

Synthesis and Some Physical Properties of New Organometallic Compounds Containing Si and Sn Atoms [†]

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Abstract: This paper reports the synthesis of two new organotin hydrides containing a (phenyldimethylsilyl)methyl ligand. It was found that the reaction of (phenyldimethylsilyl)methylmagnesium bromide in ether afforded ((phenyldimethylsilyl)methyl) trimethyltin (**3**) (72%), and with (–)-menthyl dimethyltin bromide (**4**) gave (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)dimethyltin (**5**) (84%). Bromo dealkylation of **3** with bromine in MeOH led to ((phenyldimethylsilyl)methyl)dimethyltin bromide (**6**) (82%), which upon reduction with LiAlH₄ yielded ((phenyldimethylsilyl)methyl)dimethyltin hydride (**7**) (95%). The best method for obtaining the corresponding bromostannylated derivative of compound **5**, i.e., (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl) methyltin bromide (**8**) was the exchange reaction between **4** and HgBr₂ that led to **8** with 90% yield. The reduction of bromide **8** with LiAlH₄ gave a diastereomeric mixture of (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)methyltin hydride (**9**). Some physical properties and ¹H, ¹³C, and ¹¹⁹Sn NMR of the new organotin hydrides, as well as that of their intermediate precursors are included.

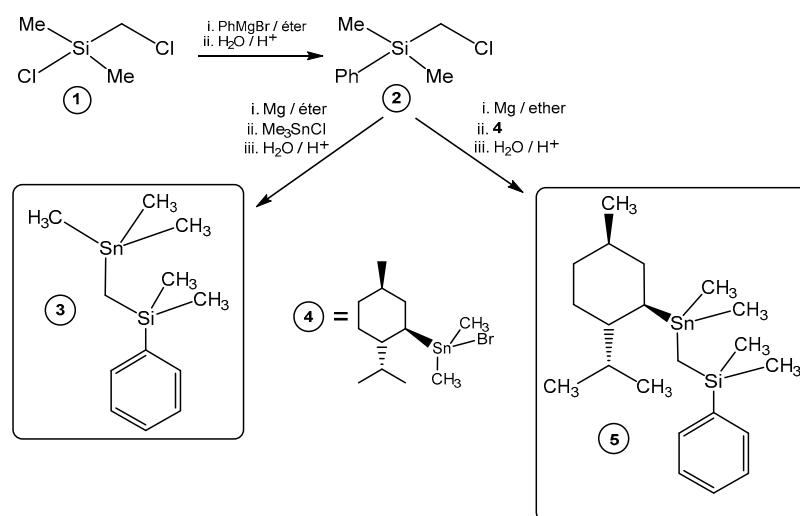
Keywords: organotin silicon compounds; tin(–)-menthyl derivatives; organotin hydrides

1. Introduction

Organotin hydrides have found many applications in organic synthesis, not only as reducing reagents, but also as intermediates in the generation of carbon–carbon bonds, and for the preparation of compounds, such as vinylstannanes, which are invaluable starting materials for cross-coupling reactions [1–3]. In previous studies, we have shown that the size of organic ligands attached to a tin atom affects not only the reactivity, but also the stereoselectivity of the reactions of these compounds [4]. We have also reported the synthesis of tin compounds containing three and two phenyldimethylsilyl)methyl ligands [5,6]. Now, following our investigations on the relationship between the steric volume of the substituents attached to the tin atom and the reactivity, as well as the stereoselectivity of the reactions of organotin hydrides, we considered it important to carry out the synthesis of (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl) methyltin hydride (**9**). This would enable us, in turn, to study the chemical properties of this new hydride that contains two bulky substituents: a (phenyldimethylsilyl)methyl group and a (–)-menthyl group attached to the tin atom.

2. Results and Discussion

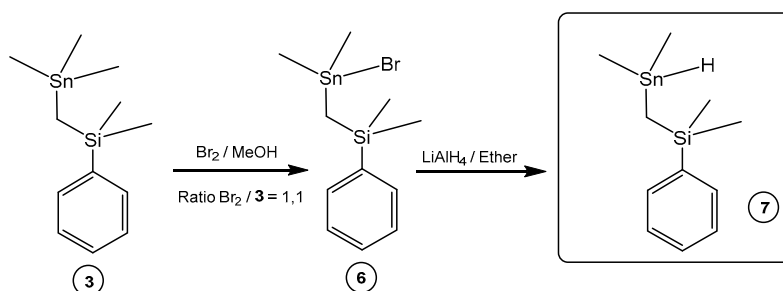
The synthesis of the starting compounds needed for the study was carried out according to Scheme 1. (Chlorodimethylsilyl)methyl chloride (**1**) is commercially available.



Scheme 1. Synthesis of starting compounds with Sn and Si atoms **3** and **5**.

((Phenyldimethylsilyl)methyl)chloride (**2**) was obtained from compound **1** following known procedures [3]. In order to develop the best protocol to reach the tin hydrides, we first obtained ((phenyldimethylsilyl)methyl)trimethyltin **3**. The alkylation of trimethyltin chloride with ((phenyldimethylsilyl)methyl)magnesium chloride in THF, using a ratio Grignard reagent/ Me_3SnCl = 1.1, afforded the new ((phenyldimethylsilyl)methyl)trimethyltin (**3**) in 72% yield. Similarly, the addition of (–)-menthylmagnesium chloride (**4**) in ether to a solution of the same Grignard reagent in THF (ratio Grignard reagent/**4** = 1.4) led to (((phenyldimethylsilyl)methyl) (1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)dimethyltin (**5**) in 84% yield.

The reaction of **3** with bromine (Scheme 2) in methanol—ratio $\text{Br}_2/\mathbf{3}$ = 1.1—led to ((phenyldimethylsilyl)methyl)dimethyltin bromide (**6**) in 82% yield (Scheme 2). The reduction of bromide **6** with LiAlH_4 in diethylether, under argon atmosphere, gave ((phenyldimethylsilyl)methyl) dimethyltin hydride (**7**) in 95% yield.



Scheme 2. Synthesis of ((phenyldimethylsilyl)methyl) dimethyltin hydride (**7**).

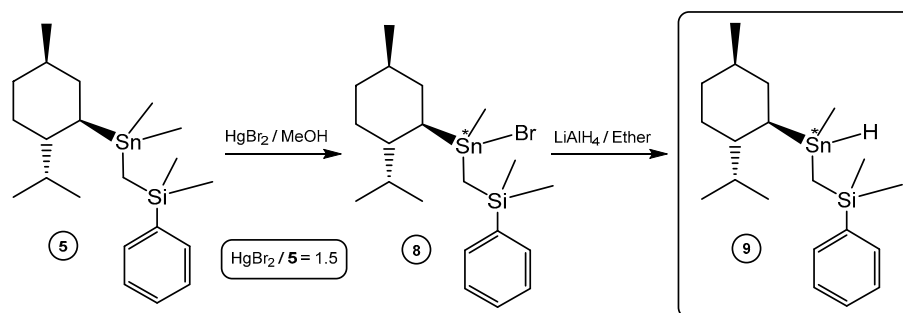
Selected values of ^1H , ^{13}C , and ^{119}Sn -NMR data of the new organotins are included in Table 1.

Table 1. Selected ^1H -, ^{13}C -, and ^{119}Sn -NMR values of ((phenyldimethylsilyl)methyl)trimethyltin (3), ((phenyldimethylsilyl)methyl)dimethyltin bromide (6), and hydride 7 ^a.

	Z N ^o		
	Me	Br	H
	Comp. 3	Comp. 6	Comp. 7
^{13}C -NMR			
Me-Sn (1J)	-7.93 (334.0)	-0.01 (362.0)	-10.46 (347.8)
-CH ₂ Sn (1J)	-5.30 (242.4)	3.88 (257.7)	-7.32 (258.0)
Me-Si [3J (C-Sn)]	0.28 (12.1)	-0.16	-0.09 (14.1)
Ph-Si-CH ₂ -Sn [3J (Ph-Sn)]	141.72 (18.4)	139.70 (20.1)	141.10 (16.6)
^1H -NMR			
Me-Sn [2J (Sn,H), Hz]	-0.02 (s, 2H, NO)	0.57 (56.7)	-0.01 (s, 3H, 56.5); 0.00 (s, 3H, 56.5)
Me-Si	0.57 (s, 6H)	0.47 s, 6H)	0.25 (s, 6H)
Sn-CH ₂	0.00 (s, 9H, 51,7)	0.72 (s, 2H)	-0.12 & -0.11 (2s, 2H)
Sn-H [1J (Sn,H)]	--	--	4.85 (m, 1H, 1739.5)
^{119}Sn -NMR			
	9	135	-96 [1J (Sn,C) = 468] [1J (Sn,H) = 1383]

^a In CDCl₃ (compounds 3 and 6) and C₆D₆ (7); chemical shifts in ppm; nJ (Sn,C) and nJ (Sn,H) coupling constants (in brackets) in Hz. Comp.: compound.

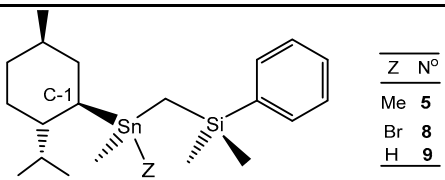
Taking into account the previous results, we carried out a study on the halogenation of compound 5 (Scheme 3). The reaction of 5 with bromine in methanol using ratios Br₂/5 = 1.1–2.2, led in all cases to mixtures of the corresponding mono- and dibromides.

**Scheme 3.** Synthesis of (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methyl cyclohexyl) methyltin hydride (9).

On the other hand, the exchange reaction between 5 and HgBr₂ in methanol using a ratio of HgBr₂/5 = 1.5 gave exclusively (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methyl cyclohexyl)methyltin bromide (8) (Scheme 3) in 87% yield. The reduction of bromide 8 with LiAlH₄ in dry diethylether under argon atmosphere, afforded (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)methyltin hydride (9) in 97% yield.

Selected values of ^1H , ^{13}C , and ^{119}Sn -NMR data of the new organotin 5, 8, and 9 are included in Table 2.

Table 2. Selected ^1H -, ^{13}C -, and ^{119}Sn -NMR values of (((phenyl dimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)dimethyltin (**5**), (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)methyltin bromide (**8**), and hydride **9** ^a.

			
Comp. 5	Comp. 8	Comp. 9	
^{13}C -NMR			
Me-Sn (1J)	-9.13 (297.5) -8.83 (298.2)	2.58 (202.1)	-13.27 (NO)
$-\text{CH}_2\text{Sn}$ (1J)	-7.19 (210.1)	1.95 (197.3)	-8.76 (NO) -8.36 (NO)
C-1-Sn (1J)	32.60 (406.8)	40.08 (426.4) 40.39 (427.0)	32.61 (NO)
Me-Si [$^3J(\text{C-Sn})$]	-7.19 (2101)	-0.32 (18.7) -0.21 (NO) -0.17 (NO) -0.07 (NO)	-11.72 (NO) -11.58 (8.6)
Ph-Si- CH_2 -Sn [$^3J(\text{Ph-Sn})$]	141.71 (15.9)	140.31 (17.7)	141.21 (14.8).
^1H -NMR			
Compound 5	-0.20–0.20 (m, 9H); 0.21–0.42 (m, 6H); 0.60–1.12 (m, 11H); 1.12–1.42 (m, 3H); 1.45–1.90 (m, 4H); 7.25–7.40 (m, 3H); 7.45–7.65 (m, 2H).		
Compound 8 ^b	0.32 (s, 6H, SiMe ₂); 0.42–0.48 (m, 2H); 0.49–0.56 (m, 3H); 0.59–0.71 (m, 2H); 0.72–0.91 (m, 8H); 0.92–1.92 (m, 9H); 7.26–7.35 (m, 3H); 7.40–7.52 (m, 2H).		
Compound 9 ^b	-0.27–0.16 (m, 9H); 0.24–0.39 (m, 6H); 0.65–1.08 (m, 9H); 1.12–1.42 (m, 3H); 1.44–1.95 (m, 3H); 4.91–5.01 [m, 1H, $^1J(\text{Sn,H})$ 1637 Hz]; 6.96–7.23 (m); 7.29–7.40 (m, 3H); 7.41–7.52 (m, 2H).		
^{119}Sn -NMR			
Comp. 5	Comp. 8	Comp. 9	
0.79	132	-214	[$^1J(\text{Sn,C}) = 464$] [$^1J(\text{Sn,H}) = 1388$]

^a In CDCl_3 (compounds **5** and **8**) and C_6D_6 (**9**); chemical shifts in ppm; $nJ(\text{Sn,C})$ and $nJ(\text{Sn,H})$ coupling constants (in brackets) in Hz. ^b Mixture of diastereomers.

These new organotin hydrides will be used in studies connected with the stereoselective reduction and hydrostannation of prochiral unsaturated systems.

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Conflicts of Interest: The authors declare no conflicts of interest.

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