

REACTIONS OF *n*-BUTYLTIN HYDRIDES WITH *n*-BUTYLTIN HALIDES\*

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## INTRODUCTION

In a previous paper<sup>1</sup> the reactions of di-*n*-butyltin dihydrides with di-*n*-butyltin dihalides to obtain di-*n*-butyltin halide hydrides were reported. This paper presents the results of investigating other exchanges between *n*-butyltin hydrides and *n*-butyltin halides.

## PROCEDURE

The reactions were followed by observing changes in infrared Sn-H stretching frequencies and changes in chemical shifts in NMR spectra. Characteristic data for each hydride involved, obtained in this and previous work, are summarized in Table I.

TABLE I  
IR AND NMR SPECTRAL DATA FOR *n*-BUTYLTIN HYDRIDES

<i>Hydride</i>	<i>Sn-H band (cm<sup>-1</sup>)</i>	<i>Chemical shift (δ, ppm)</i>	<i>References<sup>a</sup></i>
Bu <sub>2</sub> SnH	1814 <sup>b</sup>	4.84 <sup>b</sup>	[2, 3, 4, 5, 6, 7]
Bu <sub>2</sub> SnH <sub>2</sub>	1835 <sup>b</sup>	4.58 <sup>b</sup>	[2, 3, 5, 8]
BuSnH <sub>2</sub>	1801 <sup>b</sup>	4.33 <sup>b</sup>	[2, 3, 8]
Bu <sub>2</sub> SnHF	1875	7.5 <sup>b</sup>	[1]
Bu <sub>2</sub> SnHCl	1853	7.42	[1, 9]
Bu <sub>2</sub> SnHBr	1847	7.09	[1]
Bu <sub>2</sub> SnHI	1836	6.08	[1]

<sup>a</sup> References are to data previously reported. <sup>b</sup> Values obtained in this work with neat hydride.

The reactions were carried out at room temperature and, unless otherwise noted, were carried out without solvent.

\* A portion of this work, based on her undergraduate thesis, was presented by Miss Joyce Brown at the joint meeting of the Connecticut Valley Section of the American Chemical Society and the New England Association of Chemistry Teachers held at Trinity College, Hartford, Connecticut, April 10th, 1965. A portion of this work was reported by the senior author at the Second International Symposium on Organometallic Chemistry, held at Madison, Wisconsin, August 30th to September 3rd, 1965.

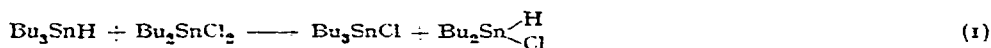
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## RESULTS AND DISCUSSION

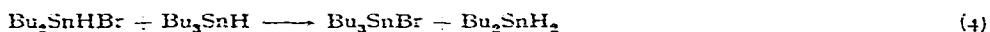
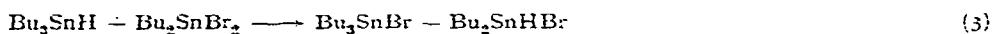
*Tri-n-butyltin hydride and di-n-butyltin dichloride*

Tri-*n*-butyltin hydride and di-*n*-butyltin dichloride were mixed in a 1:1 mole ratio. Spectra run immediately contained no absorption indicative of tri-*n*-butyltin hydride (Sn-H = 1814 cm<sup>-1</sup>;  $\delta$  = 4.90 ppm). Instead, the only absorption present was characteristic of di-*n*-butyltin chloride hydride (Sn-H = 1855 cm<sup>-1</sup>,  $\delta$  = 7.37 ppm).

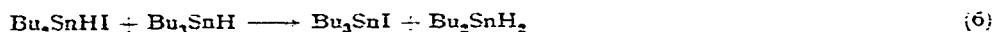
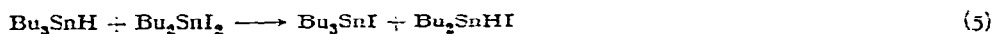
Addition of another mole of tri-*n*-butyltin hydride removed absorption characteristic of di-*n*-butyltin chloride hydride and produced absorption shown by di-*n*-butyltin dihydride (Sn-H = 1833 cm<sup>-1</sup>,  $\delta$  = 4.56 ppm). These changes are represented in eqns. (1) and (2).

*Tri-n-butyltin hydride and di-n-butyltin dibromide*

When tri-*n*-butyltin hydride and di-*n*-butyltin dibromide were mixed in a 1:1 mole ratio, a reaction occurred as shown by spectra taken immediately thereafter. Absorption shown by tri-*n*-butyltin hydride was no longer present. Instead, absorption was found characteristic of di-*n*-butyltin bromide hydride, (Sn-H = 1854 cm<sup>-1</sup>,  $\delta$  = 7.00 ppm). Addition of another mole of tri-*n*-butyltin hydride resulted in a complete loss of absorption shown by di-*n*-butyltin bromide hydride and the simultaneous appearance of absorption due to di-*n*-butyltin dihydride (Sn-H = 1836 cm<sup>-1</sup>,  $\delta$  = 4.57 ppm). These reactions are shown in eqns. (3) and (4).

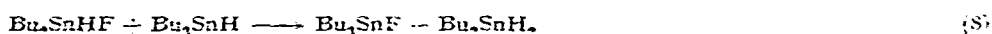
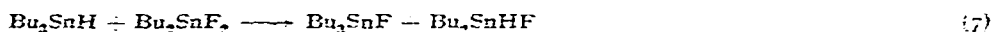
*Tri-n-butyltin hydride and di-n-butyltin diiodide*

Mixing tri-*n*-butyltin hydride with di-*n*-butyltin diiodide resulted in loss of absorption shown by tri-*n*-butyltin hydride and appearance of absorption by di-*n*-butyltin iodide hydride (Sn-H = 1835 cm<sup>-1</sup>,  $\delta$  = 6.24 ppm). Infrared spectra were of little value in determining whether the product was di-*n*-butyltin iodide hydride (Sn-H = 1836 cm<sup>-1</sup>) or di-*n*-butyltin dihydride (Sn-H = 1835 cm<sup>-1</sup>). However, NMR spectra showed that di-*n*-butyltin iodide hydride ( $\delta$  = 6.08 ppm) was present rather than di-*n*-butyltin dihydride ( $\delta$  = 4.58 ppm). Subsequent treatment with an additional mole of tri-*n*-butyltin hydride showed complete loss of the signal for the iodide hydride and the appearance of a signal for the dihydride at  $\delta$  = 4.60 ppm. These changes are represented in eqns. (5) and (6).



*Tri-n-butyltin hydride and di-n-butyltin difluoride*

When tri-*n*-butyltin hydride was mixed with di-*n*-butyltin difluoride in a 1:1 mole ratio, infrared absorption appeared at 1835  $\text{cm}^{-1}$  and 1870  $\text{cm}^{-1}$ , indicating that both di-*n*-butyltin fluoride hydride and di-*n*-butyltin dihydride were produced [eqns. (7) and (8)]. The formation of both hydrides was probably due to insufficient contact between reactants, since the reaction mixture was a very sticky semisolid material. The NMR spectrum for this reaction was difficult to obtain because of the general insolubility problem. However, by using a mixture of solvents, a very dilute solution could be obtained for which small signals were detected at  $\delta = 7.64$  ppm and 4.53 ppm, indicating the presence of di-*n*-butyltin fluoride hydride and di-*n*-butyltin dihydride, respectively. Excess tri-*n*-butyltin hydride removed the peak at  $\delta = 7.64$  ppm.

*n-Butyltin hydrides and n-butyltin trichloride*

Reactions were carried out between *n*-butyltin hydrides and *n*-butyltin trichloride with the organotin hydride in excess. Table 2 shows the IR and NMR data obtained. The product hydride appeared to be *n*-butyltin trihydride in each case. A freshly prepared authentic sample of *n*-butyltin trihydride showed Sn-H absorption at 1861  $\text{cm}^{-1}$  and a chemical shift of  $\delta = 4.33$  ppm.

TABLE 2

REACTIONS OF EXCESS *n*-BUTYLTIN HYDRIDES WITH *n*-BUTYLTIN TRICHLORIDE

Reactants		Product	Sn-H band	Chemical shift
Hydride	Chloride	hydride	( $\text{cm}^{-1}$ )	( $\delta$ , ppm)
$\text{Bu}_3\text{SnH}$ (excess)	$\text{BuSnCl}_3$	$\text{BuSnH}_3$	1869	4.23
$\text{Bu}_2\text{SnH}_2$ (excess)	$\text{BuSnCl}_2$	$\text{BuSnH}_2$	1862	4.25
$\text{Bu}_2\text{SnHCl}$ (excess)	$\text{BuSnCl}_2$	$\text{BuSnH}_2$	1861	4.20

Reactions were also carried out between these same organotin hydrides and *n*-butyltin trichloride with the trichloride in excess. In each case the initial hydride completely disappeared as a vigorous reaction occurred with deposition of solid, accompanied by rapid gas evolution. Production of a new hydride with Sn-H absorption at about 1917  $\text{cm}^{-1}$  and with a chemical shift of  $\delta =$  about 9.11 ppm was observed. This new hydride, believed to be *n*-butyltin dichloride hydride, is highly unstable, decomposing completely within a few minutes at room temperature, leaving no trace of organotin hydride. It was possible, however, during this time to obtain the data shown in Table 3. A rapid reaction between *n*-butyltin trihydride and *n*-butyltin trichloride (equal volumes of each on an infrared cell) produced absorption only at 1917  $\text{cm}^{-1}$ , indicating formation of the same hydride.

Some reactions were run at concentrations intermediate between excess organotin hydride and excess *n*-butyltin trichloride with the hope that *n*-butyltin chloride dihydride might be detected. In most cases the product hydride was only that which

TABLE 3

REACTIONS OF *n*-BUTYLTIN HYDRIDES WITH EXCESS *n*-BUTYLTIN TRICHLORIDE

Reactants		Product hydride	Sn-H band ( $cm^{-1}$ )	Chemical shift ( $\delta$ , ppm)
Hydride	Chloride			
Bu <sub>3</sub> SnH	BuSnCl <sub>3</sub> (excess)	BuSnHCl <sub>2</sub>	1917	9.11
Bu <sub>2</sub> SnH <sub>2</sub>	BuSnCl <sub>3</sub> (excess)	BuSnHCl <sub>2</sub>	1913	9.07
Bu <sub>2</sub> SnHCl	BuSnCl <sub>3</sub> (excess)	BuSnHCl <sub>2</sub>	1918	9.12

we had previously obtained. However, in some NMR spectra a small transient peak appeared at approximately  $\delta = 7.18$  ppm and in one infrared spectrum a band was present at  $1877\text{ cm}^{-1}$ . These data may indicate the presence of *n*-butyltin chloride dihydride.

In summary, from *n*-butyltin trichloride three hydrides were anticipated and three were found. In Table 4 there is summarized the information regarding these hydrides and the reasons for the assignments.

TABLE 4

HYDRIDES FROM *n*-BUTYLTIN TRICHLORIDE

IR ( $cm^{-1}$ )	NMR (ppm)	Assigned	Basis
1861	4.26	BuSnH <sub>3</sub>	Use of excess reactant hydride Comparison with an authentic sample
1877	7.18	BuSnH <sub>2</sub> Cl	Only other hydride Comparison with predicted value
1913	9.12	BuSnHCl <sub>2</sub>	Use of excess trichloride

Substitution of a chlorine for a hydrogen atom in di-*n*-butyltin dihydride results in increased Sn-H frequency in di-*n*-butyltin chloride hydride. We are thus prone to regard the hydride with the highest infrared frequency as *n*-butyltin dichloride hydride and the one with the next highest frequency as *n*-butyltin chloride dihydride. Similar reasoning may be applied to the chemical shifts. Using di-*n*-butyltin dihydride and di-*n*-butyltin chloride hydride as model compounds the infrared frequencies and NMR chemical shifts which might be expected for *n*-butyltin chloride dihydride were calculated. The predicted and observed values are shown in Table 5. We believe that the good agreement found lends support to our assignment of these two new hydrides.

TABLE 5

PREDICTED IR AND NMR VALUES FOR *n*-BUTYLTIN CHLORIDE DIHYDRIDE

	IR ( $cm^{-1}$ )	NMR (ppm)
Bu <sub>2</sub> SnH <sub>2</sub>	1835	4.58
Bu <sub>2</sub> SnHCl	1853	7.42
Shift	18	2.84
BuSnH <sub>3</sub>	1861	4.33
BuSnH <sub>2</sub> Cl		
(Predicted)	1879	7.17
(Found)	1877	7.18

## EXPERIMENTAL

All reactions involving organotin hydrides were carried out in an atmosphere of prepurified nitrogen. Tri-*n*-butyltin hydride, di-*n*-butyltin dihydride, and di-*n*-butyltin chloride hydride were prepared by established procedures<sup>10,11,9</sup>. *n*-Butyltin trihydride was prepared by a method similar to that used by Kuivila and Beumel<sup>11</sup>.

Di-*n*-butyltin dichloride and *n*-butyltin trichloride were obtained from M&T Chemicals, Inc. Di-*n*-butyltin difluoride and di-*n*-butyltin dibromide were prepared by the method of Alleston and Davies<sup>12</sup>. Di-*n*-butyltin diiodide was obtained by reaction of di-*n*-butyltin dichloride with sodium iodide in acetone<sup>1</sup>.

Infrared spectra were run using a Perkin-Elmer model 21 recording double beam spectrophotometer with sodium chloride optics. Proton magnetic resonance spectra were determined with a Varian model A-60 Analytical Nuclear Magnetic Resonance Spectrometer, using tetramethylsilane as an internal standard.

*Tri-n-butyltin hydride and di-n-butyltin dichloride*

Tri-*n*-butyltin hydride (0.19 g, 0.00066 mole) was mixed with di-*n*-butyltin dichloride (0.20 g, 0.00066 mole) at room temperature and an infrared spectrum was taken of the resulting clear solution. The only hydride absorption appeared at 1855  $\text{cm}^{-1}$ .

A sample of di-*n*-butyltin chloride hydride from di-*n*-butyltin dihydride (0.093 g, 0.00040 mole) and di-*n*-butyltin dichloride (0.12 g, 0.00040 mole) was added to tri-*n*-butyltin hydride (0.23 g, 0.00080 mole). The infrared spectrum contained only one strong band at 1833  $\text{cm}^{-1}$ .

For the NMR spectrum, tri-*n*-butyltin hydride (0.40 g, 0.00138 mole) was mixed with di-*n*-butyltin dichloride (0.42 g, 0.00138 mole). The only hydride peak,  $\delta = 7.37$  ppm down field from TMS indicated complete conversion to di-*n*-butyltin chloride hydride. Excess tri-*n*-butyltin hydride was added, and the new spectrum, containing no peak at 7.37 ppm but one at 4.56 ppm, demonstrated the further reaction to form di-*n*-butyltin dihydride.

*Tri-n-butyltin hydride and di-n-butyltin dibromide*

Tri-*n*-butyltin hydride (0.51 g, 0.00175 mole) was added to di-*n*-butyltin dibromide (0.69 g, 0.00175 mole). The infrared spectrum of the mixture contained only one hydride band, at 1854  $\text{cm}^{-1}$ . More tri-*n*-butyltin hydride was added, and the new spectrum showed absorption only at 1836  $\text{cm}^{-1}$ .

For the NMR spectrum tri-*n*-butyltin hydride (0.43 g, 0.00148 mole) was added to di-*n*-butyltin dibromide (0.58 g, 0.00148 mole). The only hydride peak appeared at  $\delta = 7.00$  ppm. The addition of excess tri-*n*-butyltin hydride removed this peak and created one at  $\delta = 4.57$  ppm.

*Tri-n-butyltin hydride and di-n-butyltin diiodide*

Tri-*n*-butyltin hydride (1.42 g, 0.00487 mole) was mixed with di-*n*-butyltin diiodide (2.37 g, 0.00487 mole), and an infrared spectrum taken of the resulting clear, colorless solution. The only hydride band appeared at 1835  $\text{cm}^{-1}$ . When tri-*n*-butyltin hydride (1.42 g, 0.00487 mole) was then added to this solution, the only hydride absorption was still at 1835  $\text{cm}^{-1}$ . No band was present for tri-*n*-butyltin hydride.

For the NMR spectrum, tri-*n*-butyltin hydride (0.38 g, 0.00129 mole) was mixed with di-*n*-butyltin diiodide (0.63 g, 0.00129 mole). The spectrum contained hydride absorption at  $\delta = 6.24$  ppm, indicative of di-*n*-butyltin iodide hydride. Upon addition of excess tri-*n*-butyltin hydride, the peak at 6.24 ppm disappeared, and one appeared at 4.60 ppm.

#### *Tri-n-butyltin hydride and di-n-butyltin difluoride*

Tri-*n*-butyltin hydride (0.28 g, 0.00095 mole) was mixed neat with di-*n*-butyltin difluoride (0.26 g, 0.00095 mole) using a dental amalgamator. The resulting mixture was an extremely sticky semisolid mass. The infrared spectrum of a smear from this mixture contained bands at both  $1835\text{ cm}^{-1}$  and  $1870\text{ cm}^{-1}$ . Formation of both hydrides may be attributable to insufficient contact between reactants.

Another sample was prepared for the determination of NMR data. To a saturated solution of di-*n*-butyltin difluoride in 5 ml of hot methanol were added a few drops of tri-*n*-butyltin hydride in pentane solution. The spectrum was taken immediately of this mixture, which had begun forming a white solid, showing peaks at  $\delta = 7.64$  ppm and 4.53 ppm. Excess tri-*n*-butyltin hydride was added, reducing the magnitude of the 7.64 ppm peak to about the same magnitude as the background.

#### *n-Butyltin hydrides and n-butyltin trichloride*

Because of the instability of the products from exchanges of *n*-butyltin trichloride, the reactions were carried out directly in NMR tubes and on infrared cells and no attempt was made to ensure exact stoichiometries.

Accordingly, to approximately 0.5 ml of tri-*n*-butyltin hydride in an NMR tube was added a dilute solution of *n*-butyltin trichloride in pentane. The spectrum of the cloudy solution was taken immediately and revealed a signal, split into three peaks, at  $\delta = 4.23$  ppm.

Similarly, a dilute solution of *n*-butyltin trichloride in pentane was mixed with excess di-*n*-butyltin dihydride in an NMR tube. The spectrum taken immediately contained peaks at  $\delta = 7.40$  ppm and 4.32 ppm, as well as at  $\delta = 4.66$  ppm, due to excess starting material. Addition of more *n*-butyltin trichloride reduced the peak at  $\delta = 4.66$  ppm, and created one at  $\delta = 7.24$  ppm, possibly due to *n*-butyltin chloride dihydride.

When *n*-butyltin trichloride was mixed neat with excess di-*n*-butyltin chloride hydride, the NMR spectrum showed absorption at  $\delta = 4.26$  ppm, as well as at  $\delta = 7.44$  ppm, due to unreacted starting material. In addition, a small peak was present at  $\delta = 7.18$  ppm, perhaps arising from *n*-butyltin chloride dihydride.

A sample of *n*-butyltin trihydride was prepared by a method similar to that of Kuivila and Beumel<sup>11</sup>. The NMR spectrum of the distilled product exhibited the hydride peak at  $\delta = 4.33$  ppm, and its infrared spectrum showed Sn-H absorption at  $1861\text{ cm}^{-1}$ .

The hydride formed in reactions of hydrides with excess trichloride was highly unstable. For this reason, special attention was required in recording spectra immediately after mixing the reactants. Within approximately 4 minutes of mixing, no evidence remained of the product hydride in either IR or NMR spectra.

A dilute pentane solution of tri-*n*-butyltin hydride (approx. 20%) was mixed in an NMR tube with excess *n*-butyltin trichloride (approx. 50% pentane solution),

and the spectrum was run within one minute of mixing, while a white or yellowish solid formed and gas was evolved. A small peak appeared at  $\delta = 9.11$  ppm.

Using solutions of similar concentrations, di-*n*-butyltin dihydride was mixed with excess *n*-butyltin trichloride, and the spectrum run immediately showed absorption at  $\delta = 9.07$  ppm.

This procedure was repeated with solutions containing di-*n*-butyltin chloride hydride and excess *n*-butyltin trichloride; the spectrum taken immediately contained a peak at  $\delta = 9.12$  ppm. In these latter two experiments also a white or yellowish solid was formed and gas was evolved.

Infrared spectra of these reactions were obtained by mixing directly on the sodium chloride cells one drop of a pure reactant with one drop of a diluted reactant (approx. 20% in pentane), and beginning the spectrum at  $2000\text{ cm}^{-1}$  within 30 seconds of mixing. The reaction mixture on the cells usually bubbled vigorously and deposited a white or yellow solid while the spectrum was being recorded. The various hydride absorptions resulting from these reactions are given in Tables 2 and 3.

One drop of *n*-butyltin trihydride mixed with one drop of *n*-butyltin trichloride on the infrared cells resulted in a spectrum containing hydride absorption only at  $1917\text{ cm}^{-1}$ .

#### ACKNOWLEDGEMENTS

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#### SUMMARY

Tri-*n*-butyltin hydride reacts with di-*n*-butyltin difluoride, di-*n*-butyltin dichloride, di-*n*-butyltin dibromide, and di-*n*-butyltin diiodide in a 1:1 mole ratio to give the respective di-*n*-butyltin halide hydrides. Subsequent reactions with tri-*n*-butyltin hydride yield di-*n*-butyltin dihydride in each case. Reactions of excess tri-*n*-butyltin hydride, di-*n*-butyltin dihydride or di-*n*-butyltin chloride hydride, respectively, with *n*-butyltin trichloride give *n*-butyltin trihydride. When excess *n*-butyltin trichloride is mixed with each of these three hydrides a new, highly unstable organotin hydride is produced which, from IR and NMR data, is believed to be *n*-butyltin dichloride hydride. The same hydride is obtained in the reaction of *n*-butyltin trihydride with *n*-butyltin trichloride. In some reactions of hydrides with *n*-butyltin trichloride, IR and NMR absorptions were found at positions predicted for *n*-butyltin chloride dihydride.

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