

Synthesis and some properties of mixed alkyl(-)menthyltin dihydrides

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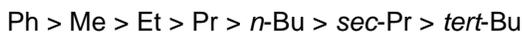
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Introduction

Organotin hydrides have found many applications in organic synthesis not only as reducing reagents [1] but also as intermediates in the generation of carbon-carbon bonds [2], and the synthesis of macrocycles *via* cyclohydrostannation [3]. Since one of the seminal papers on the reduction of carbonyl compounds with organotin hydrides (mono-, di-, and triorganotin hydrides) was published in 1961 [4], mainly the triorganotin hydrides (R_3SnH) have been used routinely for the free radical reduction of alkyl halides and many other functional groups [1,2]. It should be mentioned that at present triphenyltin- and tri-*n*-butyltin hydrides are commercially available. Triorganotin hydrides containing mixed alkyl and (-)-menthyl ligands have been reported [5].

On the other hand, there are less reports on the uses of diorganotin dihydrides (R_2SnH_2), mostly restricted to the use of Ph_2SnH_2 and $n-Bu_2SnH_2$ as reagents for the reduction of carbonyl compounds. We have not found reports on the synthesis of diorganotin dihydrides containing mixed alkyl and (-)-menthyl ligands.

In this communication, we report the synthesis of several diorganotin dihydrides containing a bulky chiral (-)-menthyl substituent and alkyl groups of increasing steric volume. The synthesis was carried out taking into account the reported sequence [6] for the easy of brominolysis of carbon-tin bonds of tetraalkyltins shown below.



Results and discussion

The synthesis of the new organotin compounds was carried out according to Scheme 1. The starting compound containing the optically pure (-)-menthyl ligand was the known (-)-menthyltrimethyltin (**1**) [4], which through brominolysis affords the also known (-)-menthyldimethyltin bromide (**2**) [4].

Dihalogenation of (-)-menthyltrimethyltin (**1**) with 2 equiv of bromine in methanol gives a mixture of (-)-menthylmethyltin dibromide (**3**) and monobromide **2**. The ^{119}Sn showed that in the mixture the ratio **3/2** was 3. As the chromatographic separation of mono and dibromides **2** and **3** was inefficient and vacuum distillation led to high losses, the mixture dissolved in ether was treated with aqueous NaOH. The (-)-menthylmethyltin oxide present in the mixture formed (**A**) precipitated as a compound with a wax like consistence, insoluble in both the aqueous and the ether layers. The oxide was washed with water, decanted, and then treated with conc. HCl. The new (-)-menthylmethyltin dichloride (**5**) thus obtained, was extracted with pentane, dried, and solvent elimination gave **5** (65% yield from **1** as a dense oil. The reduction of dichloride **5** with $LiAlH_4$ in diethylether led to (-)-menthylmethyltin dihydride (**12**) in 91% yield.

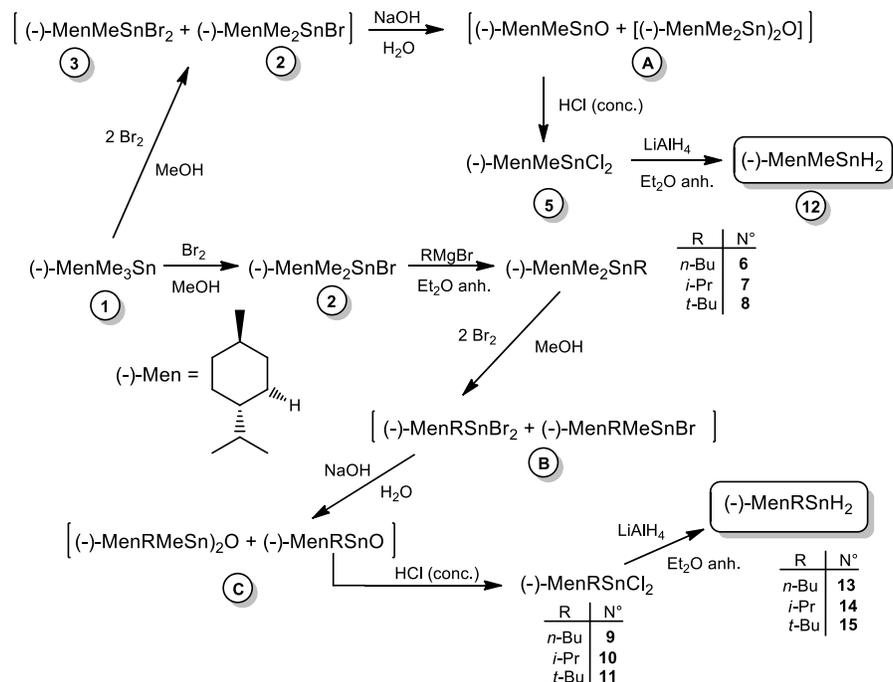
The (-)-menthyldimethyltin bromide (**2**) was alkylated *i*-propylmagnesium bromide, *n*-butyl magnesium bromide, and *t*-butylmagnesium bromide afforded the corresponding (-)-menthylalkyldimethyltin derivatives **6-8** in average yields of 82%. The reactions of tetraalkyltins **6-8** with 2 equiv of bromine in methanol led, again, to the mixtures (**B**) of the corresponding (-)-menthylalkyltin dibromides and monobromide. The mixtures **B** were dissolved in diethyl ether and

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treated with an aqueous solution of NaOH. The resulting mixtures of oxides (**C**) were handled as before, and the treatment with conc. HCl led to the corresponding (-)-menthylalkyltin dichlorides **9-11**. The reduction of dichlorides **9-11** with LiAlH₄ in diethylether under Ar atmosphere led to the (-)-menthylalkyltin dihydrides **13-15** in very good to excellent yields.



Selected values of ¹H, and ¹³C NMR data of the new organotin, i.e., compounds **5**, **6**, **9**, and **10-15**, as well as some physical properties are included in tables 1 and 2.

Table 1. ¹¹⁹Sn NMR data of compounds **5**, **6**, **9**, and **10-15** and specific optical rotatory power of diorganotin hydrides **12-15**.

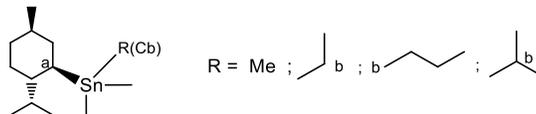
Compound N°	¹¹⁹ Sn NMR ^a			[α] _D ²⁰ (c, ^b ; benzene)
	Chemical shifts (ppm)	[¹ J(¹¹⁹ Sn, ¹³ C)] (Hz)	[¹ J(¹¹⁹ Sn, ¹ H)] (Hz)	
5	116	NO	NO	-31 (0.0208)
6	-7	NO	NO	-26.6 (0.0471)
9	109	NO	NO	-28.2 (0.0189)
10	95	NO	NO	-24.2 (0.0189)
11	79	NO	NO	-21.5 (0.0278)
12	-204	456	1346	-32.5° (0.0278)
13	-191	460	1384	-29.5 (0.0471)
14	-159	463	1387	-31.5° (0.0773)
15	-143	462	1385	-23.8 (0.0230)

^a In CDCl₃ (compounds **5**, **6**, **9**, **10,11**), and C₆D₆ (**12-15**). ^b In gr/mL.

The ¹³C NMR spectra of these compounds showed that all of them were obtained without epimerization at the menthyl carbon directly attached to tin [C(1)] atom. In all cases the 10 menthyl

resonances were clearly distinguishable, and the DEPT experiments together with the magnitude of the $^nJ(^{13}\text{C}, ^{119}\text{Sn})$ coupling constants $|^1J| > |^3J| > |^2J| > |^4J|$ enabled the easy assignment of the signals, and, therefore, to establish the structure of the new compounds.

Table 1. Selected ^1H and ^{13}C NMR values



Comp. N°	^{13}C NMR ^a			^1H NMR ^a
	Me-Sn [$^1J(^{13}\text{C}, ^{119}\text{Sn})$]	C _a -Sn [$^1J(^{13}\text{C}, ^{119}\text{Sn})$]	C _b -Sn [$^1J(^{13}\text{C}, ^{119}\text{Sn})$]	Sn-H [$^1J(^{119}\text{Sn}, ^1\text{H})$]
5	7.68 (345.6)	44.52 (507.2)	---	---
6	-11.56 (283.6) -11.49 (283.6)	31.98 (390.3)	10.13 (328.2)	---
9	---	27.83 (356.4)	50.34 (444.6)	---
10	---	33.54 (396.9)	50.83 (389.6)	---
11	---	45.06 (420.7)	51.85 (339.8)	---
12	-15.51 (328.0)	31.29 (439.5)	---	4.66 (1674)
13	---	31.89 (416.9)	7.27 (353.6)	4.67 (1626)
14	---	32.72 (395.6)	13.80 (392.8)	5.12 (1580)
15	---	51.91 (339.6)	45.18 (422.7)	5.14 (1552)

^a In CDCl_3 (compounds **5**, **6**, **9**, **10**, **11**) and C_6D_6 (**12-15**); chemical shifts in ppm; $^1J(\text{Sn}, \text{C})$ and $^1J(\text{Sn}, \text{H})$ coupling constants (in brackets) in Hz.

Dihydrides **12-15** are dense and, most of them, colorless oils. They remain active for few days in the fridge under an argon atmosphere. At the open air and r.t. they decompose in few hours. These new dihydrides will be used in studies connected with the stereoselective reduction and hydrostannation of prochiral unsaturated systems.

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References and notes

- (a) A. Davies, "Organotin Chemistry", VCH Verlagsgesellschaft, Weinheim, Alemania, 2004. b) C.J. Evans y S. Karpel, "Organotin Chemistry in Modern Technology", Elsevier, Amsterdam, 1985. c) M. Pereyre, J.P. Quintard y A. Rahm, "Tin in Organic Synthesis", Butterworths, London, 1985. d) P.G. Harrison (Editor), "Chemistry of Tin", Blackie and Son, Glasgow, 1999. e) T. Sato, "Comprehensive Organometallic Chemistry II", Vol.8, Pergamon, 1995.
- (a) Mitchell, T.N. *Organotin Reagents in Cross-coupling*, Chapter 4 in "Metal-catalyzed Cross-coupling Reactions", Armin de Meijere and François Diederich Eds.; Wiley-VCH: Weinheim, 2nd Edition, 2004; (b) "Tin Chemistry. Fundamentals, Frontiers, and Applications"; Eds.: Davies, A.G.; Gielen, M.; Pannell, K.H. and Tiekink, E.R.T. John Wiley & Sons, Chichester, 2008.
- (a) Gerbino, D. C.; Koll, L.C.; Mandolesi, S. D.; Podestá, J. C. *Organometallics* **2008**, *27*, 660. (c) Gerbino, D. C.; Scoccia, J.; Koll, L. C.; Mandolesi, S. D.; Podestá, J. C. *Organometallics* **2012**, *31*, 662.
- Kuivila, H. G.; Beumel Jr., O. F. *J. Am. Chem. Soc.* **1961**, *83*, 1246.
- Schumann, H.; Wassermann, B. C. *J. Organomet. Chem.* **1989**, *365*, C1.
- (a) M. H. Abraham, "Electrophilic Substitution at a Saturated Carbon Atom", Eds. C.H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973; p. 70 and references therein cited. (b) Gielen, M. *Acc. Chem. Res.* **1973**, *6*, 198. (c) Ingham, R.K.; Rosenmberg, S.D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459.