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SHORT COMMUNICATION

The reaction of organotin chlorides with sodium borohydride: a new preparation of organotin hydrides

An investigation of the reaction of tri-n-butyltin chloride with sodium borohydride was undertaken in an attempt to synthesize the hypothetical tri-n-butyltin borohydride. While suspensions of sodium borohydride in tri-n-butyltin chloride did not react at room temperature and were apparently unaffected by mild heating (nitrogen atmosphere), they underwent an uncontrollable decomposition at about 160° with the sudden, copious liberation of diborane and the formation of black tar in the reaction vessel. Tri-n-butyltin chloride was also found to be essentially inert at room temperature to aqueous sodium borohydride and to suspensions of sodium borohydride in the usual organic solvents, *e.g.*, ethyl ether and tetrahydrofuran.

However, a virtually instantaneous reaction occurred in which sodium chloride was precipitated without the evolution of diborane when a glycol dimethyl* ether solution of tri-n-butyltin chloride was added at room temperature to a solution of a large molar excess of sodium borohydride in the same solvent. Instead of the desired organotin borohydride, however, almost quantitative amounts of tri-n-butyltin hydride and sodium chloride expected for the equation:

$$2\,(\text{n-C}_4\text{H}_9)_3\text{SnCl} + 2\,\text{NaBH}_4 \rightarrow 2\,(\text{n-C}_4\text{H}_9)_3\text{SnH} + 2\,\text{NaCl} + \text{B}_2\text{H}_6$$

were isolated from the reaction mixture. The failure of any diborane to be evolved during the reaction is in accord with the known formation by diborane of a stable complex with sodium borohydride in glycol dimethyl ethers[1,2].

Various other organotin chlorides were similarly treated with sodium borohydride in glycol dimethyl ethers to determine the scope and utility of the procedure as a preparative method for organotin hydrides. In every case the corresponding organotin hydrides were obtained, with yields generally comparable to those from the

TABLE 1

SUMMARY OF RESULTS

Organotin hydride	*Yield (%)*		*Reference*
	NaBH₄ method	*LiAlH₄ method*	
$(CH_3)_3SnH$	92	Not reported	3
$(CH_3)_2SnH_2$	96	72[a]	3
$n\text{-}(C_4H_9)SnH_3$	16	37	4
$n\text{-}(C_4H_9)_3SnH$	96	74	4
$n\text{-}(C_4H_9)_2SnH_2$	56	66	4
$(C_6H_5)_3SnH$	82	61	4

[a] Yield of crude product.

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* Ethylene glycol dimethyl ether (monoglyme) or diethylene glycol dimethyl ether (diglyme).

reduction of the organotin chlorides by lithium aluminum hydride[3,4,5,6]. These results are summarized in Table I.

It should be noted that those organotin hydrides with normal boiling points under 100° were significantly less volatile from the reaction mixture upon pumping at less than 1 mm and room temperature than would be expected. A striking example of such diminished volatility was obtained during the analogous preparation of an organosilicon hydride. When trimethylchlorosilane was treated with excess sodium borohydride in diglyme, an entirely typical reaction occurred, with the essentially instantaneous precipitation of sodium chloride. Neither diborane nor trimethylsilane (b.p. 6.7°/760 mm[7]) were evolved from the reaction mixture at atmospheric pressure and at a room temperature of 25°. Although no additional sodium chloride was subsequently observed to form, warming the reaction mixture to 30–40° with pumping at less than 1 mm liberated trimethylsilane (84%).

Similar attempts to volatilize the organotin hydrides by warming the reaction mixture either during or after addition of the organotin chloride solution were unsuccessful, as marked thermal decomposition occurred well below temperatures at which the pure organotin hydrides are known to be stable. This thermal instability of the organotin hydrides in the reaction mixtures containing the sodium borohydride–diborane complex resembles, and is in agreement with, the report by Burg and Spielman[8] that diborane catalyzes the thermal decomposition of trimethyltin hydride. The data and observations described herein strongly imply that the initial step in the reaction of organotin chlorides with sodium borohydride is the simple metathesis to sodium chloride and an unstable organotin borohydride. The formation of an organotin borohydride as a reactive intermediate has previously been postulated by Holliday and Jeffers[9] for the reaction of tetramethyltin with aluminum borohydride.

Experimental

Filtrations, extractions, and other manipulative operations were done under nitrogen. Volatile products were separated and purified by standard high vacuum techniques, and identified from their gas-phase infrared spectra as determined on a Perkin–Elmer Model 137 Infracord Spectrophotometer with a 5 cm sodium chloride cell. Solids were identified by a comparison of their X-ray powder diffraction patterns as obtained on a General Electric XRD-5 X-ray Diffractometer, with known patterns from the American Society for Testing Materials X-ray Powder Data File, Pub. No. 48-J, ASTM, Philadelphia, 1960. Refractive indices were measured on a Bausch and Lomb Abbe-3L Refractometer.

The apparatus used throughout this study consisted of a magnetically stirred 3-neck flask fitted with gas inlet, gas outlet, and pressure-equalized dropping funnel. Atmospheric-pressure reactions were carried out under a continuous flow of nitrogen. The absence of white fumes when the effluent gas from an atmospheric-pressure reaction was passed through a pyridine bubbler was taken as an indication that diborane had not been evolved during the reaction[10]. Corroboration for this technique was obtained by an infrared examination of a sample from the pyridine bubbler for the presence of pyridineborane[11]. In those experiments conducted at a reduced pressure, the apparatus was initially flushed with nitrogen and then pumped on at less than 1 mm during the remainder of the experiment.

The glycol dimethyl ethers (Ansul Chemical Co.) employed as solvents were distilled from calcium hydride on a Todd Column. Removal of these solvents from the reaction mixtures was accomplished with a Buchler Flash Evaporator, Model PTFE-1G. Sodium borohydride (Metal Hydrides, Inc. 98% minimum) was used without additional purification. The various organotin chlorides were commercial products and had properties (m.p., b.p., or n_D^{25}) in agreement with literature values.

Examples of the method

It is recommended that organotin hydrides with normal b.p. below 100° be prepared in diglyme, since their volatility affords an easy and complete separation from the diglyme upon flash evaporation. Those organotin hydrides boiling above 100° would best be obtained in monoglyme, as the monoglyme may readily be removed from the reaction mixture by flash evaporation at a sufficiently low temperature to avoid thermal decomposition. The synthesis of tri-n-butyltin hydride from tri-n-butyltin chloride and sodium borohydride was investigated in both solvents, and will serve to illustrate the typical experimental procedures.

(*a*) *Monoglyme solvent.* Tributyltin chloride (19.204 g, 0.05900 mole) in monoglyme (140 ml) was added dropwise at atmospheric pressure to monoglyme (230 ml) containing sodium borohydride (6.2 g, 0.16 mole) and maintained at -10 to $-11°$. On addition of each drop of the tributyltin chloride solution, a seemingly instantaneous reaction occurred with the formation of a white precipitate. At no time during the 30 min required for the addition was the evolution of diborane detected. The reaction mixture was allowed to stand at -10 to $-11°$ for a few min after the last of the tributyltin chloride solution had been added. Without filtration, the entire reaction mixture was then flash evaporated at 0°/2 mm. The residue in the evaporator flask was extracted with ethyl ether, the ether extract filtered, and the ether removed at 180 mm. The clear, colorless liquid product was pumped on at 0°/< 1 mm for about 30 min to yield tributyltin hydride (16.462 g, 0.05656 mole, 96%), with an infrared spectrum identical with lit.[12]; n_D^{25} 1.4715, lit.[13,6] n_D^{25} 1.4711, extrapolated from n_D^{20} 1.4726 and n_D^{22} 1.4720.

(*b*) *Diglyme solvent.* Tributyltin chloride (33.756 g, 0.1037 mole) in diglyme (100 ml) was added dropwise at room temperature and atmospheric pressure to sodium borohydride (7.627 g, 0.2016 mole) in diglyme (250 ml). The resultant white

TABLE 2

SUMMARY OF DATA FOR OTHER ORGANOTIN HYDRIDES PREPARED BY SODIUM BOROHYDRIDE METHOD

Organotin chloride	*(moles)*	*Sodium borohydride (moles)*	*Solvent*	*Organotin hydride*	*Yield (%)*	*Comm.*
$(CH_3)_3SnCl$	0.075	0.26	diglyme	$(CH_3)_3SnH$	92	[a]
$(CH_3)_2SnCl_2$	0.057	0.30	diglyme	$(CH_3)_2SnH_2$	96	[b]
$n\text{-}C_4H_9SnCl_3$			diglyme	$n\text{-}C_4H_9SnH_3$	16	[c]
$(n\text{-}C_4H_9)_2SnCl_2$	0.033	0.17	monoglyme	$(n\text{-}C_4H_9)_2SnH_2$	56	
$(C_6H_5)_3SnCl$	0.019	0.09	monoglyme	$(C_6H_5)_3SnH$	82	[d]

[a] In the flash evaporation, solvent was retained by a 0° trap, product by a $-80°$ trap, and B_2H_6 by a $-196°$ trap. [b] Product retained by a $-126°$ trap. [c] Reaction carried out under vacuum. Extensive decomposition occurred during reaction with evolution of hydrogen and formation of yellow and red solids. Yield is the average of those from experiments at three temp. between room temp. and $-23°$. [d] Purified by short path distillation, b.p. 156–158° (0.15 mm).

precipitate was filtered off, washed with two 25 ml portions of diglyme, and dried *in vacuo* at 150°. While the dried solid gave only an X-ray pattern for sodium chloride (ASTM card No. 5–0628), it reacted with aqueous silver nitrate to form a mixture of metallic silver and silver chloride, indicating the presence in the solid also of some reducing species. After treatment with nitric acid (to destroy the reducing species), the chloride content of this solid was found to be 0.09961 mole (96% of the chloride initially available as tributyltin chloride) by the Mohr method. The diglyme filtrate was flash evaporated at 40°/2 mm immediately following the filtration to yield tributyltin hydride (16.427 g, 0.05644 mole, 54%) with identical properties to those reported for the monoglyme reaction product. A total yield of tributyltin hydride comparable to that of the sodium chloride could be obtained upon repeated flash evaporation of the diglyme filtrate from the reaction mixture. The liquid nitrogen trap protecting the vacuum pump during the flash evaporations was always found to contain diborane[14] and a minute amount of a white solid which slowly evolved diborane upon standing under vacuum at room temperature.

Table 2 summarizes the experiments leading to the other organotin hydrides. The products all had physical properties (b.p., n^t_D and/or infrared spectra) in agreement with those reported in the literature.

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