

## ELECTROSYNTHETIC ASPECTS OF ORGANOTIN COMPOUNDS

### II \*. A NOVEL SYNTHESIS OF HEXAORGANODITINS

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(Received November 26th, 1980)

#### Summary

Hexaorganoditins were prepared easily in high yield by the electrolysis of triorganotin formates in an undivided cell using a stainless steel cathode and a carbon anode.

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#### Introduction

Hexaorganoditins generally have been prepared [1] from triorganotin halides by using an alkali metal (Na, Li), or from triorganotin hydrides. A patented [2] preparation of hexabutylditin from tributyltin formate by thermolysis is of interest; however, it may also proceed by way of tributyltin hydride [3] and the thermolysis cannot be applied to triphenyltin formate. On the other hand, cyclic voltammetric analysis [4] of organometallic compounds has suggested the formation of Sn—Sn bonds in the course of electrolysis. Habeeb et al. reported [5] electrochemical halogen abstraction reactions of triorganotin halides to form hexaorganoditins using a cadmium anode in which Cd is consumed and converted to  $CdX_2$  ( $X = Cl, Br$ ). Recently, a new organic electro-synthesis reactor [6] using a divided cell with a mercury cathode has been developed for large-scale laboratory preparation of hexaorganoditins from triorganotin chlorides. However, these electro-synthetic procedures are not likely to be used as convenient synthetic methods in the laboratory. We report here a novel electro-synthesis of hexaorganoditins from various triorganotin derivatives which uses an easily available apparatus and does not require a reducing agent such as Cd or Hg.

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\* For part I see ref. 11.

TABLE I  
 ELECTROLYSIS OF R<sub>3</sub>SnX TO R<sub>3</sub>SnSnR<sub>3</sub> AT 15–25°C

R	X	Solvent <sup>a</sup> (ml)	Electrode <sup>b</sup> cathode— anode	Supporting electrolyte (mg)	Constant current (mA)	Applied voltage (V)	Electricity (F/mol(R <sub>3</sub> SnX))	Recovered R <sub>3</sub> SnX (%)	Yield (%) R <sub>3</sub> SnSnR <sub>3</sub>
Ph	OCHO	DMA(8)	C-St		100	20–60	2.5		98
	(2.0)								
Ph	OCHO	DMA(7)	Pt-Pt		50	30–70	2.5		96
	(1.5)								
Ph	OCHO	DMA(8)	C-St	Bu <sub>4</sub> NClO <sub>4</sub> (10)	50	11–13	3.0		89
	(1.5)								
Ph	OCOCH <sub>3</sub>	DMA(8)	C-St	LiClO <sub>4</sub> (5)	50	22–30	3.0	5	91
	(1.5)								
Ph	OCOCH <sub>2</sub> Ph	DMA(8)	Pt-Pt	LiClO <sub>4</sub> (10)	50	10–29	3.0	3	88
	(1.5)								
PhCH <sub>2</sub>	OCHO	DMA(8)	C-St		50	20–40	3.0	15	57
	(2.0)								
p-Tol	OCHO	DMA(7)	C-St		50	21–65	2.5		91
	(1.5)								
n-Bu	OCHO	DMA(6)	Pt-Pt		50	20–30	4.0		68
	(1.5)								
n-Bu	OCOCH <sub>3</sub>	DMA(3)	Pt-Pt	LiClO <sub>4</sub> (10)	50	15–30	4.0		59
	(0.5)								
Ph	SPh	DME(1.5)	Pt-Pt	Bu <sub>4</sub> NClO <sub>4</sub> (40)	20	23–30	4.0	20	73
	(0.3)								
Ph	SPh	DMA(5)	Pt-Pt	Bu <sub>4</sub> NClO <sub>4</sub> (20)	50	15–18	4.0		85
	(1.0)								
Ph	SC(CH <sub>3</sub> ) <sub>3</sub>	DME(1.5)	Pt-Pt	Bu <sub>4</sub> NClO <sub>4</sub> (40)	20	20–30	4.0		74
	(0.3)								
Ph	Cl	DMA(5)	C-St		50	24–9	3.5	48	46
	(1.0)								
Ph	Cl	DME(8)	Pt-Pt	Bu <sub>4</sub> NClO <sub>4</sub> (50)	50	36–60	3.5	60	26
	(2.0)								
Ph	NO <sub>3</sub>	DMA(5)	Pt-Pt		50	10–20	2.5		51
	(1.0)								
Ph	H	DMA(3)	Pt-Pt	Bu <sub>4</sub> NClO <sub>4</sub> (10)	50	22–25	1.8		91
	(0.55)								

<sup>a</sup> DMA = dimethylacetamide, DME = 1,2-dimethoxyethane, <sup>b</sup> C = carbon, St = stainless steel, Pt = platinum.

## Experimental

### General

A simple apparatus consisting of an undivided cell (a flat-bottomed beaker, 2 cm in diameter and 7 cm in height) and two plate-electrodes ( $1.5 \times 2 \text{ cm}^2$ ), was employed. Triorganotin derivatives were electrolyzed using the reaction conditions shown in Table 1.

*Preparation of hexaorganoditin compounds,  $R_3\text{SnSnR}_3$  ( $R = \text{C}_6\text{H}_5$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5\text{CH}_2$ ,  $n\text{-C}_4\text{H}_9$ )*

*i) From formates,  $R_3\text{SnOCHO}$ .* Triphenyltin formate (2 g, 5 mmol) was dissolved in dimethylacetamide (DMA) (8 ml) and electrolyzed at a constant current ( $100 \text{ mA/cm}^2$ ) without supporting electrolyte. After about 1 F/mol of electricity has passed, a white precipitate began to appear, and at the end of the electrolysis with additional 1–1.5 F/mol of electricity, precipitation was almost complete. The crystals were separated by filtration and washed with methanol followed with ether to give pure hexaphenylditin (95%). Concentration of the mother liquor gave additional (3%) ditin. Hexa-*p*-tolyliditin and hexabenzyliditin were obtained similarly.

Tri-*n*-butyltin formate (1.5 g, 4.5 mmol) was dissolved in DMA (6 ml), over which an immiscible layer of hexane was placed for extraction of the product. Electrolysis was carried out in the DMA layer with 4 F/mol of electricity using two platinum electrodes. The hexane layer was separated and concentrated in vacuo. The residue was purified by elution with hexane (30 ml) through a silica gel (ca. 10 g) column (1.5 cm in diameter). Concentration of the eluent gave pure hexabutylditin (68%).

*ii) From the sulfide,  $\text{Ph}_3\text{SnSPh}$ .* (Phenylthio)triphenyltin was dissolved together with a supporting electrolyte (tetrabutylammonium perchlorate) in DMA and electrolyzed with 4 F/mol of electricity to give hexaphenylditin (85%).

The properties of these compounds, including  $^{119}\text{Sn}$  chemical shifts, are shown in Table 2.

TABLE 2  
PROPERTIES OF  $R_3\text{SnSnR}_3$

R	m.p. ( $^{\circ}\text{C}$ ) (reported)	Anal. found (calcd.) (%)			$^{119}\text{Sn}$ chemical shift <sup>a</sup> ( $\delta$ ppm) <sup>b</sup>
		C	H	Sn	
$\text{C}_6\text{H}_5$	236–238 (232[7])	61.48 (61.77)	4.34 (4.32)	33.79 (33.91)	–144
$\text{CH}_3\text{C}_6\text{H}_4$	251–253 (251–252[8])	64.12 (64.33)	5.47 (5.40)	30.11 (30.27)	–141
$\text{C}_6\text{H}_5\text{CH}_2$	148–149 (147–148[9])	64.35 (64.33)	5.56 (5.40)	30.06 (30.27)	–45
$n\text{-C}_4\text{H}_9$					–84 (–83[10])

<sup>a</sup> Measured in  $\text{CHCl}_3$  using JEOL FX-100 at 37.08 MHz ( $30^{\circ}\text{C}$ ). <sup>b</sup> Determined relative to external tetramethyltin ( $\delta = 0$  ppm).

## Discussion

It is noteworthy that hexaphenylditin is obtained almost quantitatively by the electrolysis of triphenyltin formate without a supporting electrolyte \* in dimethylacetamide with good current efficiency. However, triphenyltin chloride gave the ditin with unsatisfactory yield under our reaction conditions and it gave the distannoxane ( $\text{ClPh}_2\text{SnOSnPh}_2\text{OH}$ ) on the electrolysis in methanol [11]. In conclusion, we wish to point out that the synthesis of ditins by Wurtz-type reactions using an active metal or by using Cd or Hg in an electrochemical reaction could be replaced by our electrosynthetic method.

## Acknowledgment

This research was supported by a Grant-in-aid from the Ministry of Education (Japan) for Scientific Research No 474240.

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\* The molecular conductivities of  $\text{Ph}_3\text{SnOCHO}$ ,  $\text{Ph}_3\text{SnCl}$ , and  $\text{Ph}_3\text{SnSPh}$  in DMA under these reaction conditions (0.257 mol/l) were 445, 346, and  $19 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively.