# *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 the (phenyldimethylsilyl)methyl ligand. It was found that the reaction of (phenyldimethylsilyl)methylmagnesium bromide in ether afforded ((phenyldimethylsilyl)methyl) trimethyltin (**3**) (72%), and with (-)-menthyldimethyltin bromide **4** gave (((phenyl dimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)dimethyltin (**5**) (84%). Bromo dealkylation of **3** with bromine in MeOH led to the corresponding monobromide **6** (82%), which upon reduction with $LiAlH_4$ yielded ((phenyldimethyl silyl)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 $HgBr_2$ that led to **8** with 90% yield. The reduction of bromide **8** with $LiAlH_4$ gave a diastereomeric mixture of (((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)methyltin hydride (**9**). Some physical properties, and $^1H$, $^{13}C$, and $^{119}Sn$ NMR of the new organotin hydrides as well as that of their intermediate precursors are included.

### *Keywords*

Organotin silicon compouns, tin-(-)-menthyl derivatives, organotin hydrides

## *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]. In previous studies we have shown that the size of the organic ligands attached to the tin atom affects not only the reactivity but also the stereoselectivity of the reactions of these compounds [2]. We have also reported the synthesis of tin compounds containing three and two phenyldimethylsilyl)methyl ligands [3]. 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-methyl cyclohexyl)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.

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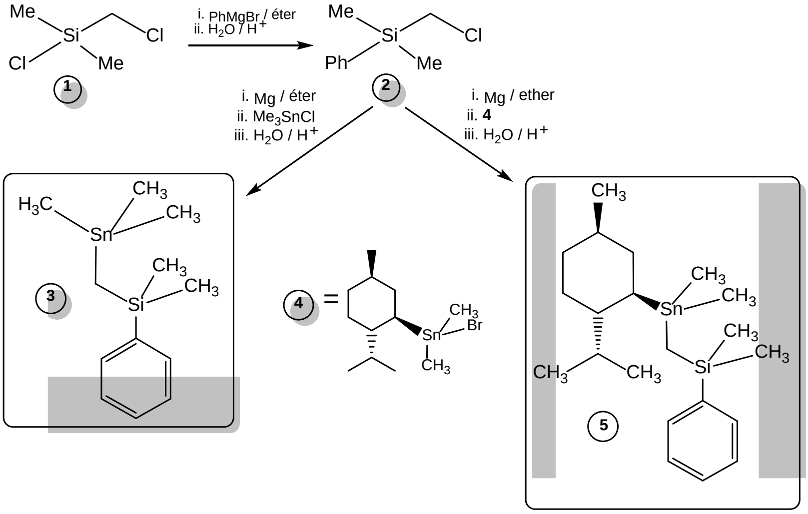
## *Results and Discussion*

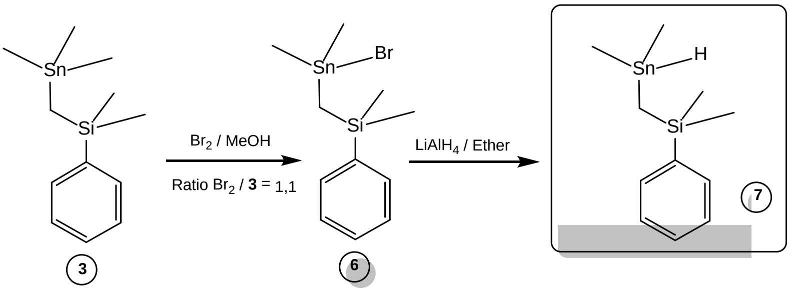
The synthesis of the starting compounds needed for the studies was carried out according to Scheme 1. (Chlorodimetilsilyl)methyl chloride (**1**) is commercially available.



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 obtained in first place **3**. The alkylation of trimethyltin chloride with (phenyldimethyl silyl)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 (-)-menthyldimethyltin bromide (**4**) in ether to a solution of the same Grignard reagent in THF - ratio Grignard reagent/**4** = 1.4 – led to ((((phenyl dimethylsilyl) methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)dimethyltin (**5**) in 84% yield.

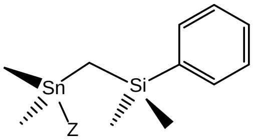
The reaction of **3** with bromine (Scheme 2) in methanol – ratio $Br_2$/**3** = 1.1 – led to ((phenyldimethylsilyl)methyl)dimethyltin bromide (**6**) in 82% yield (Scheme 2). The reduction of bromide **6** with LiAlH4 in diethylether, under argon atmosphere, gave ((phenyldimethylsilyl)methyl) dimethyltin hydride (**7**) in 95% yield.



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

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

Table 1. Selected $^{1}$H-, $^{13}$C- and $^{119}$Sn-NMR values of compounds **3**, **6** and **7**.[a]

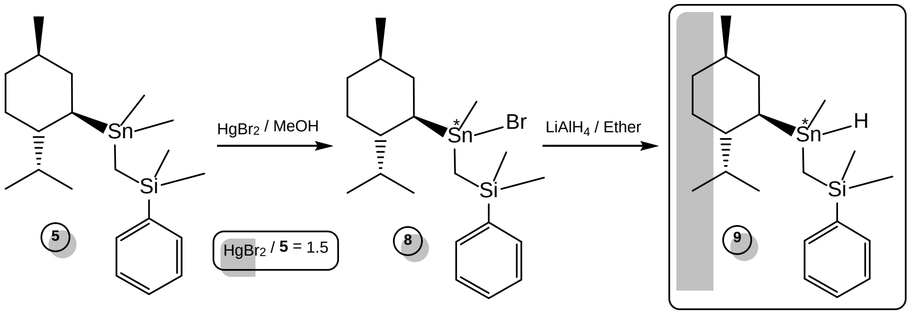


| Z | N° |
|---|---|
| Me | **3** |
| Br | **6** |
| H | **7** |

| | Comp **3**[b] | Comp.**6**[c] | Comp.**7**[d,e] |
|---|---|---|---|
| $^{13}$C-NMR | | | |
| Me-Sn ($^{1}J$) | -7.93 (334.0) | -0.01 (362.0) | -10,46 (347.8) |
| -$CH_2$Sn ($^{1}J$) | -5.30 (242.4) | 3.88 (257.7) | -7.32 (258.0) |
| Me-Si [$^{3}J$(C-Sn)] | 0.28 (12.1) | -0,16 | -0.09 (14.1) |
| Ph-Si-$CH_2$-Sn [$^{3}J$(Ph-Sn)] | 141.72 (18.4) | 139.70 (20.1) | 141.10 (16.6) |
| $^{1}$H-NMR | | | |
| Me-Sn [$^{2}J$(Sn,H), Hz] | -0.02 (s, 2H, NO) | 0.57 (56.7) | -0.01 (s, 3H, 56.5);<br>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 [$^{1}J$(Sn,H)] | -- | -- | 4.85 (m, 1H, 1739.5) |
| $^{119}$Sn-NMR | | | |
| | 9 | 135 | -96 [($^{1}$J(Sn,C) = 468)]<br>[$^{1}$J(Sn,H) = 1383] |

[a] In $CDCl_3$ (compounds **3** and **6**) and $C_6D_6$ (**7**); chemical shifts in ppm; $^{n}J$(Sn,C) and $^{n}$J(Sn,H) coupling constants (in brackets) in Hz.

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 $Br_2$/**5** = 1.1-2.2, led in all cases to mixtures of the corresponding mono- and dibromides.

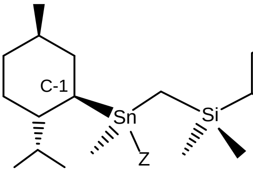


Scheme 3. Synthesis of ((((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methyl cyclohexyl)methyltin hydride (**9**)

On the other hand, the exchange reaction between **5** and $HgBr_2$ in methanol using a ratio $HgBr_2$/**5** = 1.5 gave exclusively the monobromide **8** (Scheme 3) in 87% yield. The reduction of bromide **8** with $LiAlH_4$ in dry diethylether under argon atmosphere, afforded the ((((phenyldimethylsilyl)methyl)(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)methyltin hydride (**9**) in 97% yield.

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

Table 2. Selected $^{1}$H-, $^{13}$C- and $^{119}$Sn-NMR values of compounds **5**, **8** and **9**.[a]



| Z | N° |
|---|---|
| Me | **5** |
| Br | **8** |
| H | **9** |

| | Comp. **5** | Comp. **8** | Comp. **9** |
|---|---|---|---|
| **$^{13}$C-NMR** | | | |
| Me-Sn ($^{1}J$) | -9.13 (297.5)<br>-8.83 (298.2) | 2.58 (202.1) | -13.27 (NO) |
| $-CH_2Sn$ ($^{1}J$) | -7.19 (210.1) | 1.95 (197.3) | -8.76 (NO)<br>-8.36 (NO) |
| C-1-Sn ($^{1}J$) | 32.60 (406.8) | 40.08 (426.4)<br>40.39 (427.0) | 32.61 (NO) |
| Me-Si [$^{3}J$(C-Sn)] | -7.19 (2101) | -0.32 (18.7); -0.21 (NO) -0.17 (NO); -0.07 (NO) | -11.72 (NO)<br>-11.58 (8.6) |
| Ph-Si-$CH_2$-Sn [$^{3}J$(Ph-Sn)] | 141.71 (15.9) | 140.31 (17.7) | 141.21 (14.8). |

| | |
|---|---|
| **$^{1}$H-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, $^{1}J$(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<br>[($^{1}$J(Sn,C) = 464)]<br>[$^{1}$J(Sn,H) = 1388] |

[a] In $CDCl_3$ (compounds **5** and **8**) and $C_6D_6$ (**9**); chemical shifts in ppm; $^{n}J$(Sn,C) and $^{n}$J(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.

## The authors declare no conflict of interest

***Acknowledgements.*** CONICET and UNS of Argentina supported this work. A fellowship from CIC-PBA to VFT is gratefully acknowledged.

## *References*

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