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NOTE

Reactions of tri-*n*-butyltin hydride with diorganotin dichlorides

Tri-n-butyltin hydride has been reported[1] to undergo stepwise redistributions of hydrogen and chlorine on tin with di-n-butyltin dichloride. Neumann[2] has reported that exchanges such as the following occur although no specific examples were given.

$$2R_3SnH + R'_2SnX_2 \rightleftharpoons 2R_3SnX + R'_2SnH_2 \qquad (1)$$

This communication reports the results of our investigations of stepwise redistributions of tri-n-butyltin hydride with several diorganotin dihalides. It was necessary to have spectral data for the diorganotin chloride hydrides in order to determine whether or not redistribution had occurred. The organotin halide hydrides were prepared by the general reaction[2-4] shown in eqn. (2) and their spectral data* along with those for the corresponding diorganotin dihydrides are shown in Table 1.

$$R_2SnH_2 + R_2SnCl_2 \xrightarrow[\text{temperature}]{\text{at room}} 2R_2SnClH \qquad (2)$$

Tri-n-butyltin hydride was found to react with each of the diorganotin dichlorides in a 1 : 1 mole ratio to form the corresponding diorganotin chloride hydrides.

TABLE 1

IR AND NMR SPECTRAL DATA FOR R_2SnH_2 AND R_2SnClH

R	*R_2SnH_2*		*R_2SnClH*	
	ν(Sn–H) (cm⁻¹)	*δ(SnH) (ppm)*	*ν(Sn–H) (cm⁻¹)*	*δ(SnH) (ppm)*
Methyl[a]	1850	4.27	1877	6.98
Ethyl	1835	4.59	1857	7.45
n-Propyl	1830	4.54	1853	7.59
iso-Butyl	1831	4.50	1849	7.54
n-Octyl	1830	4.54	1845	7.44
Cyclohexyl	1816	4.85	1831	7.34
Phenyl	1849	5.73	1879	7.84

[a] Reaction run with a small amount of cyclohexane present.

Addition of a second mole of tri-n-butyltin hydride converted the chloride hydrides to the corresponding dihydrides in each case. The results are summarized in eqns. (3) and (4).

$$n\text{-}Bu_3SnH + R_2SnCl_2 \rightarrow n\text{-}Bu_3SnCl + R_2SnClH \qquad (3)$$

$$n\text{-}Bu_3SnH + R_2SnClH \rightarrow n\text{-}Bu_3SnCl + R_2SnH_2 \qquad (4)$$

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* Since this article was submitted Kawakami, Saito and Okawara[5] have reported data on a number of dialkyltin halide hydrides.

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We have found the overall reactions represented by (3) and (4) to be a convenient way to prepare numerous diorganotin dihydrides. The redistribution reactions take place rapidly and quantitatively at room temperature and the product dihydride may be distilled at reduced pressure or isolated by other appropriate means. We have found the use of the relatively stable, easily prepared, and more easily handled tri-n-butyltin hydride to be preferable to lithium aluminum hydride reductions in many cases.

Experimental

All reactions involving organotin hydrides were carried out in an atmosphere of prepurified nitrogen. Tri-n-butyltin hydride and the organotin dihydrides were prepared by established procedures using lithium aluminum hydride[6-8].

Di-n-butyltin dichloride, dimethyltin dichloride, di-n-propyltin dichloride, di-iso-propyltin dichloride, di-n-octyltin dichloride, dicyclohexyltin dichloride and diphenyltin dichloride were obtained from M & T Chemicals, Inc. Diethyltin dichloride was obtained from Alfa Inorganics, Inc.

Infrared spectra were run using a Perkin–Elmer Model 21 recording double beam spectrophotometer with sodium chloride optics. All samples were run as liquid films. Proton magnetic resonance spectra were determined with a Varian Model A-60 Nuclear Magnetic Resonance Spectrometer, using tetramethylsilane as an external standard. Unless otherwise noted spectra were run neat. Infrared and proton magnetic resonance spectral data pertaining to the following experiments are to be found in Table 2. The chemical shifts reported are for the protons on tin in the organotin compound.

TABLE 2

IR AND NMR SPECTRAL DATA FOR THE PRODUCT HYDRIDE IN THE REACTION OF n-Bu_3SnH WITH R_2SnCl_2

R	1 : 1 *mole ratio*		2 : 1 *mole ratio*	
	$\nu(Sn-H)$ (cm^{-1})	$\delta(SnH)$ (*ppm*)	$\nu(Sn-H)$ (cm^{-1})	$\delta(SnH)$ (*ppm*)
Methyl[a]	1877	7.17	1848	4.43
Ethyl	1856	7.52	1829	4.69
n-Propyl[a]	1854	7.34	1832	4.58
iso-Butyl	1852	7.50	1833	4.51
n-Octyl	1849	7.42	1835	4.59
Cyclohexyl[b]	1825	7.40	1813	4.82
Phenyl[a]	1887	8.07	1858	6.07

[a] Reaction and spectra run with small amount of n-pentane present. [b] Reaction run with small amount of ether present, spectra run after ether had been removed.

Typical details are shown below for reactions involving preparations of the organotin chloride hydrides and for the stepwise reactions indicated by eqn. (3) and (4).

Preparation of di-n-propyltin chloride hydride. Di-n-propyltin dihydride (0.59 g, 0.00287 mole) was added to di-n-propyltin dichloride (0.89 g, 0.00326 mole) and mixed thoroughly at room temperature. The original absorption at Sn–H = 1830 cm^{-1} and $\delta = 4.54$ ppm shown by di-n-propyltin dihydride was completely replaced by new, single, strong absorption at Sn–H = 1853 cm^{-1} and $\delta = 7.59$ ppm, which we have assigned to di-n-propyltin chloride hydride.

Tri-n-butyltin hydride and di-n-octyltin dichloride. Di-n-octyltin dichloride (1.08 g, 0.0026 mole) was mixed with tri-n-butyltin hydride (0.714 g, 0.0025 mole) at room temperature and spectra were run immediately. No absorption remained for tri-n-butyltin hydride (Sn–H = 1814 cm^{-1}, $\delta = 4.84$ ppm) but, instead, absorption was found characteristic of di-n-octyltin chloride hydride (Sn–H = 1849 cm^{-1}, $\delta = 7.42$ ppm). Tri-n-butyltin hydride (0.748 g, 0.0026 mole) was then added removing the absorption shown by both tri-n-butyltin hydride and di-n-octyltin chloride hydride and producing absorption shown by di-n-octyltin dihydride (Sn–H = 1835 cm^{-1}, $\delta = 4.59$ ppm).

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