Convenient One-Pot Synthesis of Hexa-*n*-butylditin from Bis(tri-n-butyltin) Oxide

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Summary: Hexa-n-butylditin is prepared in high yield (83%), by reduction of bis(tri-n-butyltin) oxide with sodium borohydride in ethanol. The first stage is reduction to tri-n-butyltin hydride (not isolated), which rapidly gives hexa-n-butylditin with the loss of hydrogen under the basic reaction conditions.

Over the past 20 years organotin compounds have emerged as versatile reagents in organic synthesis.¹ Hexan-n-butylditin has found widespread use in radicalmediated reactions,² in palladium-catalyzed crosscoupling reactions,³ and as an intermediate for the syntheses of other tin metal-bound compounds.⁴ A number of procedures are available for the synthesis of hexa-*n*-butylditin starting from bis(tri-*n*-butyltin) oxide, and these are summarized in Scheme 1. Thus, reactions of bis(tri-n-butyltin) oxide with tri-n-butyltin hydride (eq 1),⁵ formic acid (eq 2),⁶ magnesium sodium, or potassium in THF (eq 3),⁷ and samarium diiodide in hexamethylphosphoramide (HMPA) (eq 4),⁸ have all been utilized for preparing hexa-n-butylditin. Fairly harsh conditions or long reaction times are required in the first three cases (eq 1-3). The reaction conditions in eq 4 are mild, but expensive samarium diiodide and toxic HMPA are utilized.

Scheme 1

$$\begin{array}{l} Bu_{3}Sn-O-SnBu_{3}+2Bu_{3}Sn-H \xrightarrow{100 \ ^{\circ}C} \\ 2Bu_{3}Sn-SnBu_{3}+H_{2}O \ (1) \end{array}$$

$$\begin{array}{c} \operatorname{Bu}_{3}\operatorname{Sn}-\operatorname{O-Sn}\operatorname{Bu}_{3}+\operatorname{HCO}_{2}\operatorname{H}\xrightarrow{200\ ^{\circ}\operatorname{C}}\\ \operatorname{Bu}_{3}\operatorname{Sn}-\operatorname{Sn}\operatorname{Bu}_{3}+\operatorname{CO}_{2}+\operatorname{H}_{2}\operatorname{O}\ (2)\end{array}$$

$$Bu_{3}Sn-O-SnBu_{3} + Mg \xrightarrow{15 h \text{ reflux}}_{THF} Bu_{3}Sn-SnBu_{3} + MgO (3)$$

$$Bu_{3}Sn-O-SnBu_{3} + 2SmI_{2} \xrightarrow{1 \text{ min}} Bu_{3}Sn-SnBu_{3} + "I_{2}SmOSmI_{2}" (4)$$

We now report that hexa-*n*-butylditin can be prepared in 83% yield by reduction of bis(tri-*n*-butyltin) oxide with sodium borohydride in ethanol at room temperature for 2 h. The conditions are extremely mild, and the workup is simple, as hexa-n-butylditin is not very soluble in ethanol. In order to gain insight into what was happening mechanistically, the reaction was monitored by ¹³C NMR spectroscopy. The first step in the process was the known reduction of tri-n-butyltin oxide with sodium borohydride to give tri-n-butyltin hydride.⁹ This reduction was complete within 5 min, and tri-n-butyltin hydride was identified as the only product in the crude reaction mixture. As time proceeded, the NMR signals for tri-*n*-butyltin hydride diminished, the initially homogeneous reaction mixture became very cloudy, and a heavy oil precipitated. NMR analysis of this precipitated oil showed it to be hexa-n-butylditin. Within 2 h less than 2% of tri-n-butyltin hydride remained in the ethanol layer.

A wide variety of reagents and conditions are known to convert alkyltin hydrides to polyalkylditins. For example, transition-metal salts,¹⁰ solvents such as dimethylformamide,^{11a} bases such as pyridine,^{11b} and even diborane¹² are known to facilitate this reaction.

At present, the mechanism, in our case, for the decomposition of tri-n-butyltin hydride to hexa-n-butylditin is unclear. To check if it was not solely a solvent effect, tri-*n*-butyltin hydride was dissolved in ethanol at room temperature. This solution was directly monitored by ¹³C NMR spectroscopy, and after 24 h only tri*n*-butyltin hydride was detected.

The other possibility was that ethoxide anion, generated by reaction of sodium borohydride with ethanol, was mediating the formation of hexa-n-butylditin. To check this, sodium borohydride was treated with 4 molar equiv of acetaldehyde, to give a solution of sodium tetraethoxyborate. This solution smoothly mediated the formation of hexa-n-butylditin from tri-n-butyltin hydride over 2 h, clearly demonstrating that tri-n-butyltin hydride is unstable in the presence of a boron ethoxide. The other possibility was that tri-*n*-butyltin ethoxide. generated by the reaction of a boron ethoxide with trin-butyltin hydride, was the true catalyst. It is known that sodium ethoxide reacts with tri-*n*-butyltin hydride. to give tri-n-butyltin ethoxide under reaction conditions similar to ours.¹³ There is precedent for reactions of alkyltin hydrides with tin alkoxides to give alkylditins,¹³ with hexa-*n*-butylditin often being formed as a byproduct in hydrostannation reactions of ketones.¹⁴ In order

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to test this hypothesis, tri-*n*-butyltin hydride was treated with tri-*n*-butyltin ethoxide in ethanol at room temperature. The tri-*n*-butyltin hydride was indeed quantitatively converted to hexa-*n*-butylditin (by NMR spectroscopy) inside 3 h, and the concentration of tri*n*-butyltin ethoxide remained constant. Thus, tri-*n*butyltin ethoxide is also capable of catalyzing formation of hexa-*n*-butylditin from tri-*n*-butyltin hydride. However, since a full 1 molar equiv of tri-*n*-butyltin ethoxide takes 3 h to catalyze the formation of hexa-*n*-butylditin, and in our reaction mixtures we cannot detect tri-*n*butyltin ethoxide by NMR spectroscopy, then it seems unlikely that tri-*n*-butyltin ethoxide is the major catalytic entity.

Finally, the stability of tri-*n*-butyltin hydride in ethanol containing 0.1 molar equiv of sodium ethoxide was investigated. The reaction took 14 h, for a complete reaction of tri-*n*-butyl hydride, giving hexa-*n*-butylditin in 86% yield.

Therefore, we conclude that ethoxide anion, generated by the reaction of sodium borohydride with ethanol, is catalyzing the formation of hexa-*n*-butylditin from tri*n*-butyltin hydride. The ready availability of starting materials, and the simplicity of this procedure, should make it the method of choice for preparing hexa-*n*butylditin.

Experimental Section

Proton-decoupled ¹³C NMR spectra were recorded at 125 MHz on a General Electric Omega 500 MHz NMR spectrometer. Chemical shifts was reported in ppm units referenced to tetramethylsilane when deuteriochloroform was used as the solvent. Tin-carbon coupling constants are quoted as the average value of ¹³C-¹¹⁷Sn and ¹³C-¹¹⁹Sn, because for couplings other than ¹J the multiplets were poorly resolved.

Hexa-n-butylditin. Sodium borohydride (143 mg, 3.8 mmol) was added in one portion to a magnetically stirred solution of bis(tri-*n*-butyltin) oxide (3 g, 5.0 mmol) in ethanol (6 mL). Inside 2 min all the sodium borohydride had dissolved and the solution was homogeneous. After 5 min, ¹³C NMR analysis showed the presence of only tri-*n*-butyltin hydride with no bis(tri-*n*-butyltin) oxide remaining. The solution was then stirred for a total of 2 h, after which time it had become

very cloudy and an oily layer had deposited. Water (10 mL) was added and the aqueous layer was extracted with methylene chloride (2 × 10 mL). The combined methylene chloride extracts were dried over magnesium sulfate, filtered, and concentrated. Vacuum distillation gave hexa-*n*-butylditin (2.42 g, 83%) as a clear oil, bp 150–152 °C/1 mmHg. The ¹³C NMR spectrum of this material was identical in every respect with that of an authentic sample of hexa-*n*-butylditin (purchased from Lancaster Synthesis), in good agreement with the literature spectrum.¹⁵ ¹³C NMR spectrum of material obtained: $\delta_{^{13}C}$ (125 MHz, CDCl₃) 30.77 (²J(C-Sn) = 16.6 Hz), 27.56 (³J(C-Sn) = 53.6 Hz), 13.7, 10.01 (¹J(C-Sn) = 236.4 Hz and ²J(Sn-Sn-C) = 38.8 Hz).

For monitoring of the reaction, ¹³C NMR spectra of authentic samples of bis(tri-*n*-butyltin) oxide, tri-*n*-butyltin hydride, tri*n*-butyltin ethoxide, and hexa-*n*-butylditin were recorded in ethanol unlocked and unshimmed. The CH₂ signal for ethanol was set to 57.35 ppm, and the chemical shifts given are referenced to this. The quality of the spectra obtained was surprisingly good. Direct monitoring of crude reaction mixtures by ¹³C NMR spectroscopy allowed quantification of the species involved.

Bis(tri-n-butyltin) oxide: $\delta_{^{13}C}$ (125 MHz, EtOH) 28.31 ($^{2}J(C-Sn) = 20.7$ Hz), 27.45 ($^{3}J(C-Sn) = 68.44$ Hz), 15.52 ($^{1}J(C-Sn) = 405.1$ Hz), 13.5.

Tri-*n***-butyltin hydride**: $\delta_{^{13}C}$ (125 MHz, EtOH) 30.36 ($^{2}J(C-Sn) = 21.2 \text{ Hz}$), 27.48 ($^{3}J(C-Sn) = 51.0 \text{ Hz}$), 13.71, 8.23 ($^{1}J(C-Sn) = 334.8 \text{ Hz}$).

Tri-*n***-butyltin ethoxide**: $\delta_{^{13}C}$ (125 MHz, EtOH) 57.35, 28.48 ($^{2}J(C-Sn) = 20.3$ Hz), 27.61 ($^{3}J(C-Sn) = 64.7$ Hz), 18.15, 15.37 ($^{1}J(C-Sn) = 387.51$ Hz), 13.59.

Hexa-n-butylditin: $\delta_{^{13}C}$ (125 MHz, EtOH) 31.12 ($^{2}J(C-Sn) = 13.6$ Hz), 27.81 ($^{3}J(C-Sn) = 53.12$ Hz), 13.62, 10.30 ($^{1}J(C-Sn) = 235.9$ Hz and $^{2}J(Sn-Sn-C) = 38.8$ Hz).

Hexa-*n*-butylditin is not very soluble in ethanol. The last spectrum is essentially of neat hexa-*n*-butylditin contaminated with a small amount of ethanol.

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