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Lewis Acid-Promoted Reduction of Bis(triorganotin) Oxides to Hexaorganoditins

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Hexalkylditin is prepared by a Lewis acid-promoted (MgCl_2) reductive reaction of bis(trialkyltin) oxide using magnesium metal as reducing agent. Hexabutyl- and hexaphenylditin are synthesized with 95% and 80% yield separately and a radical mechanism is proposed for the reaction condition. Unsymmetric ditin, $\text{Bu}_3\text{Sn-SnPh}_3$, was first synthesized by this reductive method.

INTRODUCTION

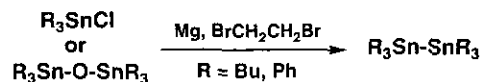
Hexaorganoditins, $\text{R}_3\text{Sn-SnR}_3$, were observed as by-products in the earliest attempts to prepare aliphatic and aromatic tetraorganotins, yet their precise modes of formation can be difficult to interpret even today.¹ Hexaorganoditins are finding increasing application in organic synthesis,²⁻⁴ as photochemically organic radical sources,⁵⁻¹⁰ or as synthetic precursors of tin-metal derivatives.^{11,12} These compounds also show interesting bactericidal and fungicidal activity.¹³ StannyI radicals $\text{R}_3\text{Sn}\cdot$, at present the most used tools for free radical synthesis, are usually obtained from triorganotin hydride or hexaorganoditin.¹⁴ Hexaorganoditins are generally prepared electrolytically¹⁵ or by reactions between organotin halides with metals, tin hydrides with tin oxides, alkoxides or amines¹⁶ and tin oxides with formic acid.¹⁷ The simplest synthetic route to hexaorganotin is the reduction of tin oxide or the coupling reaction of triorganotin chloride.¹⁸ Jousseume *et al.* reported that bis(trialkyltin) oxides can be reduced to hexalkylditins by titanium, magnesium, potassium and sodium.¹⁹ The highest available yield of hexabutyltin $\text{Bu}_3\text{Sn-SnBu}_3$ is 81%. With bis(triphenyltin) oxide, the main product is tetraphenyltin (Ph_4Sn), and the expected hexaphenylditin is produced in less than 20% yield. Unsymmetric ditin ($\text{R}_3\text{Sn-SnR}'_3$) can not easily be synthesized from the simple direct synthetic method.

RESULTS AND DISCUSSIONS

Recently, our laboratory reported an efficient synthesis of organostannane via sonochemical Barbier reaction.²⁰ When Bu_3SnCl was introduced to replace $(\text{Bu}_3\text{Sn})_2\text{O}$ in this reaction, an unexpected product, $\text{Bu}_3\text{Sn-SnBu}_3$, was generated, and no organostannane product was formed. A solu-

tion of Mg and Bu_3SnCl in dry THF was sonicated for 30 minutes. $\text{Bu}_3\text{Sn-SnBu}_3$ was created as the only product, and the highest yield achieved was 40% even at prolonged reaction time. We also observed that hexabutyltin can not be generated from bis(tributyltin) oxide under this ultrasonic condition. Interestingly, hexabutyltin can be afforded from bis(tributyltin) oxide in the presence of Lewis acid (MgBr_2) using magnesium as reducing agent under ultrasound (Scheme I). A solution of Mg, 1,2-dibromoethane and $(\text{Bu}_3\text{Sn})_2\text{O}$ was sonicated for 2 hours, and $\text{Bu}_3\text{Sn-SnBu}_3$ was produced with 45% yield. It has been proposed that MgBr_2 is generated *in situ* when Mg reacts with 1,2-dibromoethane.

Scheme I



We also observed that hexaphenylditin ($\text{Ph}_3\text{Sn-SnPh}_3$) can be generated from bis(triphenyltin) oxide with Lewis acid under this sonochemical reaction condition. It should be noted that the tetraphenyltin (Ph_4Sn) was not formed as unexpected product observed previously under this reaction condition. Therefore, we are interested in the investigations of these reductive reactions of bis(trialkyltin) oxides with different Lewis acids under ultrasound. A solution of $(\text{Bu}_3\text{Sn})_2\text{O}$ (1.0 eq.), Mg (1.2 eq) and Lewis acid (1.1 eq) in anhydrous THF was sonicated for one hour, and the reductive results are shown in Table 1. The results showed that *in situ* generated MgBr_2 is less effective than the added MgBr_2 (powder). Other Lewis acids such as MgCl_2 and ZnCl_2 can not promote the reductive reaction under sonochemical reaction conditions. Bis(tributyltin) oxide is resistant to magnesium as reducing agent in the absence of Lewis acid under

Table 1. Lewis Acid-promoted Sonochemical Reduction

$$(Bu_3Sn)_2O \xrightarrow[\text{ultrasound}]{\text{Mg, "Lewis acid"}} Bu_3Sn-SnBu_3$$

Lewis acid (eq.) ^a	Yield (time) ^b
Mg (2.3), BrCH ₂ CH ₂ Br (1.1)	45% (1 h)
Mg (1.2), MgBr ₂ (1.1)	75% (1 h)
Mg (1.2), MgCl ₂ (1.1)	N.R. ^c (2 h)
Mg (1.2), ZnCl ₂ (1.1)	N.R. ^c (2 h)

^a eq. = molar equivalent to (Bu₃Sn)₂O.^b time = ultrasonic reaction time.^c No reaction and recovery of starting material.

ultrasonic conditions. After many trials, the highest yield was 75% when MgBr₂ was introduced as Lewis acid. It should be noted that a quantitative amount of MgBr₂ is necessary for the improvement of this reductive reaction.

In our laboratory, we have observed that using thermal energy can afford different results from using ultrasound. Therefore, we used refluxing reaction conditions instead of ultrasonic conditions to investigate the Lewis acid-promoted reduction of bis(tributyltin) oxide. A solution of (Bu₃Sn)₂O (1.0 eq.), Mg (1.2 eq.), and Lewis acid (1.1 eq) in anhydrous THF was refluxed for 1-2 hours. The reductive results are shown in Table 2.

The results also showed that the added MgBr₂ is more effective than MgBr₂ generated *in situ* from Mg and 1,2-dibromoethane. Lewis acids such as TiCl₄, ZnCl₂, ZrCl₄ and CuBr do promote the reductive reaction of bis(tributyltin) oxide to hexabutylditin under the thermal reaction conditions whereas Lewis acids such as SnCl₄, AlCl₃, BF₃·OEt₂, CuCl and CuI are ineffective for the reduction of bis(tributyltin) oxide. Surprisingly, Lewis acid MgCl₂ dramatically promotes the reductive reaction under thermal conditions whereas it is ineffective when ultrasound is the energy source. Interestingly, MgCl₂ is the most effective Lewis acid that promotes the reductive reaction of bis(tributyltin) oxide to hexabutylditin in 95% yield after 2 hours refluxing (thermal reaction condition). When a catalytic amount of MgCl₂ (0.4 eq.) was introduced, the yield decreased to 69% after 2 hours of thermal reaction conditions (Table 2). We also investigated the reduction of bis(triphenyltin) oxide with Lewis acid under thermal conditions. A solution of (Ph₃Sn)₂O (1.0 eq.), Mg (1.2 eq.) and MgCl₂ (1.1 eq.) in 5 mL dry THF was refluxed for 10 hours and a yield of 80% of ditin Ph₃Sn-SnPh₃ was produced. A reasonable 74% yield of hexaphenylditin can be achieved after 4 hours of refluxing conditions. It should be noted that the formation of unexpected tetraphenyltin (Ph₄Sn) was not

Table 2. Lewis Acid-promoted Reduction of Bis(tributyltin) Oxide

$$(Bu_3Sn)_2O \xrightarrow[\text{Reflux in THF}]{\text{Mg, "Lewis acid"}} Bu_3Sn-SnBu_3$$

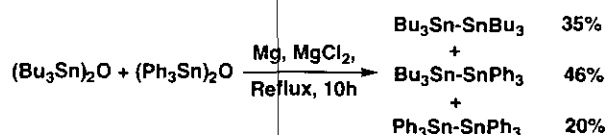
Lewis acid ^a (eq.) ^b	Yield (time) ^c
Mg (2.3), BrCH ₂ CH ₂ Br (1.1)	77% (1 h)
MgBr ₂	77% (1 h)
	84% (2 h)
	90% (1 h)
MgCl ₂	95% (2 h)
MgCl ₂ (0.4)	69% (2 h)
TiCl ₄	44% (1 h)
ZnCl ₂	57% (1 h)
ZrCl ₄	48% (1 h)
SnCl ₄	N.R. ^d (1 h)
AlCl ₃	N.R. ^d (1 h)
BF ₃ ·OEt ₂	N.R. ^d (1 h)
CuBr	23% (2 h)
CuI (or CuCl)	N.R. ^d (2 h)

^a 1.1 eq. of Lewis acid was used without indication.^b eq. = molar equivalent to (Bu₃Sn)₂O.^c time = refluxing time.^d No reaction and recovery of starting material.

observed under thermal conditions.

The mechanism of Lewis acid-promoted reduction of (R₃Sn)₂O to R₃Sn-SnR₃ may involve either an extrusion process (concerted) or a radical process (nonconcerted). In order to understand which pathways may be involved, a crossover experiment was undertaken. A solution of (Bu₃Sn)₂O (1.0 eq.), (Ph₃Sn)₂O (1.0 eq.), Mg (2.4 eq.) and MgCl₂ (2.2 eq.) in 10 mL dry THF was refluxed for 10 hours, and ditins of Bu₃Sn-SnBu₃, Bu₃Sn-SnPh₃, Ph₃Sn-SnPh₃ were produced in yields of 35%, 46%, 20%, separately (Scheme II). The results proved that a concerted mechanism is not involved in the reductive pathway because a crossover product (Bu₃Sn-SnPh₃) was generated. There is another possibility that tin-tin bond (Sn-Sn) cleavage may occur during the reductive reaction. Herewith, a solution of Bu₃Sn-SnBu₃, Ph₃Sn-SnPh₃, Mg and MgCl₂ in THF was refluxed for 10 hours, and both ditins were recovered with >98% yields individually (Scheme III). It means that Sn-Sn bond is stable under the reductive condition and the formation of hexaorganoditin compound comes from bis(trior-

Scheme II



Scheme III



* Reflux, THF, 10h

* Mg (2.4), MgCl₂ (2.2), THF, Reflux, 10h

N. R. = No reaction and recovery of starting material

ganotin) oxide. According to results from the crossover experiments, Lewis-acid promoted reduction mechanism is proposed to undergo a nonconcerted pathway.

In conclusion, we have shown that Lewis acid-promoted reductive reactions provide a convenient new route to hexaorganoditins. In particular, the preparation of hexaorganoditins from bis(triorganotin) oxides (often easily available from industrial sources) is an especially attractive method on a laboratory scale.

EXPERIMENTAL SECTION

General

The ¹H NMR (proton nuclear magnetic resonance) spectra were recorded at 300 MHz (Bruker-AC300P) with deuteriochloroform (CDCl₃, Aldrich 99.8 atom% D) as solvent and internal standard. The ¹³C NMR (carbon nuclear magnetic resonance) spectra were recorded at 75.5 MHz (Bruker-AC300P) with CDCl₃ as the solvent and the internal standard. The ¹¹⁹Sn spectra were measured in CDCl₃ using tetramethylstannane (Me₄Sn) as reference (δ 0). Infrared spectra (IR) were recorded on a BIO-RAD FTS-40 infrared spectrophotometer as a liquid film (neat) or a Nujol mull. Polystyrene was used as a standard, and the spectra are reported in reciprocal centimeters (cm⁻¹). Ultraviolet spectra (UV) were reported on a Shimadzu 3101PC spectrophotometer in the indicated solvent, and are reported in nanometers (nm). Mass spectra (MS) were recorded on VG TRIO-2000 spectrophotometers and are reported in *m/e* units for the most abundant peaks.

All experiments were carried out under a nitrogen atmosphere which was dried primarily by passing through a column of potassium hydroxide (KOH) layered with calcium sulfate (CaSO₄). Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in a recirculating still prior to use. Hexane and ethyl acetate were distilled from calcium hydride, and benzene was distilled from sodium prior to use. Thin-layer chromatography (TLC) analyses were performed on a plastic plate (or aluminum sheet) pre-coated with silica gel (Merck, 5554 Silica gel 60F₂₅₄). Visualization was accomplished by UV light or developed by spraying with a 10% phosphomolybdic acid ethanol solu-

tion. Column chromatography was performed using silica gel (Merck 230-400 mesh) and ethyl acetate/hexane mixtures as eluent. Spectral grade purification by high performance liquid chromatography (HPLC) was carried out using a Rheodyne 7000 sample injector, Jasco PU-980 intelligent pumps, Jasco RI-930 Refractive Index Detector and Phenomenex columns (Spherex 10 Silica).

The Typical Procedure for the Reduction of Bis(triorganotin) Oxide to Hexaorganoditin

A solution of bis(triphenyltin) oxide (3.0 mmol), magnesium powder (3.6 mmol) and magnesium chloride (3.3 mmol) in anhydrous THF (12 mL) is refluxed for ten hours (two hours for bis(tributyltin) oxide). The reaction mixture is cooled to room temperature, and water (20 mL) is added and extracted with diethyl ether (3 × 15 mL). The organic layer is then collected, washed with brine (15 mL), dried with MgSO₄, filtered, and the organic solvent removed under reduced pressure. Further purification is achieved by silica gel flash chromatography and a yield of 80% for hexaphenylditin (Ph₃Sn-SnPh₃) was produced. Under this reaction condition, a yield of 95% for hexabutylditin (Bu₃Sn-SnBu₃) was produced.

Bu₃Sn-SnBu₃

¹H NMR: δ 0.80-1.10 (30H, m), 1.15-1.40 (12H, m), 1.41-1.63 (12H, m). ¹³C NMR: δ 10.0, 13.7, 27.5, 30.6.

The spectral properties are in good agreement with the authentic sample purchased from Aldrich.

Ph₃Sn-SnPh₃

¹H NMR: δ 7.29-7.38 (12H, m), 7.41-7.54 (12H, m), 7.55-7.63 (6H, m). ¹³C NMR: δ 128.5, 128.8, 137.4, 139.1. ¹¹⁹Sn NMR: δ -143.9. UV (*n*-Hexane): λ_{max} = 222 nm (ε = 57,000), 247 nm (ε = 34,000). MS: (calcd. for C₃₆H₃₀Sn₂, M = 700.013). *m/z* 702 (M+2, 2), 700 (M, 2), 698 (3), 356 (5), 355 (12), 351 (base), 349 (78), 347 (50), 311 (4), 309 (8), 307 (6), 305 (4), 197 (43), 195 (32), 193 (29), 155 (10), 154 (34), 153 (10), 120 (45), 118 (35), 116 (20). The spectral properties (¹¹⁹Sn NMR) are in good agreement with those reported in the literature.¹

Bu₃Sn-SnPh₃

¹H NMR: δ 0.79 (9H, t, *J* = 7.2 Hz), 0.88-0.98 (12H, m), 1.10-1.80 (6H, m), 7.25-7.39 (6H, m), 7.40-7.61 (6H, m), 7.62-7.75 (3H, m). ¹³C NMR: δ 10.6 (*J*_{Sn-C} = 277), 13.6, 27.3 (*J*_{Sn-C} = 76), 30.4 (*J*_{Sn-C} = 19), 128.1 (*J*_{Sn-C} = 22), 128.4, 137.3 (*J*_{Sn-C} = 40), 141.0. ¹¹⁹Sn NMR: δ -145.8, -67.8. UV (*n*-Hexane): λ_{max} = 250 nm (ε = 16,960). IR (neat): 3056 (m), 2953 (s), 2925 (s), 2845 (m), 1607 (w), 1478 (w), 1458 (w), 1427 (s), 1071 (s), 997 (m), 723 (s), 697 (s). MS: (calcd. for C₃₀H₄₂Sn₂, M = 640.0418). *m/z* 643 (M+3, 3), 640 (M, 5), 585 (66), 583 (82), 581 (73), 565 (40), 563 (52),

561 (46), 529 (27), 527 (33), 525 (31), 471 (49), 469 (55), 467 (48), 199 (30), 197 (47), 195 (32), 78 (base), 77 (28), 57 (52).

The Sonochemical Reductive Procedure of Bis(tributyltin) Oxide

A solution of bis(tributyltin) oxide (1.0 mmol), magnesium powder (1.2 mmol) and magnesium bromide (1.1 mmol) in anhydrous THF (4 mL) is sonicated for two hours in a commercial ultrasonic cleaning bath²¹ (Crest 575-D, 39 kHz). The solution was passed through a short silica gel column, and the elution is collected, washed with brine (15 mL), dried with MgSO₄, filtered, and the organic solvent removed under reduced pressure. Further purification is achieved by silica gel flash chromatography and eluted with ethyl acetate/hexane. The spectral characterization is obtained by HPLC.

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Key Words

Hexaorganoditin; Bis(triorganotin) oxide; Lewis acid; Reduction.

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21. The ultrasonic cleaning bath was filled with water containing 3-5% detergent. In our laboratory, we use Decon 90 which permits much more even cavitation in the bath water.