# Some Reactions of Organotin Hydrides with Organotin Oxides and Alkoxides[1]

Albert K. Sawyer

Contribution from the Department of Chemistry, University of New Hampshire, Durham, New Hampshire. Received September 23, 1964

Reactions of organotin hydrides with organotin oxides at 100° lead to the formation of water and organotin compounds containing tin–tin bonds in all cases investigated. Tri-n-butyltin hydride with bis(tri-n-butyltin) oxide forms water and hexa-n-butylditin. Di-n-butyltin dihydride with di-n-butyltin oxide yields water and di-n-butyltin. Likewise, tri-n-butyltin hydride reacts with di-n-butyltin oxide in a 2:1 hydride–oxide ratio giving water and the previously unreported octa-n-butyltritin. This compound is also obtained from the reaction of di-n-butyltin dihydride with bis(tri-n-butyltin) oxide in a 1:1 hydride:oxide ratio. Upon mixing the reactants at room temperature, hydride–oxide exchange occurs giving tri-n-butyltin hydride and di-n-butyltin oxide. Upon heating at 100° octa-n-butyltritin is formed. Methanol is obtained in substantial yield when di-n-butyltin dihydride reacts with di-n-butyltin dimethoxide at room temperature.

Tri-n-butyltin hydride reacted with bis(tri-n-butyltin) oxide at 100° for several days to give a quantitative yield of water and hexa-n-butylditin (eq. 1). The

$$2Bu_3SnH + (Bu_3Sn)_2O \longrightarrow H_2O + 2Bu_3SnSnBu_3 \quad (1)$$
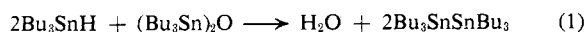
product was characterized by elemental analyses, molecular weight, and bromine titration. This titration showed the quantitative uptake of bromine expected based on 1 mole of bromine per mole of hexa-n-butylditin. This compound has been reported[2] as a by-product (2.4–15%) in the alkylation of stannic chloride or butyltin chlorides using butyl chloride and sodium.
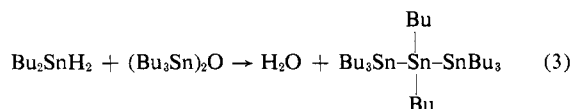
Di-n-butyltin dihydride reacted with di-n-butyltin oxide at 100° for approximately 12 hr. with no gas being evolved, to give a quantitative yield of water and di-n-butyltin (eq. 2). This reaction was also carried

$$Bu_2SnH_2 + Bu_2SnO \longrightarrow H_2O + 2/x(Bu_2Sn)_x \quad (2)$$

out in refluxing toluene. When exposed to air, the product was completely converted to di-n-butyltin oxide. Di-n-butyltin has been previously obtained by the reaction of di-n-butyltin dihydride with acetone,[3] and by the thermal decomposition of di-n-butyltin dihydride at 100°.[4]

Di-n-butyltin dihydride reacted with bis(tri-n-butyltin) oxide at 100° for approximately 8 hr. with less than 5% gas being evolved to give a quantitative yield of

(1) The author wishes to acknowledge the aid of Miss Joyce Brown in the conduct of these experiments. Thanks are also due to M and T Chemicals, Inc., for gifts of chemicals.

(2) J. G. A. Luijten and G. J. N. Van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, Middlesex, England, 1955.

(3) H. G. Kuivila and O. F. Beumel, J. Am. Chem. Soc., 83, 1246 (1961).

(4) A. K. Sawyer and H. G. Kuivila, ibid., 85, 1010 (1963).

water and a colorless liquid with a molecular weight close to that expected for octa-n-butyltritin (eq. 3).

$$Bu_2SnH_2 + (Bu_3Sn)_2O \rightarrow H_2O + Bu_3Sn\underset{\underset{Bu}{|}}{\overset{\overset{Bu}{|}}{Sn}}SnBu_3 \quad (3)$$

Upon mixing the two reactants at room temperature, an initial reaction immediately occurred with complete loss of Sn–H absorption at 1835 cm.$^{-1}$ shown by di-n-butyltin dihydride and appearance of new Sn–H absorption at 1814 cm.$^{-1}$ characteristic of tri-n-butyltin hydride. Di-n-butyltin oxide (97%) and tri-n-butyltin hydride (71%) were recovered (eq. 4). Tri-n-butyltin hydride was isolated by distillation and identified by its Sn–H infrared absorption at 1814 cm.$^{-1}$. At 100°

$$Bu_2SnH_2 + (Bu_3Sn)_2O \xrightarrow[\text{temperature}]{\text{at room}} 2Bu_3SnH + Bu_2SnO \quad (4)$$
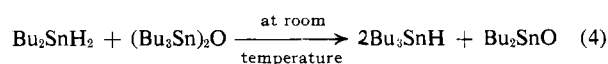
a further reaction occurred (eq. 5) forming the products finally obtained in reaction 3. The exchange of elec-

$$2Bu_3SnH + Bu_2SnO \xrightarrow{\text{at 100°}} H_2O + Bu_3Sn\underset{\underset{Bu}{|}}{\overset{\overset{Bu}{|}}{Sn}}SnBu_3 \quad (5)$$
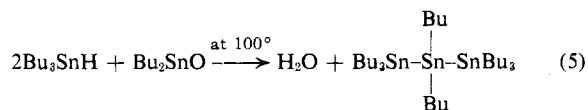
tronegative groups in reaction 4 demonstrates the superiority of di-n-butyltin dihydride over tri-n-butyltin hydride as a reducing agent. This fact has also been demonstrated by Kuivila and Beumel[3] in comparing reactions of organotin hydrides with aldehydes and ketones. Reaction 5 was carried out separately. Octa-n-butyltritin was characterized by elemental analyses, molecular weight, and bromine titration which showed the quantitative uptake of bromine corresponding to 2 moles of bromine per mole of octa-n-butyltritin. Attempted distillation of octa-n-butyltritin at reduced pressure resulted in decomposition with the formation of hexa-n-butylditin. In order to further establish that the product of reaction 5 before attempted distillation was indeed octa-n-butyltritin, rather than a mixture of hexa-n-butylditin and di-n-butyltin, absorption spectra were run in the range of 400–975 mμ. Whereas di-n-butyltin showed one absorption peak with a maximum at 820 mμ, the product of reaction 5 showed only one absorption peak with a maximum at 750 mμ. Octa-n-butyltritin gradually lost its capacity to react rapidly with bromine upon being exposed to air. This is in accord with the observation of Kraus and Greer[5] regarding the instability of 1,3-diethyl-1,1,2,2,3,3-hexamethyltritin on exposure to air. It is believed that this is the only previously reported example of a completely alkyl-substituted tritin.[5a]

(5) C. A. Kraus and W. N. Greer, ibid., 47, 2568 (1925).

In view of the formation of water in all of the reactions of organotin hydrides with organotin oxides which were tried, it was of interest to determine what would happen in the case of an organotin hydride and an organotin alkoxide. When di-*n*-butyltin dimethoxide was mixed neat with di-*n*-butyltin dihydride an exothermic reaction occurred with no gas evolution evident for a period of several days. Methanol (66%) was recovered at reduced pressure at $-70°$, and was identified by comparison with an infrared spectrum of an authentic sample. A viscous, yellow liquid having the appearance of di-*n*-butyltin remained, a portion of which was converted to di-*n*-butyltin oxide by exposure to air. This reaction forming methanol and no hydrogen was unexpected in that an analogous reaction of di-*n*-butyltin diacetate with di-*n*-butyltin dihydride quantitatively forms hydrogen and 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin.[6,7] In the diacetate-dihydride reaction di-*n*-butylacetoxytin hydride was shown to be an intermediate.[6,8] An infrared spectrum of the dimethoxide-dihydride product taken within 10 min. of mixing showed the complete disappearance of Sn-H absorption at 1835 cm.$^{-1}$ characteristic of the starting hydride and the appearance of one new broad band at 1785 cm.$^{-1}$ due to a species as yet unidentified. The simultaneous appearance of strong absorption shown by methanol in the 3000-3360-cm.$^{-1}$ region suggests its rapid formation along with the formation of some organopolytin hydride species such as $Bu_2(OCH_3)$-Sn-Sn(H)Bu$_2$, $Bu_2(H)Sn$-Sn(H)Bu$_2$, and/or others. Such species have been reported to have infrared Sn-H absorption in the 1780-1790-cm.$^{-1}$ region.[4,9] Further work is in progress on the nature of this and related reactions.

The demonstration of the formation of an alcohol in the reaction of an organotin alkoxide with an organotin hydride may have some bearing on the mechanism of the reduction of the carbonyl group by organotin hydrides. It has been postulated that the organotin hydride could add to the carbonyl group forming an intermediate organotin alkoxide which reacts further with the organotin hydride to form the alcohol.[10] Other experimenters have demonstrated that under different conditions the former reaction can occur.[11-14] This experiment is believed to be the first reported specific instance of the latter reaction. The discovery of this reaction and the reaction of an organotin hydride with an organotin oxide to form water and an organotin compound containing a tin-tin bond was previously disclosed by permission of the author.[10]

(5a) NOTE ADDED IN PROOF. The formation of some organoditins and an organotritin by reaction of organotin hydrides with organotin oxides has just recently been noted: W. P. Neumann, *et al.*, *Angew. Chem.*, **76**, 849 (1964), and W. P. Neumann and B. Schneider, **76**, 891 (1964).

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

(7) A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, **27**, 610 (1962).

(8) A. K. Sawyer and H. G. Kuivila, *ibid.*, **27**, 837 (1962).

(9) W. P. Neumann and K. Konig, *Angew. Chem.*, **74**, 215 (1962).

(10) H. G. Kuivila in "Advances in Organometallic Chemistry," Vol. I, Academic Press Inc., New York, N. Y., 1964, p. 70.

(11) W. P. Neumann, H. Niermann, and R. Sommer, *Angew. Chem.*, **73**, 768 (1961).

(12) W. P. Neumann and E. Heymann, *ibid.*, **75**, 166 (1963).

(13) R. Calas, J. Valade, and J. C. Pommier, *Compt. rend.*, **255**, 1450 (1962).

(14) J. Valade and J. C. Pommier, *Bull. soc. chim. France*, 199 (1963).

## Experimental

All reactions involving organotin hydrides and organopolytins were carried out in an atmosphere of prepurified nitrogen (Linde).

Tin analyses were carried out by the method of Gilman and Rosenberg.[15] Carbon and hydrogen analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. Water was determined by Karl Fischer titration and occasionally by direct weighing. Analyses for the presence of tin-tin bonds were carried out using approximately 1.0 $N$ bromine in carbon tetrachloride standardized using excess potassium iodide and standard thiosulfate solution.

Infrared spectra were determined with a Perkin-Elmer Model 21 recording double-beam spectrophotometer with sodium chloride optics. Unless otherwise noted, all samples were run as liquid films.

Organotin hydrides were prepared using established procedures.[3,16] Organotin oxides and methoxide were obtained for use from M and T Chemicals, Inc.

*Reaction of Tri-n-butyltin Hydride with Bis(tri-n-butyltin) Oxide.* Tri-*n*-butyltin hydride (10.36 g., 0.0356 mole) was heated with bis(tri-*n*-butyltin) oxide (10.62 g., 0.0178 mole) for 114 hr. at 100°, during which time no gas evolution was observed, and water[17] (0.0181 mole) was distilled from the reaction mixture. The colorless liquid remaining in the flask, namely hexa-*n*-butylditin, distilled at 166-167° and 0.4 mm. yielding the analytical sample (18.58 g., 0.0320 mole, 90%).

*Anal.* Calcd. for $C_{24}H_{54}Sn_2$: C, 49.69; H, 9.38; Sn, 40.92. Found: C, 49.80; H, 9.18; Sn, 40.46.

Another similar preparation was used to obtain the bromine titration for tin-tin bonds and the molecular weight. Bromine titration of the distillate obtained from this preparation showed 103% of the uptake of bromine expected, based on 1 mole of bromine per mole of hexa-*n*-butylditin. The molecular weight (by thermistor osmometer) was found to be 597 (calculated for hexa-*n*-butylditin, 580).

*Reaction of Di-n-butyltin Dihydride with Di-n-butyltin Oxide.* Di-*n*-butyltin dihydride (14.37 g., 0.0611 mole) was heated with di-*n*-butyltin oxide (15.21 g., 0.0611 mole) for about 12 hr. at 100° during which time no gas evolution was observed and water (0.86 g., 80%) was distilled from the reaction mixture. Water was characterized by a comparison of its infrared spectrum with that of an authentic sample. The viscous, yellow-green liquid remaining in the reaction flask was di-*n*-butyltin similar in its properties and its infrared spectrum to that which had previously been prepared by the thermal decomposition of di-*n*-butyltin dihydride.[4] Bromine titration showed 89% of that expected. It was further characterized by complete conversion to di-*n*-butyltin oxide on exposure to air for several days.

*Anal.* Calcd. for $C_8H_{18}OSn$: Sn, 47.69. Found: Sn, 47.77.

Di-*n*-butyltin dihydride (8.75 g., 0.037 mole) and di-*n*-butyltin oxide (9.27 g., 0.037 mole) were heated to reflux in 50 ml. of toluene for 10 hr. Water was col-

(15) H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **75**, 3592 (1953).

(16) W. J. Considine and J. J. Ventura, *Chem. Ind.* (London), 1683 (1964).

(17) Obtained in a separate experiment.

lected using a Dean–Stark separator (0.60 g., 90%). A portion of the toluene solution of di-*n*-butyltin, exposed to air for 1 day, rapidly turned to a white solid which had the properties of di-*n*-butyltin oxide.

*Anal.* Calcd. for $C_8H_{18}OSn$: Sn, 47.69. Found: Sn, 47.73.

*Reaction of Di-n-butyltin Dihydride with Bis(tri-n-butyltin) Oxide.* Di-*n*-butyltin dihydride (2.35 g., 0.0100 mole) was heated with bis(tri-*n*-butyltin) oxide (5.96 g., 0.0100 mole) for 9 hr. at 100° with less than 5% of gas evolved based on the hydride hydrogen and the recovery of water (0.0105 mole) as a distillate. The nearly colorless liquid remaining in the flask was mainly octa-*n*-butyltritin as shown by its molecular weight and bromine titration.

*Anal.* Calcd. for $C_{32}H_{72}Sn_3$: mol. wt., 813. Found: mol. wt. (thermistor osmometer, 0.098 *m* in toluene), 748.

Bromine titration showed 100% of the expected based on 2 moles of bromine per mole of octa-*n*-butyltritin. Attempted distillation gave a colorless liquid as the distillate and a yellow-green viscous liquid remaining in the flask. The colorless liquid had the properties of hexa-*n*-butylditin, which had previously been prepared.

*Anal.* Calcd. for $C_{24}H_{54}Sn_2$: Sn, 40.92; mol. wt., 580. Found: Sn, 41.00; mol. wt. (thermistor osmometer, 0.070 *m* in toluene), 559.

Upon mixing the two liquid reactants at room temperature, a reaction occurred in which a solid was formed. An infrared spectrum of the mixture taken after mixing showed the presence of tri-*n*-butyltin hydride by the Sn–H absorption at 1814 cm.$^{-1}$ and the complete loss of di-*n*-butyltin dihydride which shows Sn–H absorption at 1835 cm.$^{-1}$. The mixture was taken up in anhydrous ether and filtered giving a white solid, di-*n*-butyltin oxide (97%), as the residue.

*Anal.* Calcd. for $C_8H_{18}OSn$: Sn, 47.69. Found: Sn, 47.50.

Upon evaporation of the solvent, tri-*n*-butyltin hydride (71%) was recovered. Since it was now evident that the water-forming reaction taking place at 100° involved tri-*n*-butyltin hydride and di-*n*-butyltin oxide that reaction was carried out separately.

*Reaction of Tri-n-butyltin Hydride with Di-n-butyltin Oxide.* Tri-*n*-butyltin hydride (7.26 g., 0.0250 mole) was heated with di-*n*-butyltin oxide (3.11 g., 0.0125 mole) for 26 hr. at 100°. No gas was evolved, and water$^{17}$ (0.0129 mole) was obtained as a distillate. Octa-*n*-butyltritin remained in the flask.

*Anal.* Calcd. for $C_{32}H_{72}Sn_3$: C, 47.27; H, 8.93; Sn, 43.80. Found: C, 47.24; H, 8.79; Sn, 44.00.

Another similar preparation was used to obtain the bromine titration for tin–tin bonds and the molecular weight. Bromine titration showed 92% of that expected based on 2 moles of bromine per mole of octa-*n*-butyltritin. The molecular weight (by thermistor osmometer, 0.058 *m* in toluene) was found to be 789 (calculated for octa-*n*-butyltritin, 813).

Visible absorption spectra, using a Bausch and Lomb Spectronic 20 colorimeter, were taken in the range of 400–975 m$\mu$. Hexa-*n*-butylditin was transparent throughout the entire range. Di-*n*-butyltin showed one absorption maximum at 820 m$\mu$, whereas octa-*n*-butyltritin showed one absorption maximum at 750 m$\mu$.

*Reaction of Di-n-butyltin Dihydride with Di-n-butyltin Dimethoxide.* When di-*n*-butyltin dihydride (2.35 g., 0.0100 mole) and di-*n*-butyltin dimethoxide (2.95 g., 0.0100 mole) were mixed, an exothermic reaction occurred giving a clear, homogeneous product. Within 10 min. of mixing, an infrared spectrum was taken showing complete loss of Sn–H absorption at 1835 cm.$^{-1}$ and appearance of a new, single, strong Sn–H absorption at 1785 cm.$^{-1}$. In addition, strong absorption was found in the 3000–3500-cm.$^{-1}$ region which was not shown by either of the starting materials. Upon standing for 2 hr. at room temperature, no gas was evolved, and a yellow color developed in the mixture, which appeared to separate into two layers. About 1 day later, at 1 mm., 0.23 g. (36%) of methanol was collected in a trap at −70°. The condensate was a volatile liquid having the odor of and an infrared spectrum identical with that of an authentic sample of methanol. Over a period of several days additional methanol was collected for an over-all yield of 66%. A small portion of the yellow product upon exposure to air for several days was converted to di-*n*-butyltin oxide.

*Anal.* Calcd. for $C_8H_{18}OSn$: Sn, 47.69. Found: Sn, 47.59.

# Carbonium Ion Salts. VIII. Synthesis of Iodoborates and an Improved Route to Triphenylmethyl Iodide[1,2]

**Kenneth M. Harmon and Frank E. Cummings**

*Contribution from the Department of Chemistry, Harvey Mudd College, Claremont, California. Received July 31, 1964*

*Tropenium and triphenylcarbonium iodoborates have been prepared; these are the first characterized salts of this anion to be reported. The formation of the tropenium salt is an example of hydride ion transfer from carbon to metal. The $^{11}B$ spectra of tetrahaloborate anions have been studied in the course of this work, and an excellent route to triphenylmethyl iodide has been developed.*