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REACTION OF ORGANOTIN OXIDES, ALKOXIDES AND ACYLOXIDES WITH ORGANOSILICON HYDRIDES. NEW PREPARATIVE METHOD OF ORGANOTIN HYDRIDES*

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INTRODUCTION

The reaction involving transfer of hydrogen from silicon to some other metal atom, thus affording a novel method for the preparation of the metallic hydride, deserves investigation in view of the ease of handling of these silicon hydride and the industrial popularity which they enjoy. Organometallic hydrides are usually prepared by hydrogenation of the metal or by the exchange of metallic halide with lithium aluminum hydride or sodium borohydride. The utilization of an organosilicon hydride, as a typical hydride, involves a different and unique route particularly when trichlorosilane and its derivatives are used.

We have already reported the formation and existence of titanochloroform[1] prepared by the interaction of titanium tetrachloride and a trialkylsilicon hydride. As a second possibility, stemming from this type of reaction, the reduction of oxygen-containing organotin compounds with organosilicon hydrides could take place with the formation of an organotin hydride in good yields depending on the choice of reactants and conditions. Shortly after our presentation however, some of these, particularly the reactions of organotin alkoxides with a polymethylhydrosiloxane were reported by Itoi[2]. This paper will report work in a somewhat different area; the following equations are typical of the kind of reactions involved:

$$x\,(Bu_3Sn)_2O + 2\,(MeSiHO)_x \rightarrow 2x\,Bu_3SnH + 2\,(MeSiO_{1.5})_x \qquad (1)$$

$$(Bu_2SnO)_x + 2\,(MeSiHO)_x \rightarrow x\,Bu_2SnH_2 + 2\,(MeSiO_{1.5})_x \qquad (2)$$

The procedure is simple, involving distillation under vacuum. The results can be classified under three headings according to the reactivities of the reagents and the experimental conditions. (*a*) The distilled fraction is composed mainly of the tin hydride (eqns. 1 and 2). (*b*) In addition to the hydride, a considerable amount of siloxytin[3] compound is isolated:

$$(Bu_3Sn)_2O + Ph_3SiH \rightarrow Bu_3SnH + Bu_3SnOSiPh_3 \qquad (3)$$

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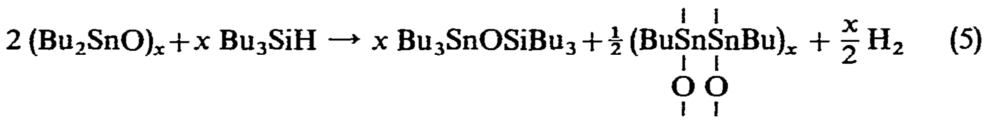
* Presented before the Symposium on the Organometallic compounds held at Osaka under the auspices of Kinki Chemical Industries Association. Paper No. 18, Nov. 20 (1964).

(*c*) Even though hydrides are initially formed, only siloxytin and ditin[4] compounds are isolated:

$$(Bu_3Sn)_2O + Bu_3SiH \rightarrow Bu_3SnH + Bu_3SnOSiBu_3 \rightarrow \tfrac{1}{2}\,Bu_3SiOSiBu_3 + Bu_3SnSnBu_3 + \tfrac{1}{2}\,H_2O \quad (4)$$



$$2\,(Bu_2SnO)_x + x\,Bu_3SiH \rightarrow x\,Bu_3SnOSiBu_3 + \tfrac{1}{2}\,(BuSnSnBu)_x + \frac{x}{2}\,H_2 \quad (5)$$

Alkyls such as propyl, butyl and octyl in the reactions covered in this paper were normal primary.

The present method thus provides a novel procedure for the synthesis of trialkyl or dialkyltin hydrides which is simpler than those previously described such as the reduction of organotin halides with lithium aluminum hydride[5] or amalgamated aluminum[6].

EXPERIMENTAL

General

All temperatures reported here are uncorrected.

(*a*) *Organotin compounds.* Bis(tributyltin) oxide (b.p. 180–189°/4, n_D^{20} 1.4868, d_4^{25} 1.172), bis(tripropyltin) oxide (b.p. 155–157°/4, n_D^{20} 1.4899, d_4^{25} 1.2586), dibutyltin oxide and monobutyltin oxide (the last two are polymers and have no m.p.) were the products of the Yoshitomi Chemical Co. Bis(triphenyltin) oxide (m.p. 124°), diphenyltin oxide (polymer) were prepared from the corresponding chlorides by treating with aqueous sodium hydroxide and subsequent thorough washing with hot water. Dimethyltin oxide and dioctyltin oxide were obtained from the Matsuda laboratory of Osaka University and were used without further purification. Tributyltin ethoxide (b.p. 110–112°/6), dibutyltin diethoxide (b.p. 119–120°/5) were prepared from the corresponding chlorides (given by Yoshitomi Chemical Co.) and sodium ethoxide respectively. Tributyltin acetate (m.p. 84.5–85°) and dibutyltin diacetate (b.p. 120–124.5°/2) were also obtained from the corresponding oxides and glacial acetic acid.

(*b*) *Organosilicon compounds.* Polymethylhydrosiloxane used was furnished by Union Carbide Co., (L-31) $(MeSiHO)_n$, where n is nearly 40 and the viscosity is 30 cps. Triphenylsilane (b.p. 178–180°/4, m.p. 45°) and tributylsilane (b.p. 78–79°/4) were synthesized from trichlorosilane and the corresponding Grignard reagents. 1,1,3,3-Tetraphenyldisiloxane was prepared by hydrolysis of the distilled diphenylchlorosilane (b.p. 140–142°/8) obtained from trichlorosilane and phenylmagnesium bromide. It was purified by vacuum distillation and by recrystallization from ethanol, (b.p. 246–8°/8, m.p. 46–9°). [Found: Si, 15.1; $H(OH)^-$*, 0.55. $C_{23}H_{22}OSi_2$ calcd.: Si, 15.0; $H(OH)^-$, 0.52%.] A lower molecular weight polymethylhydrosiloxane $Me_2HSiO(SiHMeO)_nSiHMe_2$ (n; 1–3 mainly 2) was obtained by cohydrolyzing an equimolar mixture of dimethylchlorosilane and methyldichlorosilane. [Found: $H(OH)^-$, 1.38. $C_6H_{22}O_3Si_4$ calc.: $H(OH)^-$, 1.54%.] Silicon oxyhydride, a hydrol-

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* $H(OH)^-$ shows the active hydrogen of the substance decomposed by alkali.

yzate of trichlorosilane and its co-hydrolyzate with dimethyldichlorosilane (1 : 1 mole ratio) were obtained as white gels under mild hydrolysis conditions using ice and ether.

(*c*) *General procedure.* The reactants were placed in a Claisen flask under a nitrogen atmosphere in the required mole ratio and subjected to vacuum distillation by gentle heating. When the two reactants were reactive at room temperature, the distillation was carried out after the reaction had ceased to be exothermic to avoid violent acceleration. In most cases, however, the reaction proceeded as the distillation progressed. The distilled fractions were investigated mainly by infrared spectrum but some chemical analyses were carried out on the new substances.

(*d*) *Analysis.* Elemental analyses of carbon and hydrogen were used with good agreement for the several organotin compounds. A nitrogen atmosphere was used to protect solutions containing organotin hydride and organoditin. These analyses were carried out by using approximately 0.1 *N* iodine solution in benzene standardized by standard thiosulfate in aqueous solution and tetrahydrofurane as a solvent. From the preliminary experiments, it was found that tributyltin, tripropyltin hydrides and hexabutylditin[7] reacted with iodine as shown in the following equations quantitatively without formation of hydrogen iodide when a sample in benzene was titrated with iodine solution, and the end point was very sharp. The back-titration method of the excess iodine was not used owing to the obscurity of the end point.

$$2\,Bu_3SnH + I_2 \rightarrow 2\,Bu_3SnI + H_2 \tag{6}$$

$$Bu_3SnSnBu_3 + I_2 \rightarrow 2\,Bu_3SnI \tag{7}$$

Dibutyltin dihydride, however, accompanied the formation of hydrogen iodide even when the same procedure was used. Therefore, the water extract of the acid in the benzene solution after the iodine titration was titrated against standard alkali solution and from the difference the purity of the dihydride was calculated. Several other analytical methods were tried as follows. Gas chromatography with polyethylene glycol and D.C. 550 column was tried with tributyltin hydride and dibutyltin dihydride at 110, 160 and 180°. The former converted to three fractions probably due to the disproportionation reaction, but the latter was unaffected. In general, this method seemed to be unfavourable for organotin hydride. Measuring the evolved hydrogen gas volume decomposed by formic acid or ethanolic potash with the Zerewitinoff apparatus was another possibility, but was eventually found to be inadequate.

(*A*) $(R_3Sn)_2O$

(1) *Bis(tributyltin)oxide and polymethylhydrosiloxane.* Upon mixing bis(tributyltin)oxide (40 g, 0.067 mole) and polymethylhydrosiloxane (8.0 g, 0.134 mole), a gentle evolution of heat was observed which ceased after about 30 min. By vacuum distillation there were obtained two colorless fractions, b.p. 80–114°/6 (2.8 g) and 114–116°/6 (31.2 g, 0.107 mole). A porous transparent residual mass (14.0 g) remained. The IR spectrum of the main fraction showed a strong absorption band at 1814 cm^{-1} characteristic of tributyltin hydride[8] and small absorption bands of SiH, SiMe and SiOSi bonds. Its titration analysis by iodine showed 97.6% purity, yield 79%. Redistillation of this fraction afforded the pure tributyltin hydride, b.p. 105–108°/6

(Lit. 81°/0.9), n_D^{24} 1.4694, d_4^{25} 1.0976. (Found: C, 49.05; H, 10.00. $C_{12}H_{28}Sn$ calcd.: C, 49.52; H, 9.70%.) Several other experiments were carried out with variations in amounts and mole ratios of the two reactants. The yield of the hydride was improved up to 87% at mole ratio of 1 : 2 and under the optimum condition, but when the mole ratio was 1 : 1, the yield decreased to about half and the strong absorption band of SiOSn bond at 980 cm^{-1} was recognized in the residual mass.

(2) *Bis(tributyltin) oxide and 1,1,3,3-tetraphenyldisiloxane.* Bis(tributyltin) oxide (6.0 g, 0.01 mole) was admixed with tetraphenyldisiloxane (3.8 g, 0.01 mole) and the crystals were melted by the heat generated. Successive vacuum distillations gave a fraction, b.p. 94–99°/5 (3.8 g, 0.013 mole) which was found to be tributyltin hydride by its IR spectrum. The second fraction b.p. 105–115°/5 (1.6 g) was obtained with IR spectrum showing SiH, SiOSi and SnH. These were taken to indicate a slight contamination of the siloxane fractions.

The residue was a gray viscous mass and was found to have several fused metallic tin particles in it. From the carbon tetrachloride extract of this residue, 0.5 g of white crystals were deposited which found mainly to be composed of octaphenylcyclotetrasiloxane from the mixing m.p. 160–166° with the sample made from the other route and the IR spectrum.

(3) *Bis(tributyltin) oxide and triphenylsilane.* Bis(tributyltin) oxide (10 g, 0.016 mole) was mixed with triphenylsilane (5.2 g, 0.02 mole) by gentle heating and after thorough miscibility had been attained, the material was subjected to vacuum distillation. Tributyltin hydride was first obtained as the fraction, b.p. 88–109°/4 (4.2 g), of which the purity was determined by iodine titration as 90.6%, yield 41%. The second fraction, b.p. 228–236°/4 (6.5 g), n_D^{25} 1.5507, d_4^{25} 1.156, was then obtained which was found to be almost pure (triphenylsiloxy)tributyltin on the basis of its IR spectrum comparing with the authentic sample* but contaminated slightly by hexabutylditin (2.9% by iodine titration). The yield amounted to 69%.

By a separate experiment, mole ratio 1 : 2, with heating time of one hour at 200° the purity of the obtained hydride was 95.3%, but the fraction of (triphenylsiloxyl)tributyltin b.p. 205–239°/5 was accompanied with hexabutylditin (28% by iodine titration) owing to the reaction of the formed hydride and the original tin oxide[8].

(4) *Bis(tripropyltin) oxide and polymethylhydrosiloxane.* Bis(tripropyltin) oxide (20.4 g, 0.04 mole) and polymethylhydrosiloxane (5.0 g, 0.08 mole) were admixed with water cooling. Vacuum distillation yielded two fractions. One was the fraction, b.p. 46–54°/4 (3.5 g) and another b.p. 60–89°/4 (10.5 g). The former seemed to be tripropyltin hydride which was formed during admixing of the reactants, and the latter was the hydride which was formed during the distillation. Redistillation of the two fractions gave the main distillate, b.p. 59–64°/4 (13.5 g), n_D^{25} 1.4698, d_4^{25} 1.1571, almost pure by iodine titration; yield 66%. The residue was an opaque gel (11.0 g) having unreacted Si–H bonds.

(5) *Bis(tripropyltin) oxide and triphenylsilane.* Bis(tripropyltin) oxide (11.2 g, 0.02 mole) and triphenylsilane (5.2 g, 0.02 mole) were admixed and heated at 150° for 30 min. Vacuum distillation gave three fractions, b.p. 55–83°/3 (2.7 g), 145–164°/3 (4.0 g), 165–220°/3 (7.0 g), and the residue 0.5 g. The first fraction was tripropyltin

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* The synthesis of this sample will appear in experiment C-3.

hydride having the purity of 91 %, yield 49 %, the second fraction was the unreacted oxide as the main component and the last fraction was (triphenylsiloxy)tripropyltin which showed b.p. 210–215°/3 by the redistillation, n_D^{25} 1.5689, d_4^{25} 1.185. (Found: C, 63.10; H, 7.12. $C_{27}H_{36}OSiSn$ calcd.: C, 63.91; H, 7.15 %.) The IR spectrum of this compound showed the strong absorption bands characteristic of the SnOSi bond at 980 cm^{-1}.

(6) *Bis(triphenyltin) oxide and polymethylhydrosiloxane.* Bis(triphenyltin) oxide (3.1 g, 0.0043 mole) and polymethylhydrosiloxane (1.2 g, 0.02 mole) and *p*-tert-butylcatechol (0.05 g) were admixed and gradually heated under vacuum. The reaction was recognizable at about 120° of bath temperature by solution of the oxide. The first fraction, b.p. 196–198°/5.5, included a small amount of crystals. The liquid portion was found to be triphenyltin hydride (0.9 g, 0.0026 mole, yield 32 %) by its IR spectrum which showed strong SnH absorption at 1845 cm^{-1}. An additional fraction, b.p. 198–210°/5.5, was obtained from which some crystals (1.2 g) separated. The residual mass weighed 1.3 g. These crystals together with those appearing in the preceding fraction were found to be tetraphenyltin, m.p. 223–224° (Lit. m.p. 224–225°) and mixed melting point with an authentic sample.

Comparing experiments without the inhibitor were attempted. Hexaphenylditin (titration by iodine) and tetraphenyltin*, probably derived from the intermediary triphenyltin hydride, were obtained, but no free hydride or Sn–H bond in the solid phase were seen.

(7) *Bis(triphenyltin) oxide and triphenylsilane.* Bis(triphenyltin) oxide (3.5 g, 0.005 mole), triphenylsilane (5.2 g, 0.02 mole) and tert-butylcatechol (0.05 g) were admixed and upon heating, the mixture became homogeneous at about 110°. Distillation gave no hydride, but the unreacted triphenylsilane fraction 163–173°/4 (4.3 g, 82.7 %), the higher fraction b.p. 192–210°/4 and a residue 0.8 g. From the last fraction, crystals (2.6 g) appeared, m.p. 221–224°, confirmed as tetraphenyltin by the mixing melting point test with an authentic sample.

In another experiment bis(triphenyltin) oxide (3.1 g, 0.005 mole) and triphenylsilane (2.6 g, 0.01 mole) were admixed and heated at 180–90° for 30 min. The mixture was then directly subjected to fractional extraction by using diethyl ether and benzene as solvents to avoid the possible decomposition of the intermediary products by distillation. Two products, different from the preceding experiment, were obtained. The first portion was ether soluble and from this solution 1.4 g of white precipitate was separated in which IR absorption characteristic to a SiOSn bond at 980 cm^{-1} was markedly noticeable. Recrystallization gave m.p. 136–139° and the analysis agreed with (triphenylsiloxy)triphenyltin[3]. (Found: C, 70.68; H, 4.79. $C_{36}H_{30}OSiSn$ calcd.: C, 69.14; H, 4.84 %.) From the remaining ether soluble portion, unreacted triphenylsilane (1.0 g) was recovered. The second portion was insoluble in ether but soluble in hot benzene and from its solution 1.7 g of white crystals were obtained. It had m.p. 207–215° and iodine titration and analysis (Found: C, 64.21; H, 4.29 %.) showed the composition as a mixture of hexaphenylditin[4] (65 %) and (triphenylsiloxy)-triphenyltin (Calcd.: C, 64.90; H, 4.56 %.).

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* No iodine absorption (0.1 *N* concentration) of this compound was recognized contrary to its bromine absorption, therefore, this test can be used to distinguish the accompanying hexaphenylditin from tetraphenyltin.

(8) *Bis(tributyltin) oxide and tributylsilane.* Bis(tributyltin) oxide (6.0 g, 0.001 mole) and tributylsilane (4.0 g, 0.002 mole) were admixed and then kept for 90 min at 200° under atmospheric pressure. Vacuum distillation gave a colorless liquid, b.p. 201–204°/5 (9.2 g) and almost no residue. Redistillation of this fraction showed b.p. 193–194°/4 (7.3 g), n_D^{25} 1.5041, d_4^{25} 1.161. Its IR spectrum in the region of 3800–760 cm^{-1} showed no characteristic absorptions of Si–H, SiOSi, SnH and SnOSi or the band 770 cm^{-1} which was markedly recognized in the original tin oxide. This fraction reacted with acetic acid giving needles, m.p. 85°, which showed no depression on mixing with an authentic sample of tributyltin acetate, and the iodine titration in benzene solution of the redistillate showed 82% of the uptake of iodine expected, based on 2 atoms of iodine per mole of hexabutylditin. (Found: C, 48.33; H, 9.69. $C_{24}H_{54}Sn_2$ calcd.: C, 49.69; H, 9.38%.) In a separate test an equimolar mixture of these two reactants was heated at 220° for 15 min. An IR spectrum of this intermediary state showed the presence of Sn–H bond at 1814 and SiOSn bond at 980 cm^{-1} which soon disappeared on further heating.

(9) *Bis(tributyltin) oxide and equimolar cohydrolyzate of trichlorosilane and dimethyldichlorosilane.* Upon mixing bis(tributyltin) oxide (7.5 g, 0.126 mole) with $[HSiO_{1.5}]_x[Me_2SiO]_x$ (3.8 g, 0.15 mole), a slight heat effect was noted. Vacuum distillation gave tributyltin hydride, b.p. 83–93°/4 (5.5 g, 0.189 mole) of which the purity was determined by iodine titration as 90.8%, yield 68%. The major impurity was found to be dimethylsiloxane by its IR spectrum. Contrary to these experimental results, silicon oxyhydride, $HSiO_{1.5}$, the hydrolyzate of trichlorosilane was unreactive toward bis(tributyltin) oxide using the same procedures as above.

(10) *Bis(tributyltin) oxide and a lower molecular polymethylhydrosiloxane.* Bis(tributyltin) oxide (5.9 g, 0.01 mole) and the hydrosiloxane* (1.2 g, 0.02 mole) were admixed and then a gentle evolution of heat was observed. By vacuum distillation there were obtained two fractions, b.p. 86–96°/4.5 (2.3 g) and 167–195°/4.5 (2.1 g). The first fraction was pure tributyltin hydride, yield 38% and the second was a volatile hydrosiloxane.

(B) $(R_2SnO)_n$

(1) *Dibutyltin oxide polymer and polymethylhydrosiloxane.* Dibutyltin oxide powder (12.5 g, 0.05 mole) and polymethylhydrosiloxane (6.0 g, 0.1 mole) were admixed and heated gently under vacuum. The reaction began at about 100° and dibutyltin dihydride distilled at 50–71°/3 (6.0 g, 0.0255 mole). Redistillation gave the fraction b.p. 61–69°/5, n_D^{25} 1.4702, d_4^{25} 1.179. Iodine titration of this fraction accompanied the formation of hydrogen iodide, but it was titrated by the standardized alkali solution and purity was determined as 100%, yield 51%. Its IR showed SnH absorption at 1845 cm^{-1} which corresponded to the characteristic absorption of the dihydride. A further high fraction, b.p. 103–105°/3 (0.5 g, 0.0017 mole, yield 3.4%) was found to be tributyltin hydride from the SnH absorption band appearing at 1805 cm^{-1} and this seemed to have been formed by disproportionation, since the original tin oxide contained a tributyltin component under 1%. The residue, 11.9, was a brittle white mass but gray in center owing to the presence of small dispersed particles of metallic tin.

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* This material has been explained in the article (*b*) of the experimental.

(2) *Dibutyltin oxide and* 1,1,3,3-*tetraphenyldisiloxane*. Dibutyltin oxide (4.9 g, 0.02 mole) and tetraphenyldisiloxane (7.6 g, 0.02 mole) were admixed and heated under vacuum. When the temperature reached to 100°, the oxide powder began to dissolve and a clear homogeneous solution resulted. The dihydride fraction distilled at a bath temperature of 120°, b.p. 46–60°/5 (3.7 g, 0.0157 mole, yield 78%)*.

(3) *Dibutyltin oxide and triphenylsilane.* (*a*) 1 : 1 *mole ratio.* Dibutyltin oxide (5.0 g, 0.02 mole) and triphenylsilane (5.2 g, 0.02 mole) were admixed and distilled after heating at about 100°. Besides getting dibutyltin dihydride (0.2 g, 0.00085 mole, yield 4%) and unreacted triphenylsilane (1.0 g), a fraction, b.p. 207–246°/4 (4.9 g) was obtained which was found to be (triphenylsiloxy)tributyltin with triphenylsilane (about 8%) by comparing its IR spectrum and analytical results with the compound prepared by the other method (Exp. C-3). The residue weighed 0.6 g. (*b*) 1 : 2 *mole ratio.* Dibutyltin oxide (2.5 g, 0.01 mole) and triphenylsilane (5.2 g, 0.02 mole) were admixed and heated gradually under atmospheric pressure. The oxide powder dissolved at about 100° with reaction. Vacuum distillation gave dibutyltin dihydride, b.p. 50–60°/3 (0.2 g, 0.00085 mole, yield 8.5%) of which IR spectrum showed a characteristic band of SnH at 1835 cm^{-1}. A further high fraction, b.p. 163–164°/3 (3 g), consisted of unreacted triphenylsilane. The residual viscous oil weighed 3.1 g which separated metallic tin in a small amount and in its IR spectrum of the filtrate the SiOSn bands were recognized at 980 and 945 cm^{-1}.

(4) *Dibutyltin oxide and tributylsilane.* (*a*) 1 : 1 *mole ratio.* Dibutyltin oxide (10.0 g, 0.04 mole) and tributylsilane (8.0 g, 0.04 mole) were admixed and heated at 180–190° for one hour under atmospheric pressure. The oxide gradually dissolved changing color to light yellow with slight formation of water as the reaction proceeded. Vacuum distillation gave unreacted tributylsilane, b.p. 74–86°/5 (4.3 g), a higher fraction, b.p. 188–193°/5 (9.2 g) and a residue, a brown gel (4.5 g), which showed the presence of metallic tin particle at the bottom of the flask. The IR spectrum of the second fraction showed the strong absorption band of the SiOSn bond at 980 cm^{-1}, but nothing for the Sn–H bond. By separate experiment**, this compound was shown to have the tributyl radical even though the original tin oxide was dibutyltin oxide. Analytical results also agreed showing (tributylsiloxy)tributyltin, n_D^{25} 1.4650, d_4^{25} 1.009, and the yield was calculated as 91% (calcd. according to eqn. 5). (Found: C, 57.03; H, 10.03, mol. wt., 527, $C_{24}H_{54}OSiSn$ calcd.: C, 57.03; H, 10.77%; mol. wt., 505.) (*b*) 1 : 2 *mole ratio.* Dibutyltin oxide (5.0 g, 0.02 mole) and tributylsilane (8.0 g, 0.04 mole) were heated gradually under atmospheric pressure. Upon reaching 185°, it suddenly began to bubble, but soon settled, and about 10 min later the oxide powder had dissolved completely. Distillation gave unreacted tributylsilane, b.p. 90–94°/6.5 (6.0 g, yield 75%), and a fraction, b.p. 193–203°/6.5 (4.5 g). By redistilling the latter fraction (tributylsiloxy)tributyltin, b.p. 193–198°/6 (3.3 g) was obtained in the pure state (no iodine absorption), but there was no evidence of dibutyltin dihydride.

(5) *Dioctyltin oxide and polymethylhydrosiloxane.* Dioctyltin oxide (9.0 g, 0.025 mole), polymethylhydrosiloxane (3.0 g, 0.05 mole) and benzene (10 g) as a solvent were admixed and heated gradually under atmospheric pressure. The reaction started

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* The purity of dibutyltin dihydride was found almost always near 100% if the upper liquid portion was taken as an analytical sample, even when the oxidized precipitate appeared in the bottom.

** This experiment will appear in Exp. (C-1).

at about 70° and giving a colorless viscous gel. The IR spectrum at this point showed a strong absorption characteristic of the Sn–H bond at 1840 cm^{-1}. After distilling off benzene, it was subjected to high vacuum but gave no distillate. The residue was a swelled porous mass with a gray color.

(6) *Dioctyltin oxide and tributylsilane.* Dioctyltin oxide (14.4 g, 0.04 mole) and tributylsilane (8.0 g, 0.04 mole) were admixed and heated at 150° for several minutes, then the white powder of the oxide dissolved and became a clear homogenous solution. Direct vacuum distillation of this solution gave a fraction, b.p. 81–86°/3 (7.7 g), which was mainly unreacted tributylsilane, a further fraction, b.p. 195–220°/2 (5.7 g) and a residue (yellow gel 6.5 g). In a trap, there appeared a clear liquid condensate which was found to be n-octene by its b.p. 120°/760, n_D^{25} 1.4196 and d_4^{25} 0.772 and by the absorption of bromine and the IR spectrum. Redistillation of the second fraction showed the b.p. 195–240°/2.5 which was too broad to be taken as one component, probably was a mixture of several (tributylsiloxy)trialkyltin compounds derived from the thermal rearrangement of the octyl group, n_D^{25} 1.4673 and d_4^{25} 0.9846, and the IR spectrum showed a strong absorption for SiOSn bond at 980 cm^{-1}. (Found: C, 60.15; H, 11.21. $C_{30}H_{66}OSiSn$ calcd.: C, 61.10; H, 11.28%.)

(7) *Dimethyltin oxide and polymethylhydrosiloxane.* Dimethyltin oxide (4.0 g, 0.024 mole), polymethylhydrosiloxane (11.0 g, 0.185 mole) and small pieces of iodine were admixed and allowed to stand at room temperature and under a slight vacuum. There was continuous evolution of gas which was trapped by liquid nitrogen. A liquid condensate (1.0 g) was obtained after 20 h of which the IR spectrum showed the strong absorption band characteristic of dialkyltin dihydride, SnH at 1850 cm^{-1}. The whole residual mass turned gray color after one week standing at room temperature and exposure to day light. Without using iodine as the catalyst, the reaction did not take place at room temperature even after 20 h, and merely heating of the whole mass brought solidification and coloring. No condensate was obtained.

(*C*) $R_3SnOSiR_3$

(1) *(Tributylsiloxy)tributyltin and polymethylhydrosiloxane.* (Tributylsiloxy)-tributyltin obtained in *B*-4 (11 g, 0.022 mole) and polymethylsiloxane (2.4 g, 0.04 mole) were admixed and heated to 150° (beginning of reaction) and kept at this temperature for 30 min. At this point the reaction mixture was subjected to distillation. A fraction, b.p. 111–125°/7 (6.2 g) was obtained and a transparent oil (7.0 g) remained. The IR of the distillate showed the strong absorption of the SnH bond at 1810 cm^{-1} and the remainder was superimposable on that of tributyltin hydride. Iodine titration of the hydride showed the purity as 93.1%, yield 88%.

(2) *(Tributylsiloxy)tributyltin and triphenylsilane.* (Tributylsiloxy)tributyltin (11.0 g, 0.02 mole) and triphenylsilane (5.2 g, 0.02 mole) was admixed and heated at 200° for 15 min without any recognition of reaction. The first fraction, b.p. 140–160°/6 (6.4 g) which was unreacted triphenylsilane, and the second fraction, b.p. 160–182°/6 (8.2 g) and the residual liquid (1.0 g) were obtained. The second fraction was examined as to the formation of hexabutylditin by iodine titration, but was disclosed almost pure (tributylsiloxy)tributyltin. The result shows no reaction occurrence between the two compounds. The same was in the experiment using tributylsilane instead of triphenylsilane.

(3) *(Triphenylsiloxy)tributyltin and polymethylhydrosiloxane.* (Triphenylsiloxy)-

tributyltin was prepared according to the method of Papetti and Post[3] for the preparation of (triphenylsiloxy)triphenyltin. A dry ether solution of tributyltin chloride (32.5 g, 0.10 mole) was added to sodium triphenylsilanolate (0.10 mole) in 200 ml of dry ether prepared from triphenylsilanol and naphthalene sodium in 50 ml dry THF, and refluxed for 4 h. The product was hydrolyzed with water and the ether solution was separated and concentrated. Then it was subjected to the vacuum distillation and after recovering the fraction of naphthalene and unreacted tributyltin chloride (5.4 g), a fraction was obtained, b.p. 233–235°/5 (30.6 g, 0.054 mole), n_D^{25} 1.5547, d_4^{25} 1.147. (Found: C, 63.52; H, 7.79. $C_{30}H_{42}OSiSn$ calcd.: C, 63.72; H, 7.49%.) The IR spectrum of this compound showed the strong absorption bands characteristic of the SnOSi bond at 980, 945 and 510 cm^{-1}.

This substance (5.7 g, 0.01 mole) and polymethylhydrosiloxane (0.6 g, 0.01 mole) were admixed and heated under vacuum. The first fraction appeared when the bath temperature reached 150° (higher than in the case of SnOSn compound). This fraction, b.p. 80–88°/3 (2.2 g, 0.0076 mole) was found to be almost pure tributyltin hydride by iodine titration, yield 76%. Another higher fraction, b.p. 203–238°/3 (2.5 g), the original substance and a viscous oily residue (1.6 g) were obtained.

(4) *(Triphenylsiloxy)tributyltin and triphenylsilane.* (Triphenylsiloxy)tributyltin (12.8 g, 0.0226 mole) and triphenylsilane (11.1 g, 0.042 mole) were admixed and subjected directly to vacuum distillation. Two fractions, b.p. 190–197°/6 (5.0 g), 197–204°/6 (8.5 g) and a residual oily substance (10.5 g) was obtained from which needle crystals (0.5 g) deposited. The IR spectrum of the first fraction showed no SnH (1810 cm^{-1}), but SiH absorptions due to the existance of almost pure triphenylsilane. The second fraction was a mixture of unreacted triphenylsilane, (triphenylsiloxy)tributyltin and the newly formed hexabutylditin (content 22.5%). The remaining crystals were found to be hexaphenyldisiloxane by evidence of IR and by its m.p. 225°, with no depression of the mixing m.p. with an authentic sample.

(*D*) R_3SnOEt, R_3SnOAc and $R_2Sn(OEt)_2$

(1) *Tributyltin ethoxide and polymethylhydrosiloxane.* Tributyltin ethoxide (6.7 g, 0.02 mole) and polymethylhydrosiloxane (1.2 g, 0.02 mole) were admixed. A gentle exothermic reaction occurred which ceased after 30 min. By vacuum distillation there were obtained two colorless liquid fractions, b.p. 110–122°/6 (5.0 g, yield 86%), and b.p. 122–125°/6 (1.4 g). The first fraction was composed mainly of tributyltin hydride showing the strong IR absorption band of SnH at 1805 cm^{-1}. The second fraction was tributyltin hydride contaminated more by siloxane fragments than the former.

(2) *Tributyltin acetate and polymethylhydrosiloxane.* Tributyltin acetate (7.0 g, 0.02 mole) and polymethylhydrosiloxane (2.4 g, 0.04 mole) were admixed and subjected to vacuum distillation, but no hydride was obtained, only unreacted tributyltin acetate.

(3) *Dibutyltin diethoxide and polymethylhydrosiloxane. (a) 1 : 1 mole ratio.* To dibutyltin diethoxide (8.1 g, 0.025 mole), polymethylhydrosiloxane (1.5 g, 0.025 mole) was added under cooling and thorough agitation. Vacuum distillation gave two fractions, b.p. 105–111°/6 (6.0 g) and 116–120°/6 (1.9 g). The first fraction was dibutylethoxytin monohydride $Bu_2SnH(OEt)$ which showed the strong IR absorption of SnH (1810 cm^{-1}) and ethoxy (1050–1100 cm^{-1}), n_D^{25} 1.4713, d_4^{25} 1.1040. Its purity

was determined by iodine titration as 89%, yield 75.5%. The IR spectrum of the second fraction showed strong absorption for CH_3Si and SiOSi bonds at 1260 and 1070 cm^{-1} besides the above mentioned bands. (*b*) 1 : 2 *mole ratio.* Dibutyltin diethoxide (6.5 g, 0.02 mole) and polymethylhydrosiloxane (2.4 g, 0.04 mole) were admixed under cooling. Vacuum distillation gave two fractions, b.p. 52–54°/6 (3.2 g) and 59–102°/6 (1.4 g). The first fraction was mainly dibutyltin dihydride, yield 66%. The second fraction was also the dihydride but contaminated by siloxane fragments.

(*E*) $R_3SnOSiR_3$ *and* R_3SnH

(1) *(Tributylsiloxy)tributyltin and tributyltin hydride.* (Tributylsiloxy)tributyltin (11 g, 0.02 mole) and tributyltin hydride (5.8 g, 0.02 mole) were admixed and heated at 200° for 30 min. By vacuum distillation, after recovering unreacted tin-hydride (2.0 g, 0.0069 mole) a fraction, b.p. 180–188°/3 (13.6 g) was obtained. This fraction contained 14.8% of hexabutylditin in the original unreacted siloxy tin compound determined by iodine titration.

RESULTS AND DISCUSSION

As the main purpose of this investigation was to find a new preparative method for organotin hydride, the results are first discussed when organotin hydrides were actually obtained. If the degree of their reactivities were assumed to be comparable to the starting temperature of the reactions, the liberation of heat upon admixing of the reactants and the yields of the obtained hydrides, then the order of the reactivities of organotin compounds having oxygen atom in the molecule are arranged

TABLE 1

COMPARISON OF THE YIELDS OF ORGANOTIN HYDRIDES IN THIS TYPE OF THE REACTIONS

Exp. No.	*Sn compounds (I)*	*Si compounds (II)*	*Mole ratio (I)/(II)*	*Prod.*	*Yield. (%)*	*Start temp.*[a] *(°C)*	*Heat generation in mixing*
(*A*-1)	$(Bu_3Sn)_2O$	MeHSiO	1/2	Bu_3SnH	79	R.T.	+
(*A*-2)	$(Bu_3Sn)_2O$	$(Ph_2SiH)_2O$	1/1	Bu_3SnH	65	R.T.	+
(*A*-3)	$(Bu_3Sn)_2O$	Ph_3SiH	1/2	Bu_3SnH	41	R.T.	+
(*A*-4)	$(Pr_3Sn)_2O$	MeHSiO	1/2	Pr_3SnH	66	R.T.	+
(*A*-5)	$(Pr_3Sn)_2O$	Ph_3SiH	1/1	Pr_3SnH	49	100	None
(*A*-6)	$(Ph_3Sn)_2O$[b]	MeHSiH	1/2	Ph_3SnH	32	120	None
(*A*-8)	$(Bu_3Sn)_2O$	Bu_3SiH	1/2	Bu_3SnH	0	150	None
(*A*-9)	$(Bu_3Sn)_2O$	$HSiO_{3/2}$ + Me_2SiO	1/2	Bu_3SnH	68	R.T.	+
(*B*-1)	$(Bu_2SnO)_x$	MeHSiO	1/2	Bu_2SnH_2	51	R.T.	None
(*B*-2)	$(Bu_2SnO)_x$	$(Ph_2SiH)_2O$	1/1	Bu_2SnH_2	78	120	None
(*B*-3)	$(Bu_2SnO)_x$	Ph_3SiH	1/2	Bu_2SnH_2	4	100	None
(*C*-1)	$Bu_3SnOSiBu_3$	MeHSiO	1/2	Bu_3SnH	88	150	None
(*C*-3)	$Bu_3SnOSiPh_3$	MeHSiO	1/1	Bu_3SnH	76	150	None
(*C*-4)	$Bu_3SnOSiPh_3$	Ph_3SiH	1/1	Bu_3SnH	0	150	None
(*D*-1)	Bu_3SnOEt	MeHSiO	1/1	Bu_3SnH	86	R.T.	+
(*D*-3)	$Bu_2Sn(OEt)_2$	MeHSiO	1/2	Bu_2SnH_2	66	R.T.	+

[a] R.T. = room temperature. [b] Using *p*-tert-butylcatechol as the radical inhibitor.

from Table 1 as follows,

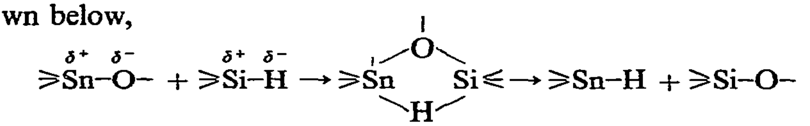
$$Bu_2Sn(OEt)_2,\ Bu_3Sn(OEt) > (Bu_3Sn)_2O > (Pr_3Sn)_2O > Bu_2SnO > Ph_3SnOSnPh_3 > Bu_3SnOSiBu_3 > Bu_3SnOSiPh_3$$

and the order of the reactivities of organosilicon hydrides can be arranged as follows from the Table 1,

$$MeSi(H)O > (Ph_2SiH)_2O > Ph_3SiH > HSiO_{3/2}\text{-}Me_2SiO \gg Bu_3SiH$$

As the weakest one in this series, tributylsilane can hardly give an organotin hydride whatever the choice of organotin compounds. It produces side reaction products such as (tributylsiloxy)tributyltin and hexabutylditin, and these results are explained by the formation of intermediary tributyltin hydride with a higher boiling point (105–108°/6) than that of tributylsilane (78–79°/6). The tin hydride remaining in the reaction system during the distillation of tributylsilane could then have an opportunity to react with the remaining organotin oxide or the newly formed siloxytin compound forming the final product of hexabutylditin.

The apparently different results of eqns. (1), (3) and (4) are also explained by the relative velocity of the tin hydride formation and consumption which are mere decomposition or reaction with the existing $(R_3Sn)_2O$ and $R_3SnOSiR_3$ compounds. The above mentioned order seems to be governed by the electron-attracting ability of the oxygen atom in the tin compounds and by the electron dative ability of the silicon atom in organosilicon hydrides modified by the functionality and the substituted organogroups. Accordingly, the fundamental reaction can be postulated to proceed through the four-centered transition state formed by electrophilic attacking of the positive silicon atom on the negative oxygen atom and by the simultaneous nucleophilic attacking of the negative hydrogen against the positive tin atom as shown below,



$$\overset{\delta+}{\geqslant Sn}-\overset{\delta-}{O}- + \overset{\delta+}{\geqslant Si}-\overset{\delta-}{H} \longrightarrow \geqslant Sn\begin{matrix}\overset{|}{O}\\ \\ H\end{matrix}Si\leqslant \longrightarrow \geqslant Sn-H + \geqslant Si-O- \qquad (6)$$

The stepwise feature of this reaction will next be discussed, namely the reaction step of organotin compounds belonging to the R_3SnOR or $R_3SnOSiR_3$ types in the simplest case, because the organotin hydride can be formed by one step as:

$$R_2SnOR' + H\text{-}Si\leqslant \longrightarrow R_3Sn\text{-}H + R'OSi\leqslant \qquad (7)$$

The reaction of the $R_3SnOSnR_3$ type, however, is more complicated, because at least two steps can be postulated to exist merely by taking it schematically,

$$R_3SnOSnR_3 + H\text{-}Si\leqslant \longrightarrow R_3Sn\text{-}H + R_3SnOSi\leqslant \qquad (8)$$

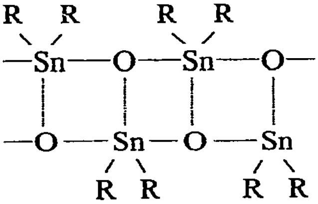
$$R_3SnOSi\ + H\text{-}Si\leqslant \longrightarrow R_3Sn\text{-}H + \geqslant SiOSi\leqslant \qquad (9)$$

In fact, there is ample support for the stepwise reaction in the experimental results of (*C*) and (*A*-1) when the mole ratio was 1:2. The distillating rate of the hydride in (*A*-1) showed a marked drop at the approximately middle point, and then the remaining portion of the hydride appeared to distill with further rise of temperature. When this reaction was carried out at equimolar ratio, its IR spectrum of the residual mass showed the strong absorption band of the SiOSn bonds at 980 cm^{-1} which proved the formation of siloxytin compound as intermediate. Another support for this stepwise reaction could be seen in experiment (*A*-3), the reaction of triphenylsilane with bis(tributyltin) oxide which gave a siloxytin compound besides the hydride as seen in eqn. (3). Glancing the whole experiments in (*C*), however, one can notice that only polymethylhydrosiloxane has the reactivity actually to give the tin hydride with siloxytin compounds among the silicon hydrides used.

Bis(triphenyltin) oxide with polymethylhydrosiloxane could give triphenyltin hydride merely when a radical inhibitor was used. With triphenylsilane and 1,1,3,3-tetraphenylsiloxane, it gave no hydride but as the side reaction products, hexaphenylditin, (triphenylsiloxy)triphenyltin and tetraphenyltin were obtained showing the strong tendency toward disproportionation of the phenyltin derivatives.

The most complicated case is the reaction of diorganotin oxide $(R_2SnO)_n$ with silanes. By the recent structural investigation of the oxide, the linear polymeric and ladder form has been assigned because of the strongly ionic interaction of tin and oxygen atoms in the molecule.

$2(R_2SnO)_n \rightarrow$



(10)

Within the scope of our experiments dibutyltin oxide was the only compound to give the dihydride in appreciable amounts. The other oxides such as diphenyltin oxide and dioctyltin oxide did not give dihydrides. All attempts to separate the compounds of the type $HR_2SnOSiR_3$ which seemed to be intermediate in the first step of the reaction failed, presumably because of the easy reactivity of SnH with SnOSi eliminating hydrogen or water, but the fact that the IR spectrum of the reaction mixture taken after the mixing of both reactants showed the presence of monohydride by the SnH absorption at 1814 cm^{-1} was evidence of the temporary existence of HSnOSi. This is the most probable mechanism for the formation of polytin or even the metallic tin found in the residual mass, but in all experiments investigated no signs of the formation of disilane Si–Si or metallic silicon were recognized. Dimethyltin oxide was extraordinarily stable to tributylsilane which indicated no reaction even at 190° for thirty minutes. To triphenylsilane there was an addition reaction liberating hydrogen at 200° for three hours but giving no appreciable distillate. To polymethylhydrosiloxane, however, it appeared that reaction occurred giving a minor yield of dimethyltin dihydride. This can be explained by the greater stability of the ladder form (eqn. 10) of dimethyltin oxide than that of dibutyltin oxide resulting from the strong coordination force between two chains attributed to the small size of the methyl groups. Diphenyltin oxide was also difficult to react with tributylsilane, reacting only with polymethylhydrosiloxane, but there was no diphenyltin dihydride even using the radical inhibitor. Dioctyltin oxide, on the other hand, reacted with tributylsilane slightly giving (tributylsiloxy)trialkyltin $R_3SnOSiBu_3$ which was taken as the thermal rearrangement product of the octyltin group upon vacuum distillation over 200°, but even with polymethylhydrosiloxane it did not give dioctyltin dihydride under similar conditions, merely showing a reaction starting at 120°. The IR spectrum at this point showed dihydride absorption at 1830 and H–SnSn[10] type absorption at 1780 cm^{-1}.

Interesting results were seen in the fact that the reaction of triphenylsilane and tributylsilane with dibutyltin oxide gave (triphenylsiloxy)- or (tributylsiloxy)tributyltin respectively as the distillable fractions resulting from the disproportionation of the products at the intermediate stage. The formation of hexaorganoditin by the reaction of bis(triorganotin) oxide and triorganosilane could be attributed to the reaction of intermediary triorganotin hydride with the original oxide or the intermediary siloxytin compounds as exp. (*E*-1).

As a $R_2Sn(OR)_2$ type reactant, dibutyltin diethoxide was very reactive and gave dibutyltin dihydride in good yield with two moles of polymethylhydrosiloxane. By equimolar reaction this gave dibutylethoxytin hydride. This is the only case in which a compound having hydrogen and oxygen atoms on the same tin atom could be isolated. The stepwise scheme of this reaction seems to be as follows;

$$Bu_2Sn(OEt)_2 + H{-}Si{\leqslant} \rightarrow Bu_2SnH(OEt) \qquad (11)$$

$$Bu_2SnH(OEt) + H{-}Si{\leqslant} \rightarrow Bu_2SnH_2 \qquad (12)$$

As organotin acetoxy derivatives, tributyltin monoacetate and dibutyltin diacetate were unreactive with silicon hydrides probably owing to the strong ionic affinity between tin and acetoxy groups. Stannous bis(2-ethylhexanoate), $Sn(O_2C_8H_{15})_2$ did not react with silane, but monobutyltin oxide $BuSnO_{3/2}$ did react. The formation of the SnH bond was shown by the IR spectrum of the reaction mixture suggesting the necessity of the existence of a hydrocarbon group attached to the tin atom in this reaction. As the silane component, silicon oxyhydride $HSiO_{3/2}$ did not react with bis(tributyltin) oxide, but the cohydrolyzate of trichlorosilane and dimethyldichlorosilane reacted with the tin oxide giving tributyltin hydride in good yield. The difference in reactivities between the two reactants may be attributed to the structures of two polymer networks.

Finally, the combination of organotin oxide with trichlorosilane, methyldichlorosilane were tried, but only the oxygen–chlorine exchange reaction took place and organotin chloride was obtained.

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SUMMARY

The reaction of organotin oxide, alkoxides and acyloxides with organosilicon hydrides was investigated by varying the mole ratio of the reactants. And it was found that Sn–O was easily cleaved by Si–H giving Sn–H. Several organotin hydrides, such as tributyltin hydride, tripropyltin hydride and dibutyltin dihydride were ob-

tained in good yields. For triphenyltin hydride and dimethyltin dihydride, it was necessary to use a radical inhibitor or iodine as a promoter and even then the yields were poor. New compounds of the type SiOSn, such as (tributylsiloxy)tributyltin, (triphenylsiloxy)tributyltin and (triphenylsiloxy)tripropyltin were also obtained.

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