of pyridine there were precipitated crystals which were filtered, washed with pyridine, and allowed to stand over silica gel for 12 hr. to obtain 3.8 g. (52.8%) of dipyridino adduct, m.p. 101–103° (reported m.p. 99°[9]), which gave the correct analysis for tin.

On dissolving the dipyridino adduct in benzene there precipitated a white cloggy mass which could not be recrystallized from any solvent, but dissolved in ethanol or pyridine forming a clear solution. This monopyridino adduct decomposed on heating over 220°.

Anal. Calcd. for $C_{11}H_{15}Br_2NSn$: Sn, 26.99. Found; Sn, 26.53.

Attempted hydrogenation of diallyltin dibromide. In a usual hydrogenation apparatus a solution of 10.4 g. (0.03 mole) of diallyltin dibromide in 100 ml. of absolute ethanol was shaken with hydrogen in the presence of about 1 g. of Raney nickel (W-2[21]). During 8 hr. of shaking no absorption of gas was observed.

The same procedure using Raney nickel (W-6[21]) was also unsuccessful.

KYÔTO, JAPAN

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[21] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL AND THERMIT CORPORATION AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Partial Hydrolysis of Dialkyltin Dihalides

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Some unexpected results obtained during recent work on various organotin compounds have led us to reexamine the products obtained by Johnson, Fritz, *et al.*,[3,4] from the reaction of dialkyltin dichlorides with certain amines and alcohols. These authors believe their products to be tetraalkyldichloroditins. We have repeated the reaction and closely studied the products. It is demonstrated that the products obtained are actually bis(dialkylchlorotin) oxides.

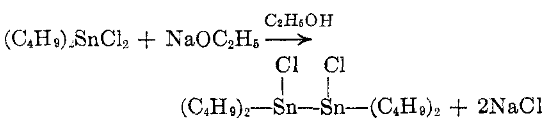
Hexaalkyl (aryl) ditins have been known for a good number of years[2] and the tin-tin bond in these compounds is widely accepted. The ditins readily react with bromine (or other halogens) at room temperature and give a metallic silver deposit on treatment with alcoholic silver nitrate. They are easily prepared by the reaction of the corresponding trialkyl (aryl) tin chloride with sodium, either in liquid ammonia or in high boiling solvents (1).

$$(C_6H_5)_3SnCl + 2Na \xrightarrow{\text{(liq. NH}_3\text{)}} (C_6H_5)_3SnNa + NaCl \qquad (1)$$

$$(C_6H_5)_3SnNa + (C_6H_5)_3SnCl \longrightarrow \underset{\text{I}}{(C_6H_5)_3Sn{-}Sn(C_6H_5)_3} + NaCl$$

The hexaarylditins (I) are generally solids and are oxidatively stable whereas the hexaalkyl ditins are generally high boiling liquids of lesser stability.

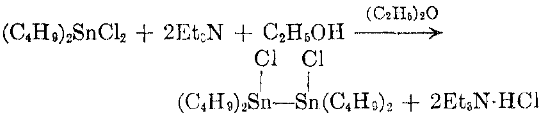
In 1954, Johnson and Fritz[3] reported a new type of tin compound, tetrabutyldichloroditin (II), from the reaction of an ethanolic solution of dibutyltin dichloride with sodium ethoxide (2).



$$(C_4H_9)_2SnCl_2 + NaOC_2H_5 \xrightarrow{C_2H_5OH} (C_4H_9)_2{-}\overset{\overset{\text{Cl}}{|}}{Sn}{-}\overset{\overset{\text{Cl}}{|}}{Sn}{-}(C_4H_9)_2 + 2NaCl \qquad (2)$$

II

In 1955 the reaction was extended to several dialkyltin dichlorides and to diphenyltin dichloride.[4] It was also reported that various amines in combination with ethanol brought about the same reaction (3).



$$(C_4H_9)_2SnCl_2 + 2Et_3N + C_2H_5OH \xrightarrow{(C_2H_5)_2O} (C_4H_9)_2\overset{\overset{\text{Cl}}{|}}{Sn}{-}\overset{\overset{\text{Cl}}{|}}{Sn}(C_4H_9)_2 + 2Et_3N{\cdot}HCl \qquad (3)$$

More recently Sawyer and Kuivila[5] have reported the preparation of similar ditin compounds with negative substituents on the tin atoms—*e.g.*, tetrabutylditin diacetate, tetraphenylditin dibenzoate. These preparations required the use of alkyltin hydrides to reduce the tin from a valence of four to a formal valence of three. These ditin products consumed stoichiometric amounts of bromine instantaneously.

In attempts to repeat the reaction of Johnson, Fritz, Halvorson, and Evans,[4] with di-*n*-butyltin dichloride, we have obtained yields of 95%, but the analyses of the products were consistently low in tin—*e.g.*, 42.8%, 42.6% as compared with a calculated value of 44.2%. These analyses were carried out in the Metal and Thermit laboratories where the procedure used has proved to be extremely reliable for many hundreds of tin compounds (see Experimental). The melting points, 110–112°, were sharp and identical with those obtained by Johnson, *et al.* Further recrystallization gave a material melting 1–2° higher but did not improve the analysis. Furthermore, this product

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[1] University of New Hampshire, Durham, N. H.

[2] (a) E. Krause and R. Pohland, *Ber.*, **57**, 532 (1924). (b) *Cf.* E. Krause and A. Von Grosse, *Die Chemie der Metall-Organischen Verbindungen*, Gebrüder Borntrager, Berlin, pp. 356–361 (1937).

[3] O. H. Johnson and H. E. Fritz, *J. Org. Chem.*, **19**, 74 (1954).

[4] O. H. Johnson, H. E. Fritz, D. O. Halvorson, and R. L. Evans, *J. Am. Chem. Soc.*, **77**, 5857 (1955).

[5] A. K. Sawyer and H. G. Kuivila, *J. Am. Chem. Soc.*, **82**, 5958 (1960).

did *not* decolorize bromine, whereas tetraalkyldiacyloxyditins are known to take up bromine quantitatively.[5]

In order to identify the reaction product obtained, dibutyltin dichloride dissolved in methanol was treated with water, precipitating a white solid, m.p. 105-107°. Recrystallization from acetone gave white crystals, m.p. 111-112°, with 42.5% tin. This compound gave no depression in melting point when mixed with the product from the Johnson-Fritz reaction. Indeed, when dibutyltin dichloride was stirred with water alone, the insoluble material isolated was again identical to the previous products melting at 111-112°.

During attempts to prepare tetrabutylditindichloride from dibutyltin dihydride and dibutyltin dichloride, oxygen was bubbled through the mixture precipitating the same product as above, m.p. 112-114°.

The product obtained appears to be essentially the same material reported as $(C_4H_9)_2SnCl_2 \cdot (C_4H_9)_2SnO$,[6] m.p. 109-110°, and of the type discussed in a monograph by Luijten and van der Kerk.[7] Indeed, a comparison of the melting points of a number of products obtained by Johnson, Fritz *et al.*, with those of the corresponding complexes previously reported, brings out a distinct similarity as shown in Table I.

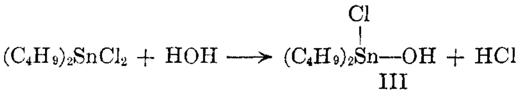
TABLE I

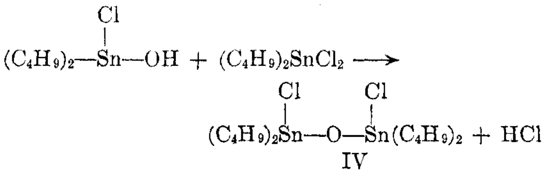
MELTING POINTS OF THE REACTION PRODUCTS FROM THE DIALKYLTIN DICHLORIDE-AMINE-ALCOHOL REACTION

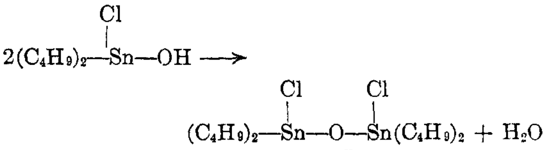
R_2SnX_2		Reported by Johnson, Fritz,[3,4] *et al.*	Reported as $R_2SnX_2 \cdot R_2SnO$
R	X		
Ethyl	Cl	174-176°	176°[a]
Propyl	Cl	120.5-121.5°	124°[b]
Butyl	Cl	111-112°	109-110°[c] 114-115°[d]
Butyl	Br	102-103°	108°[c,e]
Phenyl	Cl	185-187°	187°[f]

[a] See ref. 7. [b] P. Pfeiffer and O. Brack, *Z. Anorg. U. Allgem. Chem.*, **87,** 229-234 (1941). [c] See ref. 6. [d] This work. [e] T. Harada, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **42,** 178-180 (1947) [now *J. Sci. Research Inst.* (*Tokyo*)]. [f] B. Aronheim, *Ann.*, **194,** 145-175 (1878).

As the melting point of our material is quite sharp and the analyses are consistently good, we regard the material as a pure compound, bis-(dibutylchlorotin) oxide, IV, and propose its formation as follows:


$$(C_4H_9)_2SnCl_2 + HOH \longrightarrow (C_4H_9)_2\overset{\overset{Cl}{|}}{Sn}-OH + HCl \qquad (4)$$
III


$$(C_4H_9)_2-\overset{\overset{Cl}{|}}{Sn}-OH + (C_4H_9)_2SnCl_2 \longrightarrow (C_4H_9)_2\overset{\overset{Cl}{|}}{Sn}-O-\overset{\overset{Cl}{|}}{Sn}(C_4H_9)_2 + HCl \qquad (5)$$
IV

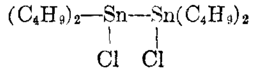
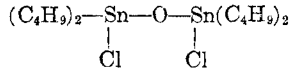
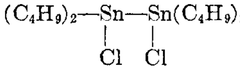
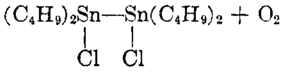

$$2(C_4H_9)_2-\overset{\overset{Cl}{|}}{Sn}-OH \longrightarrow (C_4H_9)_2-\overset{\overset{Cl}{|}}{Sn}-O-\overset{\overset{Cl}{|}}{Sn}(C_4H_9)_2 + H_2O \qquad (6)$$
IV

The intermediate dibutylchlorotin hydroxide, III, m.p. 105-107°, can be considered to be a hydrated form of IV. It is difficult to purify and characterize since it readily loses water to form IV when heated in solvents. Evidence for its existence is threefold: (1) Elementary analysis (see Experimental). (2) Molecular weight determination—calcd. for $C_8H_{19}ClOSn$: 285.4, Found: 250. 3) Karl Fischer titration: 0.500 moles H_2O per mole of III required by Equation (6); 0.508 moles H_2O found.

To demonstrate conclusively that the product of the dichlorotin-amine-alcohol reaction is not a ditin, the 1,1,2,2-tetrabutyl-1,2-dichloroditin (II) was successfully synthesized by the treatment of 1,1,2,2-tetrabutyl-1,2-diacetoxyditin with hydrogen chloride.[8] It has a melting point of 25-27°, a tin analysis of 44.0% (required—44.2%), and consumes 0.994 mole of bromine instantaneously.

TABLE II

REACTION PRODUCTS OF DIBUTYLTIN DICHLORIDE

Product	M.P.	% Sn	% Cl
 $(C_4H_9)_2-\underset{Cl}{\underset{\vert}{Sn}}-\underset{Cl}{\underset{\vert}{Sn}}(C_4H_9)_2$	Theory	44.22	13.2
 $(C_4H_9)_2-\underset{Cl}{\underset{\vert}{Sn}}-O-\underset{Cl}{\underset{\vert}{Sn}}(C_4H_9)_2$	Theory	42.95	12.8
$(C_4H_9)_2SnCl_2 + N(C_2H_5)_3 + C_2H_5OH$	110-112 115-116	43.97	13.06
Johnson, Fritz[3,4]		44.15	12.85
$(C_4H_9)_2SnCl_2 + N(C_2H_5)_3 + C_2H_5OH$	111-112	42.6	
This work		43.11	12.85
$(C_4H_9)_2SnCl_2 + (C_4H_9)_2SnO$	112-114	—	—
$(C_4H_9)_2SnCl_2 + H_2O$	112-113	—	—
$(C_4H_9)_2SnH_2 + (C_4H_9)_2SnCl_2 + O_2$	112-114	42.5	—
 $(C_4H_9)_2-\underset{Cl}{\underset{\vert}{Sn}}-\underset{Cl}{\underset{\vert}{Sn}}(C_4H_9)_2$ Sawyer[5]	25-27	44.0	—
 $(C_4H_9)_2\underset{Cl}{\underset{\vert}{Sn}}-\underset{Cl}{\underset{\vert}{Sn}}(C_4H_9)_2 + O_2$ Sawyer[5]	111-113	—	—

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(6) British Patent **711,564,** July 7, 1954; *Chem. Abstr.*, **49,** 14797 (1955).

(7) J. G. A. Luijten and G. J. M. van der Kerk, *Investigations in the Field of Organotin Chemistry,* Tin Research Institute, Fraser Road, Greenford, Middlesex, England, p. 8.

(8) A. K. Sawyer and H. G. Kuivila, soon to be published.

This product is oxidatively unstable, losing about 6% of its reducing capacity in one day in spite of special precautions to keep it away from air. When treated with oxygen, this ditin is converted quantitatively to IV.

CONCLUSION

All the data available on the products of the dibutyltin dichloride reaction are given in Table II. On the basis of these results it is concluded that the products of Johnson and co-workers are actually bis(dialkyl-halotin) oxides (IV), rather than ditin compounds as claimed. Furthermore, these oxides are very stable compounds, readily formed by partial hydrolysis of the disubstituted tin dichlorides. That this stability is representative of the class of compounds will be shown in further papers.

EXPERIMENTAL[9]

Dibutylchlorotin hydroxide (III). Dibutyltin dichloride (150 g.) was dissolved in 300 ml. of methyl alcohol and treated with a large volume of water. A white solid formed and was filtered, powdered with a mortar and pestle, and reslurried with more water. The solid was again filtered and dried under reduced pressure, yielding 132 g. (93%) of a white solid, m.p. 105–107°. The infrared spectrum showed a small band at 3509 cm.$^{-1}$

Anal. Calcd. for $C_8H_{19}ClOSn$: Sn, 41.75; Cl, 12.47. Found: Sn, 40.71; Cl, 12.39.

The molecular weight was determined in chloroform by the isopiestic method of Barger[10] except that the solutions were measured gravimetrically rather than volumetrically.

Anal. Calcd: 285.4; Found: 250. Attempts to recrystallize led to dehydration and yielded only compound IV.

Bis-(dibutylchlorotin) oxide (IV). (a) Using the procedure of Johnson, Fritz, *et al.*[3,4] 0.025 mole of dibutyltin dichloride in 50 ml. anhydrous ether reacted with 0.025 mole of triethylamine and 20 ml. of absolute ethanol. After removal of the amine hydrochloride, 5.27 g. of a white solid, m.p. 111–113°, was obtained. Recrystallization from acetone yielded 3.37 g., m.p. 112–114°.

Anal. Calcd. for $C_{16}H_{36}Cl_2OSn$: Sn, 42.95; Cl, 12.80. Found: Sn, 42.6, 43.11; Cl, 13.06, 12.85.

(b) When Compound III was recrystallized from acetone, a white solid resulted, m.p. 112–113°, which gave no depression in a mixed melting point determination with the product from (a).

(c) Dibutyltin dichloride 9 g. (0.03 mole) and 7.5 g. (0.03 mole) of dibutyltin oxide were melted to a clear solution and allowed to cool. The solid, when recrystallized from acetone, melted 112–114°.

(d) In the course of another investigation, dibutyltin dihydride and dibutyltin dichloride were mixed in equimolar quantities and oxygen bubbled into the mixture. A solid product was obtained which was shown by melting point and mixture melting point to be identical with the product obtained by the procedure of Johnson and Fritz.[4,5] Recrystallization from petroleum ether (b.p. 40–60°) gave a solid m.p. 112–114°.

Anal. Calcd. for $C_{16}H_{36}Cl_2OSn_2$: Sn, 42.95; Found Sn, 42.51, 42.44.

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(9) Melting (or decomposition) points are uncorrected. Tin analyses were done in duplicate by the method of Farnsworth and Pekola. This method has been extremely reliable for many hundreds of analyses (M. Farnsworth and J. Pekola, *Anal. Chem.*, **31**, 410–414 (1959).

(10) A. Steyermark, *Quantitative Organic Microanalysis*, Blakiston Co., Philadelphia, p. 292 *ff.* (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Influence of the Metallic Cation of Certain Organometallic Compounds on the Courses of Some Organic Reactions[1,2]

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AND CHARLES R. HAUSER

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The ratios of ionization of the α-hydrogen *versus* addition to the carbonyl group of acetophenone by phenylpotassium phenylsodium, and phenyllithium were approximately 10:1, 1.5–2:1 and 1:23, respectively. Similar results were obtained in certain related reactions. They are interpreted on the basis of the influence of the metallic cation. The 1,2- *versus* 1,4-addition of the reagents to benzalacetophenone was studied.

The courses of certain organic reactions with strongly basic or nucleophilic anions are known to be influenced considerably by the metallic cation associated with the anion. Two examples are the substitution *versus* elimination reactions of alkyl halides with alkali diethylamides or phenylalkalies[4] and the condensation of alkali esters with the carbonyl group of ketones *versus* the ionization of their α-hydrogen.[5] In both examples the lithium reagent favors the nucleophilic reaction at the carbon, and the sodium reagent the basic attack at the hydrogen.

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(1) Supported by the Office of Ordnance Research, U. S. Army, and by the Office of Naval Research.

(2) A portion of this work was reported at the Philadelphia meeting of the American Chemical Society, April 1950.

(3) On leave from the University College, Dublin, Ireland.

(4) W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **24**, 416 (1959).

(5) C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 4756 (1953); C. R. Hauser and W. R. Dunnavant, *J. Org. Chem.*, **25**, 1296 (1960).