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Synthesis and some reactions of mixed (−)-menthyltin hydrides

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Abstract

The synthesis and physical properties of dineophyl(−)menthyltin (**4**) and methylneophyl (−)menthyltin (**9**) hydrides as well as that of their organotin precursors are described. Whereas the reduction of acetophenone with **4** afforded (−)-(S)-1-phenylethanol in 40% ee, the reduction of the same ketone with dimethyl(−)menthyltin hydride yielded the alcohol with only a 7% ee. Full ^{1}H, ^{13}C, and ^{119}Sn NMR data are given.

Keywords: Tin; Hydrides; Asymmetric synthesis

1. Introduction

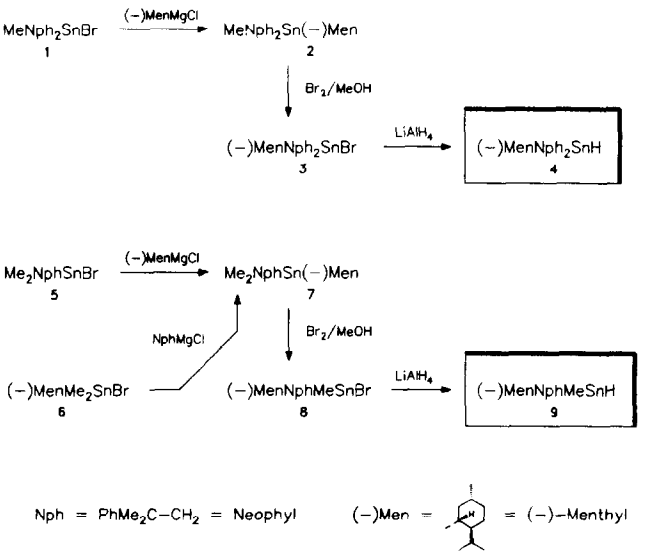
The increasing importance of organotin hydrides in organic synthesis has been evaluated in recent books and reviews [1]. The reduction of gem-dihalides [2] with organotin hydrides as well as the addition of these hydrides to activated olefins [3] takes place stereoselectively. In connection with some studies aiming to determine if any correlation exists between the observed stereoselectivity and the size of the organic ligand attached to the tin atom, we have recently reported the synthesis and some chemical properties of various neophyltin derivatives [4,5], as well as the chemo- and stereoselective reduction and deuteration of (pivaloyloxy)methyl 6,6-dihalopenicillanates with trineophyltin hydride [6] and deuteride [7], respectively.

Taking into account their possible application in the stereoselective transformation of organic prochiral molecules, we considered of interest the synthesis of organotin hydrides containing a combination of bulky and chiral ligands. As the chiral ligand we have chosen the (−)-menthyl group because, besides economic advantages, it can be bound to the tin atom with complete stereoselectivity via the corresponding Grignard reagent as reported by Schumann et al. [8]. In the present paper we report the synthesis, physical properties, and some reactions of dineophyl(−)-menthyltin hydride (**4**) and methylneophyl(−)-menthyltin hydride (**9**).

2. Results and discussion

Organotin hydrides **4** and **9** were obtained according to Scheme 1.

Dineophyl(−)-menthyltin hydride (**2**) was obtained in 88% yield by addition of (−)-menthylmagnesium



Scheme 1.

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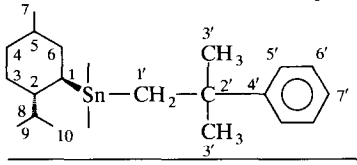
chloride [9] in THF to the known [4] methyldineophyltin bromide (**1**) in benzene (molar ratio Grignard/organotin 1.1). The reaction of **2** with bromine in methanol (molar ratio bromine/**2** 1.1) led to monobromodemetallation, i.e. dineophyl(−)menthyltin bromide (**3**) in 93% yield, which upon reduction with lithium aluminum hydride in ether yielded **4** (92%). The addition of neophylmagnesium chloride in ether to a solution of dimethyl(−)-menthyltin bromide (**5**) [8] in benzene led to dimethylneophyl(−)-menthyltin (**7**) in 91.6% yield. The same compound **7** was obtained by addition of (−)-menthylmagnesium chloride in THF to a solution of the known [4] dimethylneophyltin bromide in benzene (89% yield). The reaction of **7** with bromine in methanol (molar ratio bromine /**7** 1.1) gave a mixture of diastereoisomeric methylneophyl (−)-menthyltin bromides (**8**) in quantitative yield, which upon reduction with lithium aluminum hydride in ether led to a mixture of the corresponding methylneophyl-(−)-menthyltin hydrides (**9**) in 95.4% yield. All attempts to separate this mixture, either by column chromatography or by kugelrohr distillation, failed.

The ^{13}C, and ^{119}Sn NMR spectra of the new organotin hydrides **4** and **9**, and of their precursors are summarized in Table 1.

The ^{13}C NMR chemical shifts (Table 1) were assigned through the analysis of the multiplicity of the signals by means of DEPT experiments and taking into account the magnitude of $^{n}J(^{13}C, ^{119}Sn)$ coupling constants. The use of the Karplus-type relationship existing between the value of the $^{3}J(C, Sn)$ coupling constants and the dihedral angle [10], enables us to deduce the stereochemistry of the (−)-menthyl ligands. Thus, the $^{3}J(C, Sn)$ values ranging from ca. 58 to 78 Hz for

Table 1
^{13}C and ^{119}Sn NMR data of compounds **2–4** and **7–9** [a]



	Compound **2**	Compound **3**	Compound **4** [b]	Compound **7**	Compound **8**	Compound **9** [b]
δC_1 (^1J)	32.61 (373.1)	40.71 (373.1)	32.49 (391.4)	31.88 (390.6)	39.88 (352.4)	32.18 (404.4)
						32.33 (406.8)
δC_2 (^2J)	46.13 (15.3)	45.77 (13.7)	46.39 (16.4)	46.33 (15.6)	45.48 (19.2)	47.37 (17.8)
					45.66 (14.0)	47.44 (17.8)
δC_3 ($^3J_{trans}$)	26.49 (57.7)	26.52 (78.6)	26.71 (61.0)	26.44 (59.4)	26.17 (78.2)	27.21 (61.0)
δC_4 (^4J)	35.31 (NO)	33.72 (9.2)	35.78 (NO)	35.43 (6.6)	34.71 (NO)	36.21 (NO)
δC_5 ($^3J_{trans}$)	35.00 (62.6)	34.85 (76.3)	35.45 (NO)	35.09 (63.4)	34.79 (75.2)	35.85 (63.6)
						35.94 (63.6)
δC_6 (^2J)	40.36 (16.8)	39.44 (19.8)	41.86 (16.4)	40.59 (16.7)	39.39 (28.4)	42.07 (17.8)
						42.42 (17.8)
δC_7	22.48	22.18	22.79	22.53	22.24	23.21
δC_8 ($^3J_{gauche}$)	32.65 (18.3)	33.72 (25.9)	33.31 (NO)	32.94 (19.0)	33.19 (23.5)	33.80 (17.8)
					33.74 (26.4)	33.91 (17.8)
δC_9	21.94	21.72	22.16	21.97	21.68	22.60
δC_{10}	15.64	15.85	15.72	15.51	15.38	16.12
$\delta C_{1'}$ (^1J)	29.36 (304.4)	37.73 (283.1)	29.19 (321.9)	29.81 (321.4)	38.00 (346.8)	29.57 (338.2)
	30.34 (299.8)	39.20 (282.3)	29.77 (316.6)			30.00 (338.2)
$\delta C_{2'}$ (^2J)	37.97 (17.5)	38.14 (21.4)	37.64 (19.1)	38.07 (18.9)	38.18 (NO)	38.25 (22.8)
	38.01 (18.3)	38.23 (21.4)	37.68 (19.8)		38.27 (NO)	
$\delta C_{3'}$ (^3J)	32.56 (29.0)	32.11 (35.1)	31.65 (28.2)	32.85 (32.6)	31.26 (31.9)	32.68 (33.0)
	32.95 (29.8)	32.31 (35.1)	32.41 (NO)	33.06 (31.0)	31.71 (NO)	33.04 (30.6)
	33.05 (30.5)	32.92 (43.5)	32.61 (31.3)		31.96 (NO)	33.10 (33.0)
	33.25 (NO)	33.05 (42.0)	33.29 (38.1)			33.44 (35.6)
$\delta C_{4'}$ (^3J)	151.48 (20.3)	150.55 (25.2)	151.19 (19.8)	151.40 (21.6)	150.04 (23.7)	151.47 (20.2)
	151.57 (20.3)	150.63 (27.5)	151.31 (22.9)			
$\delta C_{5'}$	127.91	128.23	128.43	127.96	128.47	128.83
$\delta C_{8'}$	125.24	125.22	125.69	125.14	124.79	125.96
$\delta C_{7'}$	125.27	125.81	125.86	125.32	126.05	126.30
Sn-CH_3 (^1J)	−7.53 (278.5)	–	–	−9.59 (289.2)	−0.52 (278.4)	−12.10 (305.0)
				−9.63 (289.5)		
^{119}Sn	−36.1	89.5	−137.2	−21.8	110.0	−114.0
					115.2	−117.2

[a] In $CDCl_3$, except when otherwise stated; chemical shifts, δ, in ppm with respect to TMS (^{13}C spectra) and Me_4Sn (^{119}Sn spectra); $^{i}nJ(Sn,C)$ coupling constants in Hz (in brackets); NO = not observed. [b] In C_6D_6.

carbons C-3 and C-5 of the menthyl group in all the compounds included in the Table 1, indicate dihedral angles of about 180° between these carbons and the tin moiety attached to C-1, i.e. *anti* positions with respect to the alkylstannyl group. On the other hand, the values between 18 and 26 Hz found in all cases for the ^3J(C, Sn) coupling constants of C-8 suggest a dihedral angle of ca. 60°, i.e. a *gauche* position with respect to the stannyl substituent. From the previous discussion it is possible to conclude that in these compounds the organotin moiety occupies an equatorial position in the cyclohexane ring of the (−)-menthyl group. These results are in agreement with those obtained by Schumann et al. [8b].

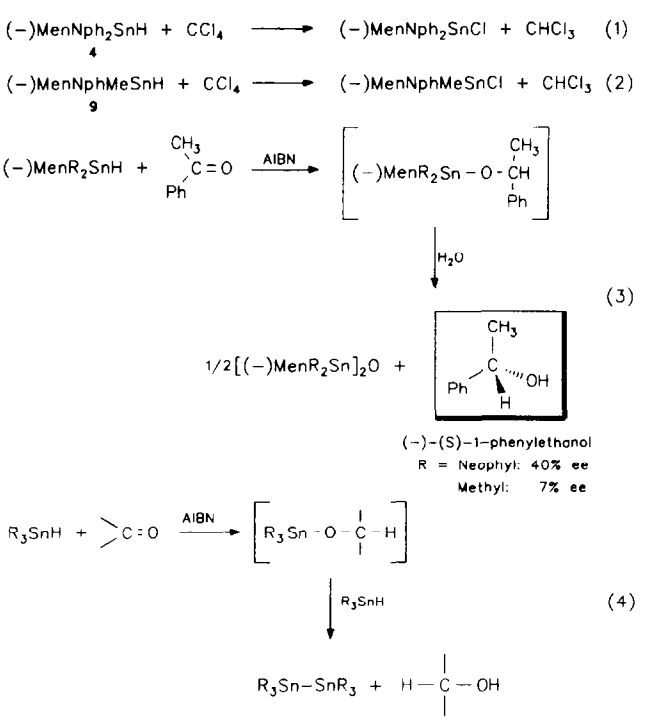
The ^{13}C NMR spectra of prochiral compounds **2**–**4** show two resonances for C-1′, C-2′, and C-4′, and four signals for C-3′ of the neophyl group. This multiplicity of resonances could be connected with the steric crowding rather than any effect of the chiral menthyl ligand. Thus, replacing one of the neophyl ligands in compound **2** by a methyl group, the multiplicity of the resonances belonging to carbons C-1′–C-4′ disappears as shown by the ^{13}C NMR spectrum of dimethylneophyl(−)-menthyltin (**7**). Furthermore, we have also found the same multiple resonances in organotin compounds containing two neophyl groups and two achiral organic ligands. On the other hand, the multiple resonances of some signals observed in the ^{13}C NMR spectra of compounds **8** and **9** could be ascribed to the fact that these compounds consist of mixtures of the corresponding diastereoisomers.

The ^{119}Sn NMR spectra of compounds **8** and **9** show the resonances corresponding to the two diastereoisomers in each case.

Dineophyl(−)-menthyltin hydride (**4**) is a dense colourless liquid which decomposes very slowly in the air: after fifteen days on the bench the IR spectrum does not show significant changes. In a refrigerator and under nitrogen, a sample of **4** has been kept for six months without noticeable decomposition. The mixture of methylneophyl(−)-menthyltin hydrides (**9**), is a colourless liquid which decomposes faster than hydride **4**: after fifteen days the intensity of the Sn–H band in the IR spectrum reduces to ca. 10%. Organotin hydrides **4** and **9** are readily soluble in common organic solvents such as pentane, hexane, benzene, toluene, diethylether, and THF.

In order to compare the reactivity of hydrides **4** and **9** with that of other organotin hydrides, both hydrides were allowed to react with carbon tetrachloride (Eqs. (1) and (2), Scheme 2).

It was found that the decomposition of a 0.077 M solution of **4** (Scheme 2, Eq. (1), $n = 0$) and **9** (Scheme 2, Eq. (1), $n = 1$) in carbon tetrachloride at 25°C, took about 55 min in the case of **4** and ca. 5 min in the case of **9** (reactions followed by IR spectroscopy by observing the disappearance of the Sn–H absorption). These results show that whereas the reactivity of methylneophyl(−)-menthyltin hydride (**9**) is within the range of that of the "more common" triorganotin hydrides (Me, ^{n}Bu, Ph) [11], dineophyl(−)-menthyltin hydride (**4**) reacts more slowly. However, **4** reacts faster than trineophyltin hydride, which under the same conditions reacts in 2 h [5].



Scheme 2.

In order to test possible applications of dineophyl(−)-menthyltin hydride (**4**) in asymmetric synthesis, we carried out the reduction of the prochiral acetophenone with this hydride (Eq. (3), Scheme 2). Thus, a mixture of **4** and acetophenone (molar ratio **4**/ketone 2) was irradiated under nitrogen and with a catalytic amount of AIBN for 24 h. After this time, the IR spectrum of the mixture showed the disappearance of the C = O group. The ^{1}H NMR of the crude product showed at 4.5 ppm two superimposed quartets of different intensity, corresponding to the two diastereoisomeric alkoxystannanes. This clearly shows that the addition of the hydride is selective. After hydrolysis and the usual work-up, the crude product was chromatographed (silica gel 60) and pure (S)-(−)-1-phenylethanol was recovered in 27.6% yield, enantiomeric excess (ee) 40.3%. We were not able to recover more alcohol from other fractions of the chromatography which were contaminated with the organotin oxide.

Two facts should be noted here: first that although the IR spectrum showed the disappearance of the C=O group, it showed no OH band. Secondly, under the same reaction conditions but using a 1.5 molar ratio

hydride/ketone after 24 h the IR spectrum showed no appreciable reduction of the C=O group. These facts indicate that although it has been demonstrated [11], that in the reduction of carbonyl compounds with normal organotin hydrides (Bu, Ph) usually a 100% excess of hydride is needed in order to obtain the free alcohol [Eq. (4), Scheme 2], this does not apply to the reductions with dineophyl (−)menthyltin hydride (**4**) where in order to free the alcohol addition of water is needed. These facts could be connected with the low reactivity of hydride **4** compared with that of the "normal" organotin hydrides, and therefore in the reductions carried out with **4** the excess of hydride could act just by mass effect speeding up the reaction.

These results compare well with those obtained by Seebach, who obtained enantiomeric excesses of 30% [12] and 42% [13] in the reduction of acetophenone with lithium aluminum hydride complexed with chiral diols.

In order to determine the effect of the size of the organic ligands on the asymmetric induction exerted by the (−)-menthyl group attached to the tin atom, we carried out the reduction of acetophenone with dimethyl(−)-menthyltin hydride (obtained according to Schumann [8]) under the same reaction conditions as above. A dramatic change in enantioselectivity was observed: the reduction took place with just 7.1% ee. Therefore, in the case of mixed (−)-menthyltin hydrides the enantioselectivity which can be achieved in the reduction of prochiral ketones does depends upon the size of the other organic ligands attached to the tin atom.

It should be added that the excess of hydride in the reductions using dineophyl(−)-menthyltin hydride (**4**) can be easily recovered (just percolation through a silica gel 60 column), and that the bis(dineophyl(−)-menthyltin) oxide formed can also be easily transformed in the hydride **4** by reduction with borane in THF [14], i.e. the organotin reagent can be recovered for further use.

Similar studies with methylneophyl(−)-methyltin hydride (**9**) were not attempted due to the fact that we could not separate the mixture of diastereoisomers.

3. Experimental section

The NMR spectra were determined partly at Dortmund University (Germany) (^{1}H, ^{13}C and ^{119}Sn), using a Bruker AM 300 instrument, and partly at IQUIOS (Rosario, Argentina) with a Bruker AC 200 instrument (^{1}H and ^{13}C). Infrared spectra were recorded with a Perkin-Elmer 599B spectrophotometer. Microanalyses were performed at Dortmund University. Specific rotations were measured with a Polar L-fP, IBZ Messtechnik. Sample irradiations were carried out in an irradiator constructed in this Institute which consisted of four water-cooled mercury lamps (two of 250 W and two of 400 W): temperature at the sample site: 25 °C. All the solvents and reagents used were analytical reagent grade. Dimethylneophyltin bromide (**1**) and methyldineophyltin bromide (**6**) [4], dimethyl (−)menthyltin hydride [8] were synthesized by known procedures.

3.1. Alkylation reactions via Grignard reagents. Reaction of methyldineophyltin bromide (1) with (−)-menthylmagnesium chloride. Synthesis of methyldineophyl(−)-menthyltin (2)

To a stirred solution of **1** (21.9 g, 0.0456 mol) in benzene (25 ml), at room temperature and under nitrogen atmosphere, was added dropwise a solution of (−)-menthylmagnesium chloride in ether (27 ml, 1.86 M, 0.050 mol). The reaction mixture was heated under reflux for 3 h and left overnight, at room temperature, under stirring. Then HCl 10% was added (ca. 10 ml). The organic layer was decanted, washed three times with water and dried over anhydrous magnesium sulfate. The solvent and impurities were removed under reduced pressure. Compound **2** was obtained as an oil (32.11 g, 0.041 mol, 90.2%). $[\alpha]_D^{20}$ −22.51° (c, 0.79; benzene); n_D^{20}: 1.5522. ^{1}H NMR ($CDCl_3$) −0.32 (s, 3H, ^2J(Sn, H) 47.6); 0.65 (d, 3H, ^3J(H, H) 6.9); 0.77 (d, 3H, ^3J(H, H) 6.6); 0.89 (d, 3H, ^3J(H, H) 6.7); 0.98(m, 1H); 1.20 (dd, 2H, ^2J(H, H) 9.5), ^3J(H, H) 9.6); 1.279 (s, 2H); 1.28 (s, 2H); 1.29 (s, 12H); other aliphatic signals: 1.36–1.68 (m, 7H); 7.14–7.30 (m, 10H). Analysis: Found: C, 68.64; H, 9.30. $C_{31}H_{48}Sn$ calcd.: C, 69.02; H, 8.97%.

Under similar experimental conditions, compound **7** was obtained by two different ways. (a) Compound **5** reacted with (−)-menthylmagnesium chloride to give **7** in 92% of yield. (b) Compound **6** reacted with neophylmagnesium chloride [2] yielding **7** (87%). b.p. 128–130 °C/0.75 mm. $[\alpha]_D^{20}$: −25.5° (c, 2.00; benzene). ^{1}H NMR ($CDCl_3$) −0.198 (s, 3H, ^3J(Sn, H) 48.7); −0.192 (s, 3H, ^3J(Sn, H) 48.7); 0.72 (d, 3H, ^3J(H, H) 6.7); 0.84 (d, 3H, ^3J(H, H) 5.6); 0.93 (d, 3H, ^3J(H, H)5.9); other aliphatic signals: 1.09–1.83 (m, 18H); 7.12–7.45 (m, 5H). Analysis: Found: C, 63.02; H, 9.41. $C_{22}H_{38}Sn$ calcd.: C, 62.73; H, 9.10%.

3.2. Bromo/methyl exchange reactions. Reaction of methyldineophyl(−)-menthyltin (2) with bromine. Synthesis of dineophyl(−)-menthyltin bromide (3)

To a stirred solution of **2** (22.12 g, 0.041 mol) in MeOH (123 ml), cooled at 0°C and in the dark, was added dropwise a solution of bromine (6.55 g, 0.041 mol) in MeOH (45 ml). After stirring overnight, at room temperature, the solvent was removed under

reduced pressure and **3** was obtained in a quantitative yield (24.8 g, 0.041 mol). n_D^{20} 1.5665; $[\alpha]_D^{20}$ −23.18° (c, 1.06; benzene). ^{1}H NMR ($CDCl_3$) 0.80 (d, 3H, ^3J(H, H) 6.7); 0.85 (d, 3H, ^3J(H, H) 6.4); 1.00 (d, 3H, ^3J(H, H) 6.7); 1.24 (m, 1H); 1.46 (s, 4H); 1.49 (s, 12H); other aliphatic signals: 1.52–1.84 (m, 9H); 7.27–7.40(m, 10H). Analysis: Found: C, 59.14; H, 7.42. $C_{30}H_{45}BrSn$ calcd.: C, 59, 62; H, 7.51%.

Under the same experimental conditions, compound **7** reacted with bromine to give **8**, as a diastereoisomeric mixture, in 81% yield; b.p. 108–112°C/0.05 mm. $[\alpha]_D^{20}$ −19.25° (c, 2.00; benzene). ^{1}H NMR ($CDCl_3$) 0.23 (s, 3H, ^3J(Sn, H) 48.8); 0.30 (s, 3H, ^3J(Sn, H) 48.8); 0.69 (d, 3H, ^3J(H, H) 6.8); 0.73 (d, 3H, ^3J(H, H) 6.7); 0.84 (d, 3H, ^3J(H, H) 6.2); 0.87 (d, 3H, ^3J(H, H) 4.7); 0.89 (d, 3H, ^3J(H, H) 6.4); 0.93 (d, 3H, ^3J(H, H) 5.5); 1.00–2.18 (36H) series of multiple signals from which clearly emerge four singlets at 1.44, 1.46, 1.49 and 1.53; 7.16–7.41(m, 10H).

3.3. Reduction of the trialkyltin bromides. Reaction of dineophyl(−)-menthyltin bromide (3) with lithium aluminium hydride. Synthesis of dineophyl(−)-menthyltin hydride (4)

To a suspension of 1.55 g (0.041 mol) of lithium aluminium hydride in anhydrous ether (92 ml), at 0°C and under nitrogen atmosphere, was added dropwise, a solution of **3** (24.5 g, 0.0405 mol) in anhydrous ether (63 ml). The reaction mixture was left stirring at room temperature for 5 h. Then it was decomposed with a saturated solution of ammonium chloride (ca. 10 ml), the organic layer washed with water and dried over magnesium sulfate and the solvent distilled off under reduced pressure. After percolation through a chromatographic column (silicagel 60), compound **4** was obtained as a transparent liquid (20 g, 0.038 mol, 94%); n_D^{20} 1.5528; $[\alpha]_D^{20}$ −25.97° (c, 0.85; benzene). IR (Sn–H) 1811 cm^{-1}. ^{1}H NMR ($CDCl_3$) 0.66 (d, 3H, ^3J(H, H) 6.8); 0.83 (d, 3H, ^3J(H, H) 6.5); 0.89 (d, 3H, ^3J(H, H) 6.8); 1.30 (s, 2H); 1.32 (s, 12H); 1.34 (s, 2H); 4.89 (m, 1H, ^1J(Sn, H) 1618.2); other aliphatic signals: 0.94–1.17 (4H) and 1.42–1.74 (6H); 7.03–7.29(m, 10H). Analysis: Found: C, 68.91; H, 8.83. $C_{30}H_{46}Sn$ calcd.: C, 68.58; H, 8.82%.

Under similar conditions, hydride **9** was obtained as a diastereoisomeric mixture, from the reaction of **8** with lithium aluminium hydride in 95% yield. $[\alpha]_D^{20}$ −17.4° (c, 3.00; benzene). IR ν(Sn–H) 1790 and 1795 cm^{-1}. ^{1}H NMR (C_6D_6) 0.01 (s, 3H, ^3J(Sn, H) 59.0); 0.02 (s, 3H, ^3J(Sn, H) 53.1); 0.77(d, 3H, ^3J(H, H) 6.8); 0.79 (d, 3H, ^3J(H, H) 6.8); 0.91 (d, 6H, ^3J(H, H) 6.2); 0.95 (d, 3H, ^3J(H, H) 6.8); 0.96 (d, 3H, ^3J(H, H) 6.8); 1.15 (d, 3H, ^3J(H, H) 7.0); 1.17 (d, 3H, ^3J(H, H) 7.0); 4.97 (m, 2H, ^1J(Sn, H) 1493.4); other aliphatic signals: 1.00–1.86 (30H); 7.05–7.40 (m, 10H).

3.4. Reduction of acetophenone with dineophyl(−)-menthyltin hydride (4) and dimethyl(−)menthyl tin hydride (10). Synthesis of (−)-(S)-1-phenylethanol

A mixture of acetophenone (0.360 g, 0.003 mol), **4** (3.04 g, 0.006 mol) and a catalytic amount of ABIN was irradiated under nitrogen atmosphere and with stirring for 24 h. After this time the IR spectrum showed no C=O band. Then a few drops of water were added to liberate the alcohol, and the resulting mixture was extracted with ether and dried with magnesium sulfate. After solvent elimination under reduced pressure, the mixture was chromatographed in a silica gel 60 column. Pure (−)-(S)-1-phenylethanol (0.101 g, 0.000827 mol, 27.6%) was eluted with petroleum ether/diethylether (3:1), as an enriched racemic mixture; $[\alpha]_D^{20}$ −2.75° (c, 0.75; MeOH); ee = 40.3%. It is to note that even though by spectroscopy the reduction was quantitative, we could not recover more alcohol from other fractions of the chromatography which were contaminated with organotin oxide.

Under the same reaction conditions, a mixture of acetophenone (0.360 g, 0.003 mol) and **10** (1.74 g, 0.006 mol), after column chromatography, yielded pure (−)-(S)-1-phenylethanol (0.225 g, 0.00184 mol, 61.4%), eluted with petroleum ether/diethylether (3:1); $[\alpha]_D^{20}$ −3.3° (c, 5.11; MeOH); ee = 7.09%. As previously, we could not recover more alcohol from other fractions contaminated with the organotin oxide.

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