DI-*n*-BUTYLTIN HALIDE HYDRIDES

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(Received December 2nd, 1964)

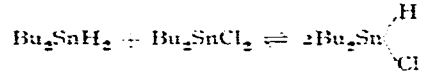
INTRODUCTION

The preparation of di-*n*-butyltin chloride hydride by hydride–halide exchange has been previously reported[1]. Since this was the first example of the preparation of an organotin halide hydride, it was of interest to carry out reactions to prepare other related organotin halide hydrides, and to study their reactions. This paper presents the results of our investigation of the exchange reactions of di-*n*-butyltin dihydride with di-*n*-butyltin difluoride, di-*n*-butyltin dichloride, di-*n*-butyltin dibromide and di-*n*-butyltin diiodide respectively. Very recently, Neumann and Pedain[2] have reported the preparation of several other organotin halide hydrides and their synthetic use, particularly through additions to olefinic and acetylenic systems.

RESULTS AND DISCUSSION

Di-n-butyltin chloride hydride[1]

In the case of di-*n*-butyltin dihydride with di-*n*-butyltin dichloride in a 1:1 mole ratio a reaction occurred upon mixing at room temperature which gave a product with a single Sn–H absorption band in the infra-red at 1853 cm^{-1} along with disappearance of the absorption shown by di-*n*-butyltin dihydride at 1835 cm^{-1}. This behavior indicated that the reaction shown in equation 1 had occurred essentially completely to the right and that the new absorption at higher frequency was that


$$Bu_2SnH_2 + Bu_2SnCl_2 \rightleftharpoons 2Bu_2Sn\begin{matrix}H\\Cl\end{matrix} \qquad (1)$$

for di-*n*-butyltin chloride hydride. That the reaction could be reversed, however, was shown by the fact that attempted distillation at reduced pressure gave di-*n*-butyltin dihydride and di-*n*-butyltin dichloride[1].

Di-n-butyltin bromide hydride

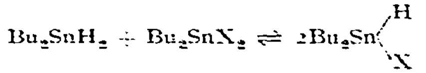
In the case of di-*n*-butyltin dihydride and di-*n*-butyltin dibromide in a 1:1 mole ratio at room temperature similar results were obtained with a new single Sn–H absorption band in the infrared appearing at 1847 cm^{-1} which is believed to be due to the presence of di-*n*-butyltin bromide hydride.

Di-n-butyltin iodide hydride

In the case of di-*n*-butyltin dihydride and di-*n*-butyltin diiodide in a 1:1 mole ratio at room temperature there appeared to be no change in the region of absorption in the infrared on mixing, with the observed absorption at 1836 cm^{-1}. By analogy with the two previous cases it might be reasoned that a reaction had occurred and that the absorption observed at 1836 cm^{-1} was that for di-*n*-butyltin iodide hydride rather than di-*n*-butyltin dihydride. This is not unreasonable in view of the decrease in frequency observed in going from the organotin chloride hydride to the organotin bromide hydride and from the closeness of electronegativities of hydrogen and iodine. The problem to be resolved was whether or not the product obtained on mixing was the expected di-*n*-butyltin iodide hydride or a mixture of the two reactants. We were not able in the two latter cases to crystallize a portion of the product from a solvent at —70° as was the case for the organotin chloride hydride. In the case of the organotin chloride hydride the product crystallized from ether was shown to be identical to that remaining in solution by refractive indices, infrared spectra, melting points, and analyses, all of which corresponded to the theoretical for di-*n*-butyltin chloride hydride[1].

Proton magnetic resonance and infrared spectral data

It has recently been reported[3,4] and observed also in these laboratories, that different organotin hydrides show characteristic chemical shifts for the protons on tin in their NMR spectra. The problem with the organotin iodide hydride was resolved by proton magnetic resonance spectra taken of di-*n*-butyltin dihydride and of mixtures of the dihydride with each of the dihalides, respectively. In the case of the solid di-*n*-butyltin fluoride hydride spectra were run on a dilute solution of the hydride in methanol, in which the hydride was slightly soluble. In each case, upon mixing the reactants in equimolar quantities at room temperature, a new single resonance peak appeared, shifted downfield from the main peak shown by di-*n*-butyltin dihydride. Simultaneously the peak shown by the dihydride disappeared. These results clearly show that, in all of the cases investigated, the reaction indicated below occurs essentially completely to the right on mixing.



$$Bu_2SnH_2 + Bu_2SnX_2 \rightleftharpoons 2Bu_2Sn\begin{matrix}H\\X\end{matrix} \qquad (2)$$

(where X = F, Cl, Br, and I)

The effect of substituting more electronegative groups for one of the hydride hydrogens on the chemical shift due to the other proton attached to the same tin atom is shown in Table 1. There is a progressive shift in δ values in going through the sequence H, I, Br Cl, and F.

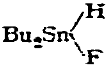
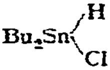
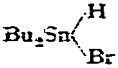
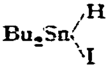
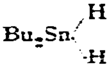
Since NMR spectra showed the product of mixing di-*n*-butyltin dihydride with di-*n*-butyltin diiodide to be solely di-*n*-butyltin iodide hydride, it follows that the infrared absorption obtained at 1836 cm^{-1} is that for Sn–H absorption in the organotin halide hydride.

Di-n-butyltin fluoride hydride

In the case of di-*n*-butyltin dihydride with di-*n*-butyltin difluoride considerable difficulty was encountered because of the lack of solubility at room temperature of both di-*n*-butyltin difluoride and the product obtained on mixing. The product was a

TABLE 1

NMR CHEMICAL SHIFTS AND Sn–H STRETCHING FREQUENCIES FOR DI-*n*-BUTYLTIN HALIDE HYDRIDES AND DI-*n*-BUTYLTIN DIHYDRIDE

Organotin hydrides	*NMR chemical shifts*[a] *δ*[b]	*Infrared frequencies Sn–H band (cm⁻¹)*
 $\mathrm{Bu_2Sn}{<}^{\mathrm{H}}_{\mathrm{F}}$	7.56	1875
 $\mathrm{Bu_2Sn}{<}^{\mathrm{H}}_{\mathrm{Cl}}$	7.42	1853
 $\mathrm{Bu_2Sn}{<}^{\mathrm{H}}_{\mathrm{Br}}$	7.09	1847
 $\mathrm{Bu_2Sn}{<}^{\mathrm{H}}_{\mathrm{I}}$	6.08	1836
 $\mathrm{Bu_2Sn}{<}^{\mathrm{H}}_{\mathrm{H}}$	4.58	1835

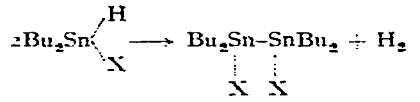
[a] For the proton attached to the tin atom. [b] In parts per million from tetramethylsilane.

sticky solid making it difficult to obtain a complete reaction. Warming for a few minutes at 100° helped but additional heating at 100° resulted in rapid decomposition with gas evolution. In the infrared, upon grinding the reactants in nujol with a slight excess of di-*n*-butyltin difluoride, a new Sn–H band was found at 1875 cm⁻¹ along with a shoulder at 1835 cm⁻¹. In the best of these cases the new band comprised at least 70 % of the total Sn–H absorption. In numerous preparations we were not able to completely eliminate the shoulder at 1835 cm⁻¹ due to the starting hydride. Since the size of this shoulder varied from one preparation to another we are prone to attribute its presence to a lack of complete reaction because of the difficulties mentioned previously with a solid reactant and a solid product, rather than to some equilibrium mixture such as has been shown to exist in the case of di-*n*-butyltin acetate hydride[5]. The new band at 1875 cm⁻¹ we believe is due to di-*n*-butyltin fluoride hydride. This absorption, as might be expected, lies at a higher frequency than that for the other organotin halide hydrides of the series. An infrared spectrum of a dilute solution prepared by mixing equimolar quantities of di-*n*-butyltin difluoride and di-*n*-butyltin dihydride in methanol, showed complete conversion to di-*n*-butyltin fluoride hydride.

Some properties of di-n-butyltin halide hydrides

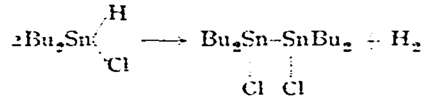
All four of these organotin halide hydrides were quite stable to decomposition involving loss of hydrogen at room temperature. They were, however, not as stable as the parent hydride, di-*n*-butyltin dihydride. For example, di-*n*-butyltin chloride hydride showed no gas evolution during the first ten hours after its formation. By eighteen hours very slow gas evolution had started and over an additional forty hours approximately 10% of the theoretical amount was collected. A small amount of metallic tin also accompanied the decomposition. The decomposition of each of these hydrides at 100° was complete over periods ranging from 20 minutes for the organotin fluoride hydride to six hours for the bromide hydride with nearly quantitative formation of hydrogen. A small amount of tin was obtained in each case but that for di-*n*-butyltin fluoride hydride, varying from a trace to eight percent. By contrast, at 100° di-*n*-butyltin dihydride required eight or more hours to reach a stage in gas evolution (about 70%) at which spectra show no more dihydride present but only absorption for some polytin hydride species at about 1785 cm^{-1}. Prolonged heating was required to remove this last hydride, and no tin was formed in the overall reaction, in which the final product was di-*n*-butyltin[6].

The other main decomposition product might be expected to be a 1,1,2,2-tetra-*n*-butylditin 1,2-dihalide as shown by the following general equation:



$$2\,\mathrm{Bu_2Sn}{\left\langle{}^{\mathrm{H}}_{\mathrm{X}}\right.} \longrightarrow \mathrm{Bu_2}\underset{\mathrm{X}}{\mathrm{Sn}}-\underset{\mathrm{X}}{\mathrm{Sn}}\mathrm{Bu_2} + \mathrm{H_2} \qquad (3)$$

1,1,2,2-Tetra-*n*-butylditin 1,2-dichloride has been reported[7] and its extreme sensitivity for oxidation to bis(di-*n*-butyltin chloride) oxide noted. Due to this, and the fact that the reaction is accompanied by a small amount of a tin-forming reaction, this compound was not obtained analytically pure, but the thermal decomposition yielded a product whose bromine titration showed the formation of 0.97 moles of tin–tin bonds for each two moles of di-*n*-butyltin chloride hydride taken. Upon exposure to air the product was converted to bis(di-*n*-butyltin chloride) oxide. It appears likely then, that, in the case of the thermal decomposition of di-*n*-butyltin chloride hydride the main reaction is the following:

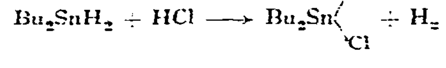


$$2\,\mathrm{Bu_2Sn}{\left\langle{}^{\mathrm{H}}_{\mathrm{Cl}}\right.} \longrightarrow \mathrm{Bu_2}\underset{\mathrm{Cl}}{\mathrm{Sn}}-\underset{\mathrm{Cl}}{\mathrm{Sn}}\mathrm{Bu_2} + \mathrm{H_2} \qquad (4)$$

Exposure to air in the case of di-*n*-butyltin chloride hydride gave bis(di-*n*-butyltin chloride) oxide. Reactions of di-*n*-butyltin chloride hydride with hydrochloric acid and with acetic acid formed hydrogen in each case and di-*n*-butyltin dichloride and di-*n*-butyltin acetate chloride, respectively[1].

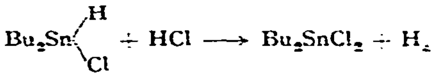
Reaction of di-n-butyltin dihydride with hydrochloric acid in a 1:1 mole ratio

When di-*n*-butyltin dihydride was treated with hydrochloric acid and dioxane at room temperature in a 1:1 mole ratio, abrupt cessation of gas evolution occurred when one mole of hydrogen had been evolved. At this point an infrared spectrum showed only Sn–H absorption at 1853 cm^{-1} corresponding to the formation of di-*n*-butyltin chloride hydride by equation (5).



$$\mathrm{Bu_2SnH_2} + \mathrm{HCl} \longrightarrow \mathrm{Bu_2Sn}{\left\langle{}^{\mathrm{H}}_{\mathrm{Cl}}\right.} + \mathrm{H_2} \qquad (5)$$

Upon further standing very slow gas evolution occurred, in one case giving ten per cent of the hydride hydrogen in the organotin chloride hydride along with a few per cent of tin, in forty hours. Reaction of di-*n*-butyltin dihydride with an excess of hydrochloric acid and dioxane quantitatively gives hydrogen and di-*n*-butyltin dichloride. The demonstration of the formation of di-*n*-butyltin chloride hydride using a 1:1 mole acid/hydride ratio suggests that with excess acid reaction (5) occurs followed by reaction (6).



$$Bu_2Sn(H)(Cl) + HCl \longrightarrow Bu_2SnCl_2 + H_2 \qquad (6)$$

Reaction (6) has been carried out separately[1]. An analogous case has been reported in the reaction of di-*n*-butyltin dihydride with acetic acid, in a 1:1 mole ratio, except that when the acetic acid was used up the dihydride and the organotin acetate hydride were found to exist in a mobile equilibrium[5]. Also no tin was deposited and the subsequent gas evolution and formation of the ditin diacetate were more rapid. Noltes and Van der Kerk have observed that di-*n*-propyltin dihydride and hydrochloric acid in a 1:1 mole ratio at −70° form a product which, when distilled, yields di-*n*-propyltin dihydride and di-*n*-propyltin dichloride[8]. Since it has been shown that di-*n*-butyltin chloride hydride gives di-*n*-butyltin dihydride and di-*n*-butyltin dichloride on attempted distillation, it seems likely, although it remains to be shown, that di-*n*-propyltin chloride hydride was present before distillation.

EXPERIMENTAL

All reactions involving organotin hydrides were carried out in an atmosphere of prepurified nitrogen. Analyses for the presence of tin–tin bonds were carried out using approximately 1.0 *N* bromine in carbon tetrachloride standardized with excess potassium iodide and standard thiosulfate solution. Infrared spectra were run using a Perkin-Elmer model 21, recording double beam spectrophotometer with sodium chloride optics. Unless otherwise noted all samples were run as liquid films. All melting points are uncorrected. NMR spectra were run neat, except for di-*n*-butyltin fluoride hydride, with a Varian Associates A60 NMR spectrometer. Di-*n*-butyltin dihydride was prepared by established procedures[9]. Di-*n*-butyltin difluoride and di-*n*-butyltin dibromide were prepared by the method of Alleston and Davies[10]. Di-*n*-butyltin dichloride was obtained from M & T Chemicals, Inc. and redistilled before use. Di-*n*-butyltin diiodide was obtained by reaction of di-*n*-butyltin dichloride with sodium iodide in acetone, n_D^{25} 1.6022, having properties identical to those reported by Seyferth *et al.*[11].

Di-n-butyltin fluoride hydride

When 0.61 g (0.0026 mole) of di-*n*-butyltin dihydride and 0.70 g (0.0026 mole) of di-*n*-butyltin difluoride were ground together at room temperature in a mortar, a sticky solid resulted. An infrared spectrum of this product, run as a nujol mull, showed new absorption at 1875 cm^{-1} with a shoulder remaining at 1835 cm^{-1}. It was estimated that there was at least a 70 % conversion to the new hydride. The product was essentially insoluble in all of a wide variety of solvents tried. The positions of Sn–H absorption of this hydride and of all of the other organotin halide hydrides are summarized in Table 1. When the product above was heated at 100° for twenty minutes 70 % of gas was evolved, based on the hydride hydrogen, unattended by any trace of tin in the solid product. An infrared spectrum showed that no hydride remained.

Equimolar amounts (0.00369 moles) of both reactants in methanol (25 ml) gave a solution in which both IR and NMR spectra showed complete conversion to di-*n*-butyltin fluoride hydride.

Di-n-butyltin chloride hydride

By the method previously reported[1], di-*n*-butyltin dihydride (2.35 g, 0.0100 mole) was mixed with di-*n*-butyltin dichloride (3.04 g, 0.0100 mole) and an infrared spectrum immediately taken. This spectrum showed no Sn–H absorption characteristic of the starting hydride at 1835 cm^{-1} but instead, new, single, strong absorption at 1853 cm^{-1}. When this product was heated at 100° for three hours, gas was evolved corresponding to 100 % of the theoretical based on hydride hydrogen. About 1 % of tin was recovered along with a clear liquid containing no hydride.

In a separate experiment 5.88 g (0.0250 mole) of di-*n*-butyltin dihydride and 7.60 g (0.0250 mole) of di-*n*-butyltin dichloride were mixed, and heated at 100° until no hydride remained. The liquid product contained a trace of tin (0.07 %) which was removed by filtration of an anhydrous ether solution of the product. Upon evaporation of the ether, bromine titration of the product for the presence of tin–tin bonds showed 97 % of the uptake of bromine expected of 1,1,2,2-tetra-*n*-butylditin 1,2-dichloride. A small amount of the product on exposure to air was converted within a few hours to bis(di-*n*-butyltin chloride) oxide as shown by melting point (110–112°). A mixture melting point with an authentic sample showed no depression. The readiness of the ditin to undergo oxidation to the bis(tin chloride) oxide has been previously noted[7].

Di-n-butyltin bromide hydride

Di-*n*-butyltin dihydride (0.60 g, 0.00255 mole) was mixed with di-*n*-butyltin dibromide (1.009 g, 0.00255 mole) at room temperature and an infrared spectrum taken immediately after mixing. No Sn–H absorption at 1835 cm^{-1} shown by the starting hydride remained, but in its place was found new, single, strong absorption at 1847 cm^{-1}. Attempts to isolate the di-*n*-butyltin bromide hydride from solvent at −70° were unsuccessful. When 0.0100 moles each of di-*n*-butyltin dihydride and di-*n*-butyltin dibromide were mixed and heated at 100° for six hours, 97 % gas evolution occurred based on the hydride hydrogen present. At this time an infrared spectrum showed that no hydride remained. Some tin (8 %) was formed.

Di-n-butyltin iodide hydride

Di-*n*-butyltin dihydride (1.39 g, 0.0059 mole) was mixed with di-*n*-butyltin diiodide (2.88 g, 0.0059 mole) at room temperature and an infrared spectrum immediately taken. Strong Sn–H absorption at 1836 cm^{-1} was present. Since the starting hydride absorbed at 1835 cm^{-1}, attempts were made to isolate di-*n*-butyltin iodide hydride from petroleum ether at −70° without success. NMR spectra were run of di-*n*-butyltin dihydride and of equimolar mixtures of di-*n*-butyltin dihydride with each of the di-*n*-butyltin dihalides. The chemical shifts for the proton attached to the tin atom in each case are shown in Table 1. When 0.0100 mole each of di-*n*-butyltin dihydride and di-*n*-butyltin diiodide were mixed and heated at 100° for two hours, 96 % of gas was evolved based on the hydride hydrogen present. At this time an infrared spectrum of the product showed that no hydride remained. A trace of tin was observed in the liquid product.

Reaction of di-n-butyltin dihydride with hydrochloric acid in a 1:1 mole ratio

To 2.08 g (0.00885 mole) of di-*n*-butyltin dihydride was added with stirring 0.00885 mole of 6.05 *N* hydrochloric acid along with 1.00 ml of dioxane. Hydrogen was rapidly evolved (corrected volume 197 ml, 100 %) whereupon gas evolution ceased. An infrared spectrum of the product showed the absence of absorption at 1835 cm^{-1} such as shown by di-*n*-butyltin dihydride and the appearance of absorption at 1853 cm^{-1} characteristic of di-*n*-butyltin chloride hydride. In a separate experiment di-*n*-butyltin chloride hydride was allowed to stand at room temperature and the amount of gas evolved was measured as a function of time. At the end of ten hours a small amount of finely divided tin was present although no gas had been collected. By the end of eighteen hours very slow gas evolution had started and approximately 10 % of the theoretical amount, based on equation 3, was collected over the next forty hours.

ACKNOWLEDGEMENTS

The authors are grateful for support of this work by grants from the Central University Research Fund of the University of New Hampshire. Mr. EARL HANSON assisted in this work under these grants. Miss JOYCE BROWN assisted in this work under an NSF Undergraduate Research Participation Grant to the University of New Hampshire during the summer of 1964. We are grateful to the National Science Foundation for this support. We also are indebted to M & T Chemicals for gifts of chemicals, to Drs. KENNETH ANDERSEN and JOHN MANGRAVITE for running NMR spectra and to the National Science Foundation for a grant, G-22718, to purchase the NMR spectrometer.

SUMMARY

Reactions of di-*n*-butyltin dihydride with di-*n*-butyltin dihalides lead to the formation of di-*n*-butyltin halide hydrides. By this method di-*n*-butyltin fluoride hydride, di-*n*-butyltin chloride hydride, di-*n*-butyltin bromide hydride, and di-*n*-butyltin iodide hydride were prepared. Infrared and proton magnetic resonance spectra were obtained showing characteristic Sn–H stretching frequencies in the infrared and characteristic chemical shifts in the magnetic resonance spectra. Di-*n*-butyltin chloride hydride was shown to be formed during the reaction of di-*n*-butyltin dihydride with hydrochloric acid in dioxane with a 1:1 acid/hydride ratio. Thermal decomposition of di-*n*-butyltin chloride hydride at 100° gave mainly hydrogen and 1,1,2,2-tetra-*n*-butylditin 1,2-dichloride.

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