stored in a vacuum desiccator over potassium hydroxide pellets and maintained under reduced pressure (25 mm.) for 18 hr. In this manner 26.8 g. (84% over-all) of di-*n*-butylvinyltin acetate was obtained. In an analogous manner the other organotin acetates listed in Table III were prepared and crude samples, suitable for testing, of di-*n*-butylvinyl-, diphenyl-*n*-hexyl-, divinyl-*n*-decyl-, divinyl-*n*-hexyl- and divinyl-*n*-octyltin acetate were obtained.

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RAHWAY, N. J.

[CONTRIBUTION FROM THE MELLON INSTITUTE]

The Preparation and Properties of Some Silylmethyl and Silylpropyl Substituted Tin Compounds

BY ROBERT L. MERKER AND MARY JANE SCOTT[1]

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The preparation and properties of compounds possessing the structures $[\mathrm{XMe_2Si(CH_2)}_m]_2\mathrm{SnR_2}$ and $\mathrm{XMe_2SiCH_2SnR_3}$, where X is hydrogen, ethoxyl or oxygen ($\mathrm{O}_{1/2}$), are described. The two six-membered cyclic siloxanes, $\underline{\mathrm{Me_2SiCH_2SnMe_2CH_2SiMe_2O}}$ and $\underline{\mathrm{Me_2SiCH_2SnBu_2CH_2SiMe_2O}}$ are the first reported compounds containing both tin and silicon in the same ring system. The addition of dimethylhydrogensilylmethyltributyltin to vinyldimethylchlorosilane using chloroplatinic acid as a catalyst proceeded smoothly resulting in a fair yield of the β-adduct.

Introduction

A number of hybrid organotin–organosilicon compounds have been previously reported in the literature by Rochow and Seyferth[2,3] and Post and Papetti.[4] The compounds reported by Rochow and Seyferth were of the type, ($\mathrm{X_2SiMeCH_2SnR_3}$) and, therefore, were capable of forming polymeric materials containing organotin substituents in the side chains. The other compounds reported by Seyferth[3] and Post and Papetti[4] were all trimethylsilylmethyl substituted tin compounds and hence did not possess a reactive functional group on the silicon which could lead to the formation of polymers.

The intent of this present investigation was the preparation of hybrid organotin–organosiloxane monomers (preferably as siloxane cyclics) which could on polymerization yield polymers having both tin and silicon in the backbone chain. One of the more promising classes of compounds falling into this category possessed the structures $[\mathrm{XMe_2Si(CH_2)}_m]_2\mathrm{SnR_2}$ (chain extending species) and ($\mathrm{XMe_2SiCH_2SnR_3}$) (end-blocking species). This paper, however, is restricted to a discussion of the preparation, the properties and a few of the reactions of such compounds. The results of polymerization studies will be reported at a later date.

Discussion

The dimethylhydrogensilylmethyl and dimethylhydrogensilylpropyl tin compounds were prepared utilizing the reaction

$$n\mathrm{HMe_2Si(CH_2)}_m\mathrm{MgCl} + (\mathrm{R}_{(4-n)})\,\mathrm{SnCl}_n \xrightarrow[\text{ether}]{\text{ethyl}} [\mathrm{HMe_2Si(CH_2)}_m]_n\mathrm{SnR}_{(4-n)} + n\mathrm{MgCl_2} \quad (1)$$

where $m = 1$ or 3, $n = 1$ or 2, and R was methyl or butyl. The dimethylhydrogensilylmethyl- and dimethylhydrogensilylpropylalkyl tin compounds so prepared were found to be quite stable to cleavage under basic conditions in either absolute ethanol or aqueous ethanol at reflux temperatures. Thus it was possible to convert them to the corresponding ethoxyl derivatives in nearly quantitative yields

$$[\mathrm{HMe_2Si(CH_2)}_m]_n\mathrm{SnR}_{(4-n)} + n\mathrm{EtOH(abs.)} \xrightarrow{\text{NaOEt}} [\mathrm{EtOMe_2Si(CH_2)}_m]_n\mathrm{SnR}_{(4-n)} + n\mathrm{H_2} \quad (2)$$

The compounds in which $m = 1$ and $n = 2$ were smoothly converted to the six-membered cyclic siloxanes on hydrolysis in moderately dilute solution in aqueous ethanol.

$$\mathrm{(HMe_2SiCH_2)_2SnR_2} + \mathrm{HOH} \xrightarrow[\text{EtOH}]{\text{NaOH}} \underline{\mathrm{Me_2SiCH_2SnR_2CH_2SiMe_2O}} + 2\mathrm{H_2} \quad (3)$$

These are the first well characterized compounds reported which contain both tin and silicon in a cyclic ring system.

It is of interest that under the reaction conditions employed (reaction 3), nearly quantitative yields of the six-membered cyclic siloxanes were obtained. Attempts to prepare the ten-membered cyclic from the propyl derivative ($m = 3$) under identical conditions were unsuccessful and yielded

$$[\mathrm{HMe_2Si(CH_2)_3}]_2\mathrm{SnMe_2} + \mathrm{HOH} \xrightarrow[\text{EtOH}]{\text{NaOH}} (\mathrm{Me_2Si(CH_2)_3SnMe_2(CH_2)_3SiMe_2O}\text{–})_x + 2\mathrm{H_2} \quad (4)$$

only linear polysiloxanes. A small yield of the ten-membered cyclic, however, was obtained by thermally cracking the linear polysiloxanes under alkaline conditions.

$$(\mathrm{Me_2Si(CH_2)_3SnMe_2(CH_2)_3SiMe_2O}\text{–})_x \xrightarrow[\Delta]{\text{KOH}} \underline{\mathrm{Me_2Si(CH_2)_3SnMe_2(CH_2)_3SiMe_2O}} \quad (5)$$

A compound in which $m = 1$ and $n = 1$, dimethylhydrogensilylmethyltributyl tin or its ethoxy

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[1] Multiple Fellowship on Silicones sustained by the Dow-Corning Corporation and Corning Glass Works.

[2] D. Seyferth and E. G. Rochow, *J. Polymer Sci.*, **18**, 543 (1955).

[3] D. Seyferth, THIS JOURNAL, **79**, 5881 (1957).

[4] H. W. Post and S. Papetti, *J. Org. Chem.*, **22**, 526 (1957).

derivative, on similar hydrolysis in either basic or acidic medium, respectively, yielded the corresponding disiloxane.

$$2\mathrm{HMe_2SiCH_2SnBu_3} + \mathrm{HOH} \xrightarrow[\mathrm{EtOH}]{\mathrm{OH^-}} (\mathrm{Bu_3SnCH_2SiMe_2})_2\mathrm{O} + 2\mathrm{H_2} \quad (6)$$

$$2\mathrm{EtOMe_2SiCH_2SnBu_3} + \mathrm{HOH} \xrightarrow[\text{dioxane}]{\mathrm{H^+}} (\mathrm{Bu_3SnCH_2SiMe_2})_2\mathrm{O} + 2\mathrm{EtOH} \quad (7)$$

In general, it was felt that reaction 1 followed by reaction (3) was a more satisfactory method for the preparation of pure cyclic organotin organosiloxanes than employing the reaction

$$(\mathrm{ClCH_2Me_2Si})_2\mathrm{O} + 2\mathrm{Mg} \xrightarrow{\text{ethyl ether}} (\mathrm{ClMgCH_2Me_2Si})_2\mathrm{O}$$

$$(\mathrm{ClMgCH_2Me_2Si})_2\mathrm{O} + \mathrm{R_2SnCl_2} \longrightarrow (\mathrm{Me_2SiCH_2SnR_2CH_2SiMe_2O}\text{-})_x + 2\mathrm{MgCl_2} \quad (8)$$

$$(\mathrm{Me_2SiCH_2SnR_2CH_2SiMe_2O}\text{-})_x \xrightarrow[\Delta]{\mathrm{KOH}} \underbrace{\mathrm{Me_2SiCH_2SnR_2CH_2SiMe_2O}}$$

The use of above resulted not only in low yields of desired products, but also in products that were extremely difficult to separate from the impurities arising from side-Grignard reactions.

Numerous investigators have described the addition of organosilicon hydrides across double bonds of various unsaturated compounds using peroxide,[5] platinum-on-carbon[6] and, more recently, chloroplatinic acid[7] catalysts. Seyferth[8] reports that the additions of trichlorosilane and methyldichlorosilane to triethylvinyltin are catalyzed by benzoyl peroxide but do not proceed in the presence of platinum catalysts. He tentatively suggests the possibility that organotin compounds might function as platinum catalyst poisons. It, therefore, was of interest to attempt the addition of one of these novel tin-containing organosilicon hydrides to an unsaturated compound employing platinum catalysis. The attempted addition

$$\mathrm{Bu_3SnCH_2SiMe_2H} + \mathrm{CH_2{=}CHSiMe_2Cl} \xrightarrow{\mathrm{H_2PtCl_6{\cdot}6H_2O}} \mathrm{Bu_3SnCH_2SiMe_2CH_2CH_2SiMe_2Cl} \quad (9)$$

proceeded smoothly giving a fair yield of β-adduct. Hence, the difficulties encountered by Seyferth might have been due to some property of the vinyl–tin link, differing from that of the vinyl–silicon link. On the basis of the above work, it might be predicted that analogous organotin–organosilicon hydrides will react with other unsaturated compounds, in this way providing an attractive method for the preparation of a large number of new organotin–organosilicon compounds.

The properties and analyses for the compounds prepared are shown in Table I. In addition to elemental analysis for tin, silicon, carbon and hydrogen, proof of structure was furnished by the specific

TABLE I

PROPERTIES AND ANALYSES FOR SOME SILYLMETHYL AND SILYLPROPYL SUBSTITUTED TIN COMPOUNDS

	Compound	Boiling pt. °C.	Boiling pt. Mm.	$n^{25}D$	d^{25}_4	R_D Obsd.	R_D Theory	Si, % Obsd.	Si, % Theory	Sn, % Obsd.	Sn, % Theory	H, % Obsd.	H, % Theory	C, % Obsd.	C, % Theory
I	$(\mathrm{Me_2HSiCH_2})_2\mathrm{SnMe_2}$	101	20	1.4743	1.108	0.2537	0.2544	..	..	..	..	8.40	8.20	32.40	32.57
II	$\underbrace{\mathrm{Me_2SiCH_2SnMe_2CH_2SiMe_2}}_{\mathrm{O}}$	95	21	1.4743	1.203	.2338	.2340	18.6	18.2	38.6	38.4	7.29	7.18	30.47	31.09
III	$(\mathrm{Me_2HSiCH_2})_2\mathrm{SnBu_2}$	130	5	1.4810	1.043	.2727	.2717	14.5	14.9	31.4	31.4	9.68	9.57	43.93	44.35
IV	$(\mathrm{Me_2EtOSiCH_2})_2\mathrm{SnBu_2}$	186	15	1.4655	1.056	.2620	.2625	11.9	12.0	25.4	25.4	9.65	9.49	46.25	46.28
V	$\underbrace{\mathrm{Me_2SiCH_2SnBu_2CH_2SiMe_2}}_{\mathrm{O}}$	170[a]	25	1.4800	1.113	.2552	.2549	..	..	..	..	..	..	...	...
		170[b]	25	1.4805	1.116	.2549	.2549	14.0	14.3	30.6	30.2	9.03	8.72	43.33	42.76
VI	$(\mathrm{Me_2HSi(CH_2)_3})_2\mathrm{SnMe_2}$	146	15	1.4730	1.052	.2667	.2665	15.4	16.0	34.7	33.8	9.35	9.19	40.73	41.04
VII	$\underbrace{\mathrm{Me_2Si(CH_2)_3SnMe_2(CH_2)_3SiMe_2}}_{\mathrm{O}}$[c]	148	16	1.4840	1.157	.2472	.2487	..	..	..	..	..	..	...	...
VIII	$\mathrm{Bu_3SnCH_2SiMe_2H}$	133	5	1.4764	1.047	.2696	.2690	9.10	7.73	32.5	32.7	9.85	9.99	48.68	49.50
IX	$\mathrm{Bu_3SnCH_2SiOEtMe_2}$	147	5	1.4682	1.053	.2640	.2640	7.80	6.90	29.3	29.2	..	..	...	...
X	$(\mathrm{Bu_3SnCH_2SiMe_2})_2\mathrm{O}$[d]	240	<0.1	1.4852	1.102	.2599	.2601	8.5	7.6	30.7	32.1	..	..	...	...
XI	$\mathrm{Bu_3SnCH_2SiMe_2CH_2CH_2SiMe_2Cl}$[e]	180	30	1.4836	1.066	.2680	.2680	11.6	11.6	24.4	24.5	..	..	...	...
XII	$(\mathrm{Bu_3SnCH_2SiMe_2CH_2CH_2SiMe_2})_2\mathrm{O}$	..	...	1.4850	1.045	.2742	.2727	...	...	..	..	..	..	...	...

[a] Prepared by thermally cracking coupled Grignard product of $(\mathrm{ClCH_2Me_2Si})_2\mathrm{O}$ and $\mathrm{Bu_2SnCl_2}$. [b] Prepared from compound IV. [c] Cryoscopic mol. wt. obsd. 361.6, theor. 365.1. [d] Viscosity at 25° = 9.624 cs.; at 76.2° = 3.359 cs.; $E_{\text{visc.}}$ = 4272 cal.; cryoscopic mol. wt. obsd. 756.0, theor. 740.4. [e] Neut. equiv. obsd. 476.2, theor. 483.8.

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[5] J. L. Speier, Ruth Zimmerman and J. A. Webster, THIS JOURNAL, **78**, 2278 (1956).

[6] G. H. Wagner, U. S. Patent 2,637,738; May 5, 1953.

[7] J. L. Speier, J. A. Webster and G. H. Barnes, THIS JOURNAL, **79**, 974 (1957).

[8] D. Seyferth, *J. Org. Chem.*, **22**, 1252 (1957).

refractions calculated from the values of Warrick.[9] The structures proposed for each compound were further verified through analysis of the infrared and H^1 n.m.r. spectra obtained.

From the infrared spectrum observed for $(Bu_3SnCH_2Me_2Si)_2O$, it is evident that the stretching absorption band for the Si–O–Si bond is shifted from the normal 9.38 μ position to a higher wave length of 9.73 μ. This effect of tin located on the α-carbon atom on the position of the infrared absorption band for the siloxane bond was also observed for $\underline{Me_2SiCH_2Me_2SnCH_2Me_2SiO}$ (9.87 μ) and $\underline{Me_2SiCH_2Bu_2SnCH_2Me_2SiO}$ (9.87 μ). The shift in band position for these two compounds is slightly larger than that seen for $(Bu_3SnCH_2Me_2Si)_2O$ and probably results from a slight amount of strain in the 6-membered ring. When tin is substituted in the γ-position as in the compound, $\underline{Me_2Si(CH_2)_3Me_2Sn(CH_2)_3Me_2SiO}$, the Si–O–Si band was evidenced at the normal position of 9.38 μ.

Experimental

Starting Materials.—Chloromethyldimethylsilane ($n^{25}D$ 1.4165, d^{25}_4 0.888) and γ-chloropropyldimethylsilane ($n^{25}D$ 1.4310, d^{25}_4 0.884), were prepared by the reduction of chloromethyldimethylchlorosilane and γ-chloropropyldimethylchlorosilane, respectively, with lithium aluminum hydride. The methods employed were essentially the same as those used by Nebergall[10] for the preparation of phenylsilane from phenyltrichlorosilane. Vinyldimethylchlorosilane was obtained from the Dow Corning Corporation and was used without further purification. *sym*-Bis-chloromethyltetramethyldisiloxane was prepared through hydrolysis of chloromethyldimethylchlorosilane. Dimethyltin dichloride, dibutyltin dichloride and tributyl tin chloride were obtained from the Metal and Thermit Corp., Rahway, N. J., and were used without further purification.

Preparation of Compounds I, Bis-(dimethylhydrogensilylmethyl)-dimethyltin; III, Bis-(dimethylhydrogensilylmethyl)-dibutyltin; and VI, Bis-(dimethylhydrogensilylpropyl)-dimethyltin (See Table I).—The method used in preparing compounds I, III and VI can be illustrated by considering the preparation of I. Following the usual Grignard Reaction procedure, a solution of 50 g. (0.465 mole) of chloromethyldimethylsilane in 150 ml. of anhydrous diethyl ether was added dropwise to 12.4 g. (0.465 g. at.) of magnesium shavings in a flask equipped with a stirrer and condenser. The rate of addition was regulated to maintain reflux. To this Grignard reagent solution was then added dropwise a solution of 40.8 g. (0.185 mole) of dimethyltin dichloride in 300 ml. of diethyl ether. The products were refluxed for one hour after completion of the addition, then diluted with 100 ml. of benzene, washed with 5% hydrochloric acid solution and water, and dried over anhydrous sodium sulfate. Solvents were removed at atmospheric pressure and fractional distillation at reduced pressure yielded 48.2 g. of I, properties given in Table I. Compounds I, III and VI were obtained in yields of 82, 66.6 and 75.5% of theory, respectively, based on the weight of tin compound added in each case.

Preparation of Compound II, Cyclo-oxy-(bis-dimethylsilylmethyl)-dimethyltin).—In the preparation of II, 22.6 g. (0.077 mole) of I, $(Me_2HSiCH_2)_2SnMe_2$, was refluxed with 70 ml. of absolute ethanol, 4 g. water and 0.2 g. KOH catalyst. After the evolution of the theoretical volume of hydrogen in four hours, the reaction products were diluted with benzene, washed and distilled. The solvents were removed at atmospheric pressure, and fractional distillation at reduced pressure yielded 20.4 g. of II, a yield of 86.6%. Properties are summarized in Table I.

Preparation of Compound IV, Bis-(dimethylethoxysilylmethyl)-dibutyltin.—Compound IV was prepared by refluxing 25.6 g. (0.0675 mole) of III, $(Me_2HSiCH_2)_2SnBu_2$, with 30 g. of absolute ethanol to which 0.2 g. of sodium had been added. After four hours, the equivalent volume of hydrogen had been evolved. The reaction mixture was neutralized with glacial acetic acid and distilled at reduced pressure yielding 26.1 g. of product (83% of theory) possessing the properties described in Table I.

Preparation of Compound V, Cyclo-oxy-(bis-dimethylsilylmethyldibutyltin). Preparation of Compound Va.—The cyclic Va was prepared by the addition of dibutyltin dichloride to the di-Grignard reagent of *sym*-bis-chloromethyltetramethyldisiloxane, and subsequent thermal cracking in the presence of potassium hydroxide. In the usual fashion for Grignard reactions a solution of 125 g. (0.54 mole) of $(ClCH_2Me_2Si)_2O$ in 400 ml. of anhydrous diethyl ether was added dropwise to 26.2 g. (1.08 g. at.) of magnesium at a rate to maintain reflux. To this Grignard reagent was added dropwise 153.3 g. (0.505 mole) of dibutyltin dichloride in 200 ml. of diethyl ether. Upon completion of the addition, the reaction products were refluxed for one hour, then washed with water and 1% sodium hydroxide until neutral. After the addition of 1 g. of powdered potassium hydroxide and removal of solvents at atmospheric pressure, the residue was cracked at 5 mm. pressure and 220° pot temperature. From fractional distillation of the cracked products was obtained a 37% yield based on dibutyltin dichloride of cyclic Va, the properties of which are shown in Table I.

Attempts to prepare the pure dimethyltin analog (compound II) by this procedure were unsuccessful because of the difficulty in isolating this compound from impurities, which boiled in approximately the same range. The purest sample of II obtained by this method possessed the properties $n^{25}D$ 1.4691, d^{25}_4 1.159 and R_D 0.2401. The properties of the pure compound prepared by the method discussed previously are listed in Table I.

Preparation of Compound Vb.—Compound Vb was prepared from compound IV by refluxing 18 g. (0.0386 mole) of IV, 70 ml. of absolute ethanol, 0.2 g. of KOH and 5 g. of water for two hours. The reaction products were diluted with 60 ml. of benzene, washed with water, and dried over anhydrous sodium sulfate. After removal of solvents at atmospheric pressure, fractional distillation at reduced pressure yielded 13.4 g. of V, a yield of 92%.

Preparation of Compound VII, Cyclo-oxy-(bis-dimethylsilylpropyldimethyltin).—Compound VII was prepared by ethanolysis of compound VI, $[Me_2HSi(CH_2)_3]_2SnMe_2$, followed by hydrolysis and subsequent thermal cracking of the polysiloxane. This was accomplished by refluxing 20.5 g. (0.0574 mole) of VI, 70 ml. of absolute ethanol, 5 g. of water and 0.2 g. of potassium hydroxide until an equivalent volume of hydrogen had been evolved. At the start of the reflux period the reaction mixture contained two phases indicating that the bis-(dimethylhydrogensilylpropyl)-dimethyltin (VI) was not completely soluble in the alcohol-water mixture. As reaction proceeded, the mixture became homogeneous, presumably due to the formation of the soluble ethoxy intermediate. At the end of reaction, two phases were again apparent, resulting from the formation of the siloxane which was insoluble in this system. The reaction products were diluted with 80 ml. of benzene, washed with water, and dried over anhydrous sodium sulfate. After solvents were removed at atmospheric pressure, no distillable product was obtained to a pot temperature of 170° at 14 mm. pressure. After the addition of 0.2 g. of powdered KOH, the mixture was thermally cracked at ultimate vacuum to a pot temperature of 250°. Fractional distillation of the cracked products yielded compound VII, yield 20.4%, properties outlined in Table I.

Preparation of Compound VIII, Dimethylhydrogensilylmethyltributyltin.—Compound VIII was prepared by Grignard reaction in which a solution of 140.3 g. (1.29 moles) of $ClCH_2Me_2SiH$ in 300 ml. of anhydrous diethyl ether was added dropwise to 31.4 g. (1.29 g. at.) of magnesium shavings in a flask equipped with condenser and stirrer. Following this was added dropwise 260 g. (0.8 mole) of Bu_3SnCl dissolved in 100 ml. of diethyl ether. At the completion of the addition the reaction mixture was refluxed 45 minutes, washed with dilute HCl and with water, and dried over anhydrous sodium sulfate. Fractional distillation yielded 290 g. of VIII, 99% of theory based on weight of tin compound used. Properties and analyses are given in Table I.

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(9) E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

(10) W. H. Nebergall, *ibid.*, **72**, 4702 (1950).

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

BY M. V. GEORGE, GLEN D. LICHTENWALTER AND HENRY GILMAN

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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.