Synthesis and some properties of mixed alkyldi-(−)-menthyltin hydrides

Cristian A. Vitale and Julio C. Podestá *

Instituto de Investigaciones en Química Orgánica, Universidad Nacional del Sur, Avenida. Alem 1253, 8000 Bahía Blanca, Argentina

The synthesis and physical properties of methyldi-(−)-menthyltin 4 and neophyldi-(−)-menthyltin 7 hydrides as well as those of their organotin precursors are described. The reaction of hydrides 4 and 7 with carbon tetrachloride shows that the reactivity of 4 is within the range of the more common triorganotin hydrides while the organotin hydride 7 reacts more slowly. A study of the reduction of acetophenone with both hydrides shows that whereas the reduction with 4 leads to (−)-(*S*)-1-phenylethanol (8.8% optical purity), the reduction with 7 affords (+)-(*R*)-1-phenylethanol (6.6% optical purity); these results indicate that some degree of asymmetric induction can be achieved. Full ^{1}H, ^{13}C and ^{119}Sn NMR data are given.

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.[1] In previous studies carried out with trineophyltin hydride and deuteride,[2] as well as with mixed methylneophyltin hydrides,[3] we have found 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.

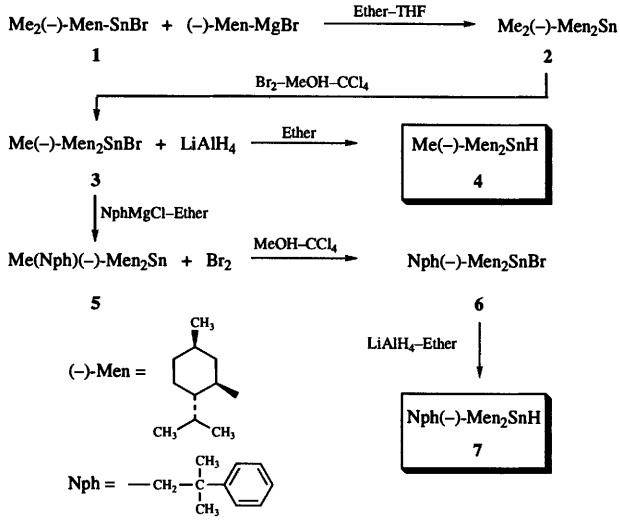
More recently, we considered of interest the synthesis of organotin hydrides containing a combination of bulky and chiral ligands for possible application in the stereoselective transformation of organic prochiral molecules. As the chiral ligand we chose the (−)-menthyl group because, besides economic advantages, it can be bound to the tin atom with complete stereoselectivity *via* the corresponding Grignard reagent. The first part of these studies, which has recently been reported,[4] included the synthesis and some reactions of organotin compounds containing one (−)-menthyl ligand combined with mixed methyl and neophyl groups.

In the present paper we report the synthesis, physical properties and some reactions of methyldi-(−)-menthyltin hydride **4** and neophyldi-(−)-menthyltin hydride **7**.

Results and discussion

The new organotin hydrides were obtained according to Scheme 1.

The addition of a solution of the known[5] dimethyl-(−)-menthyltin bromide **1** in diethyl ether to (−)-menthylmagnesium chloride in THF[6] (molar ratio Grignard:organotin = 1.5:1) gave dimethyldi-(−)-menthyltin **2** (87.5%). The reaction of a solution of **2** in carbon tetrachloride–methanol (see Experimental section) with bromine in methanol (molar ratio bromine:**2** = 1.1:1) led to methyldi-(−)-menthyltin bromide **3** (78%), which upon reduction with lithium aluminium hydride in diethyl ether yielded the corresponding methyldi-(−)-menthyltin hydride **4** (99%). Similarly, the addition of **3** in diethyl ether to neophylmagnesium chloride in the same solvent (molar ratio Grignard:3 = 1.5:1) led to methylneophyldi-(−)-menthyltin **5** (87%). The reaction of a solution of **5** in carbon tetrachloride–methanol (see Experimental section) with bromine in methanol (molar ratio bromine:**5** = 1.1:1) gave neophyldi-(−)-menthyltin bromide **6** (90%), which upon reduction with lithium aluminium hydride led to neophyldi-(−)-menthyltin hydride **7** (92%).



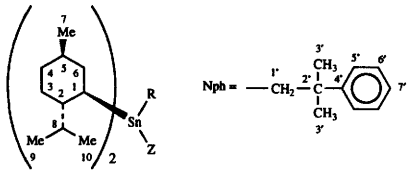
Scheme 1 Synthesis of methyldi-(−)-menthyltin hydride **4** and neophyldi-(−)-menthyltin hydride **7**

The ^{13}C and ^{119}Sn NMR spectra of the new organotin hydrides **4** and **7**, as well as those 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,[7] enabled us to deduce the stereochemistry of the (−)-menthyl ligands. Thus, the $^{3}J(C, Sn)$ values in the range 55–71 Hz for carbons C-3 and C-5 of the menthyl group in all the compounds included in Table 1, indicate dihedral angles of *ca.* 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 in the range *ca.* 18–28 Hz found for the $^{3}J(C, Sn)$ 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.*[8]

The ^{13}C NMR spectra of compounds **3**–**7** show in most cases more than one resonance for each carbon. This multiplicity of

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



Comp.	2	3	4	5	6	7
Z	Me	Br	H	Me	Br	H
R	Me	Me	Me	Nph	Nph	Nph

	Comp. **2**	Comp. **3**	Comp. **4**[b]	Comp. **5**	Comp. **6**	Comp. **7**[b]
δ C-1 (^1J)	32.81 (269.6)	40.21 (271.5)	33.40 (NO)	33.14 (350.9)	41.90 (253.6)	33.60 (335.7)
		41.73 (271.5)	33.70 (NO)	33.77 (352.6)	42.36 (249.2)	
δ C-2 (^2J)	46.49 (15.3)	46.15 (14.2)	47.71 (15.2)	46.23 (14.4)	46.11 (14.0)	47.06 (15.2)
		46.23 (10.8)	48.00 (16.6)	46.33 (14.4)	46.24 (15.2)	47.33 (15.2)
δ C-3	26.61 (56.0)	26.44 (73.4)	27.40 (58.6)	26.68 (55.0)	26.72 (71.2)	26.96 (58.5)
($^3J_{trans}$)		26.51 (72.2)			26.79 (71.2)	27.01 (58.0)
δ C-4 (^4J)	35.50 (NO)	34.97 (NO)	36.31 (NO)	35.44 (NO)	34.91 (NO)	35.92 (NO)
		35.05 (NO)		35.46 (NO)	34.98 (NO)	
δ C-5	35.20 (61.0)	34.89 (56.0)	36.10 (NO)	35.18 (58.2)	35.06 (71.2)	35.71 (62.3)
($^3J_{trans}$)			36.20 (NO)	35.22 (NO)	35.18 (71.2)	
δ C-6 (^2J)	41.19 (17.8)	40.07 (23.5)	42.80 (16.5)	40.85 (16.7)	40.01 (16.6)	42.48 (16.5)
		40.56 (24.7)	43.30 (16.5)	41.48 (17.3)	40.56 (21.6)	43.17 (17.8)
δ C-7	22.57	22.29	22.87	22.61	22.38	22.88
δ C-8	33.44 (17.8)	34.53 (NO)	34.10 (19.1)	33.20 (NO)	34.22 (22.8)	31.92 (28.0)
($^3J_{gauche}$)			34.50 (19.1)		34.49 (22.8)	
δ C-9	22.05	21.81	22.70	22.00	21.89	22.26
		21.89	23.30			22.21
δ C-10	15.81	15.69	16.41	15.91	16.17	15.91
		15.91		16.01	16.30	16.01
δ C-1′ (^1J)	—	—	—	28.03 (281.6)	37.47 (241.6)	28.74 (240.3)
δ C-2′ (^2J)	—	—	—	38.01 (18.2)	38.46 (22.9)	37.70 (19.1)
δ C-3′ (^3J)	—	—	—	32.75 (NO)	32.29 (30.6)	33.25 (NO)
				33.58 (NO)	33.34 (38.2)	33.33 (NO)
						33.79 (NO)
						33.85 (NO)
δ C-4′ (^3J)	—	—	—	151.59 (18.9)	150.94 (25.6)	151.16 (19.1)
δ C-5′	—	—	—	127.94	128.26	128.38
δ C-6′	—	—	—	125.27	125.36	125.79
δ C-7′	—	—	—	125.27	125.80	125.91
Sn-Me (^1J)	−11.56 (267.8)	−3.31 (244.5)	−13.71 (282.2)	−9.22 (257.0)	—	—
^{119}Sn	−17	127	−90	−36	96	−120

[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); [a]J(Sn,C) coupling constants in Hz (in brackets); NO = not observed. [b] In C_6D_6.

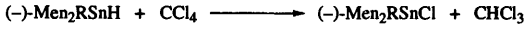
signals could be connected with the steric crowding rather than any effect of the chiral menthyl ligands, as shown in previous work by our group.[4]

In order to compare the reactivity of hydrides **4** and **7** with that of other organotin hydrides, both hydrides were reacted with carbon tetrachloride according to Part A, Scheme 2.

It was found that the decomposition of a 0.077 M solution of **4** and **7** in carbon tetrachloride, at 25 °C, took *ca.* 15 min in the case of **4** and 60 min in the case of **7** (reactions were followed by IR spectroscopy by observing the disappearance of the Sn–H absorption). These results show that both hydrides react more slowly than the more common triorganotin hydrides (Me, Bu, Ph)[9] and faster than trineophyltin hydride, which under the same reaction conditions reacts in 2 h.[2a] It is noteworthy that the reactivity of hydride **7** is almost the same as that shown by dineophyl-(−)-menthyltin hydride.[4]

The hydrostannation of activated olefins by means of organotin hydrides with bulky organic ligands is affected by steric factors. Thus, whereas trineophyltin hydride[2a] and dineophyl-(−)-menthyltin hydride[4] do not add to methyl α,β-disubstituted propenoates, their corresponding derivatives obtained by replacing one of the bulky neophyl ligands by a methyl group, *i.e.* methyldineophyl- and methylneophyl-(−)-menthyltin hydrides, will add normally under free radical conditions.[3,10] These results indicate that, according to the steric volume of the organic ligands, triorganotin hydrides could be divided into two main classes; those which will add normally to trisubstituted activated olefins and those which will not add. In order to test into which class organotin hydrides **4** and **7** should be included and, therefore, to determine their possible uses as hydrostannation reagents, the addition of both hydrides to methyl (*E*)-α,β-diphenylpropenoate under free radical conditions was attempted and, as can be seen in

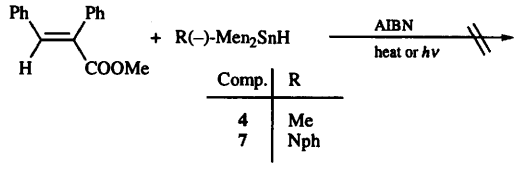
Part A)



Hydride	R	Time[a] (min)
4	Me	15
7	Nph	60

[a] 0.077 M solution in CCl_4 (25 °C)

Part B)

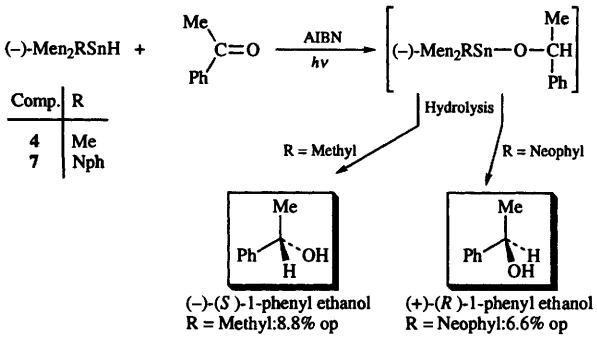


Comp.	R
4	Me
7	Nph

Scheme 2 Reactivities of organotin hydrides **4** and **7**

Scheme 2 (Part B), without any success. The fact that organotin hydride **4** which has a methyl ligand attached to the tin atom does not add suggests that the combined bulk of the two (−)-menthyl groups is enough to hinder the addition.

In order to test possible applications of hydrides **4** and **7** in asymmetric synthesis, we carried out the reduction of prochiral acetophenone with both hydrides (Scheme 3). Thus, a mixture



Scheme 3 Reduction of acetophenone with organotin hydrides **4** and **7**

of **4** and acetophenone (molar ratio **4**:ketone = 2.3:1) was irradiated under nitrogen with a catalytic amount of AIBN for 2.5 h. After this time, the IR spectrum of the mixture showed the disappearance of the C=O group. After hydrolysis with acetic acid and the usual work-up, the crude product was first distilled using a Kugelrohr system and then chromatographed (reversed phase, LiChroprep RP-18) to give (−)-(*S*)-1-phenylethanol in *ca.* 69% yield, optical purity (op) 8.8%. Following the same procedure, the reduction of acetophenone with organotin hydride **7** afforded (+)-(*R*)-1-phenylethanol in *ca.* 72% yield after 52 h irradiation (op 6.6%).

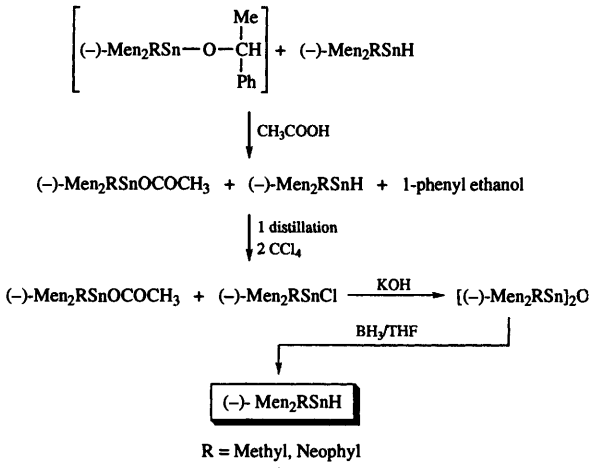
We have also found that in order to obtain the complete reduction of the C=O group it is necessary to use an excess of more than 100% of tin hydride, and that although the IR spectra showed the disappearance of the C=O they showed no OH band. These results confirm those obtained in previous studies;[4] namely, that in reductions with organotin hydrides having bulky substituents, the excess of hydride does not free the alcohol from the stannoxane[9] and acts just by mass effect speeding up the reaction.

Our studies also confirm[4] that it is possible to achieve asymmetric induction using organotin hydrides with chiral ligands. It is noteworthy that the stereochemistry of the reduction products obtained with the organotin hydrides **4** and **7** are *S* and *R* respectively, although the optical purities in each case are modest. Thus, the reduction of acetophenone with **4** gives a mixture enriched in (−)-(*S*)-phenylethanol, whilst **7** gives a mixture enriched in its enantiomer, (+)-(*R*)-phenylethanol.

The fact that the reduction with hydride **4** is remarkably faster than with hydride **7** clearly shows the effect of the size of the organic ligand on the reactivity of these hydrides.

It should be added that the starting hydrides used in these reactions could be recovered in good yields following Scheme 4.

The product of the reaction between an excess of organotin hydrides (**4** and **7**) and acetophenone consists of a mixture of the corresponding stannoxane and the organotin hydride. The mixture was diluted in diethyl ether and allowed to react with acetic acid for 2 h. It gave a mixture of 1-phenylethanol, organotin hydride and the corresponding stannoxane. This result shows that the reaction between acetic acid and organotin hydrides **4** and **7** is very slow. The 1-phenylethanol was distilled off using a Kugelrohr system and the crude residue was treated first with carbon tetrachloride–to convert the hydride into the corresponding chloride–and then with NaOH (0.5 M) in order to convert both the organotin chloride and the acetate into the corresponding oxide. The reduction of the organotin oxides



Scheme 4 Recovery of organotin hydrides **4** and **7** from the reduction products

with borane in THF[11] led to the corresponding organotin hydrides. By this procedure we were able to recover an average of 76% of the starting organotin hydrides.

Experimental

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). *J* Values are given in Hz. IR spectra were recorded with a Perkin-Elmer 599B spectrophotometer. Microanalyses were performed at Dortmund University and at INQUIMAE (University of Buenos Aires, Argentina). Specific rotations, given in units of 10^{-1} deg cm^2 g^{-1} 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. Dimethyl-(−)-menthyltin bromide **1** was prepared as described.[5]

Alkylations *via* Grignard reagents

Synthesis of dimethyldi-(−)-menthyltin 2 and methylneophyldi-(−)-menthyltin 5. To a stirred solution of (−)-menthylmagnesium chloride in THF (1.54 M; 192 ml, 0.295 mol), at 0 °C and under a nitrogen atmosphere, was added dropwise a solution of dimethyl-(−)-menthyltin bromide **1** (72.69 g, 197.5 mmol) in diethyl ether (180 ml). The reaction mixture was heated under reflux for 5 h and then left for 24 h at room temperature with continued stirring. It was then treated with 10% aq. HCl (*ca.* 50 ml). The organic layer was decanted, washed three times with water, dried ($MgSO_4$) and evaporated under reduced pressure. The resulting oil was purified by column chromatography (silica gel 60). Elution with light petroleum (bp 30–65 °C) gave compound **2** (73.9 g, 87.6%) as an *oil*; n_D^{20} 1.5088; $[\alpha]_D^{20}$ −48.3 (*c* 0.84 in benzene); $\delta_H(CDCl_3)$ −0.15 (6 H, s, $^2J_{Sn,H}$ 44.6), 0.75 (6 H, d, $^3J_{H,H}$ 6.6), 0.84 (6 H, d, $^3J_{H,H}$ 7.2), 0.92 (6 H, d, $^3J_{H,H}$ 7.3) and 0.96–1.84 (20 H, m) (Found: C, 61.72; H, 10.50. $C_{22}H_{44}Sn$ requires C, 61.84; H, 10.38%).

Under the same experimental conditions, methyldi-(−)-menthyl bromide **3** (see next experiment) reacted with neophylmagnesium chloride to give after 30 h of heating under reflux compound **5** which was purified by column chromatography. Compound **5** was eluted with light petroleum (bp 30–65 °C) as an *oil* (87.2%); n_D^{20} 1.5338; $[\alpha]_D^{20}$ −39.4 (*c* 1.7 in benzene); $\delta_H(CDCl_3)$ −0.30 (3 H, s, $^2J_{Sn,H}$ 44.8), 0.69 (3 H, d, $^3J_{H,H}$ 7.2), 0.72 (3 H, d, $^3J_{H,H}$ 7.2), 0.80 (3 H, d, $^3J_{H,H}$ 6.9), 0.83 (3

H, d, $^3J_{H,H}$ 5.6), 0.89 (3 H, d, $^3J_{H,H}$ 6.8), 0.90 (3 H, d, $^3J_{H,H}$ 6.8), 0.98–1.82 (28 H, m) and 7.12–7.41 (5 H, m) (Found: C, 68.18; H, 9.86. $C_{31}H_{54}Sn$ requires C, 68.26; H, 9.98%).

Bromo/methyl exchange reactions

Synthesis of methyldi-(−)-menthyltin bromide 3 and neophyldi-(−)-menthyltin bromide 6. To a stirred solution of **2** (73.8 g, 172.7 mmol) in MeOH (250 ml) and CCl_4 (250 ml), cooled at 0 °C and in the dark, was added dropwise a solution of bromine (27.6 g, 172.7 mmol) in methanol (250 ml). After the mixture had been stirred for 12 h at room temperature, it was evaporated under reduced pressure to give an oily residue which was chromatographed (silica gel 60). Compound **3**, eluted with light petroleum (bp 30–65 °C), crystallized from MeOH as a white *solid*, mp 58.5–60 °C (66.31 g, 78%); $[\alpha]_D^{20}$ −47.1 (*c* 1.58 in benzene); $\delta_H(CDCl_3)$ 0.57 (3 H, s, $^2J_{Sn,H}$ 43.0), 0.81 (3 H, d, $^3J_{H,H}$ 6.7), 0.82 (3 H, d, $^3J_{H,H}$ 6.7), 0.87 (6 H, d, $^3J_{H,H}$ 6.1), 0.97 (6 H, d, $^3J_{H,H}$ 6.7) and 1.05–2.10 (20 H, m) (Found: C, 51.28; H, 8.32. $C_{21}H_{41}BrSn$ requires C, 51.25; H, 8.40%).

Under the same experimental conditions, compound **5** reacted with bromine to give **6**, as an *oil* (89.8%); n_D^{20} 1.5541; $[\alpha]_D^{20}$ −33.4 (*c* 1 in benzene); $\delta_H(CDCl_3)$, 0.76–1.95 (46 H, m) (superimposed signals) and 7.16–7.46 (5 H, m) (Found: C, 58.98; H, 8.46. $C_{30}H_{51}BrSn$ requires C, 59.04; H, 8.42%).

Reduction of organotin bromides 3 and 5 with $LiAlH_4$

Synthesis of methyldi-(−)-menthyltin hydride 4 and neophyldi-(−)-menthyltin hydride 7. To a suspension of $LiAlH_4$ (1.55 g, 41.0 mmol) in anhydrous diethyl ether (90 ml), at 0 °C and under a nitrogen atmosphere, was added dropwise a solution of **3** (20 g, 40.6 mmol) in anhydrous diethyl ether (65 ml). The reaction mixture was stirred at room temperature for 5 h after which it was treated with saturated aqueous NH_4Cl (*ca.* 10 ml). The organic layer was separated, washed with water, dried ($MgSO_4$) and then concentrated by removal of the solvent by distillation under reduced pressure. Percolation of the residue through a chromatographic column (silica gel 60) using light petroleum (bp 30–65 °C) as eluent gave compound **4** as a transparent *liquid* (16.45 g, 98%); n_D^{20} 1.5031; $[\alpha]_D^{20}$ −52.9 (*c* 1.64 in benzene); $\nu_{Sn,H}$(film) 1850 cm^{-1}; $\delta_H(C_6D_6)$ −0.32 (3 H, s, $^2J_{Sn,H}$ 47.6), 0.94 (3 H, d, $^3J_{H,H}$ 4.6), 0.95 (3 H, d, $^3J_{H,H}$ 4.4), 0.99 (6 H, d, $^3J_{H,H}$ 4.2), 1.08 (6 H, d, $^3J_{H,H}$ 4.6), 1.20–2.46 (20 H, m) and 5.27 (1 H, m, $^1J_{Sn,H}$ 1531.8) (Found: C, 61.12; H, 10.32. $C_{21}H_{42}Sn$ requires C, 61.03; H, 10.24%).

Under similar conditions, hydride **7** was obtained as a *liquid* (93%), from the reaction of **6** with $LiAlH_4$; n_D^{20} 1.5342; $[\alpha]_D^{20}$ −45.7 (*c* 1.17 in benzene); $\nu_{Sn,H}$(film) 1795 cm^{-1}; $\delta_H(C_6D_6)$ 0.79 (3 H, d, $^3J_{H,H}$ 6.8), 0.82 (3 H, d, $^3J_{H,H}$ 6.8), 0.86–2.03 (40 H, m), 5.21 (1 H, m, $^1J_{Sn,H}$ 1533.0) and 6.96–7.51 (5 H, m) (Found: C, 67.71; H, 9.94. $C_{30}H_{52}Sn$ requires C, 67.80; H, 9.86%).

Reduction of acetophenone with organotin hydrides 4 and 7

Synthesis of (−)-(*S*)- and (+)-(*R*)-1-phenylethanol. A stirred mixture of acetophenone (0.5 g, 4.1 mmol), hydride **4** (4 g, 9.68 mmol) and a catalytic amount of AIBN was irradiated under a nitrogen atmosphere for 2.5 h. After this time the IR spectrum showed no C=O band. The reaction mixture was diluted with anhydrous diethyl ether (10 ml) after which it was treated with a solution of acetic acid (0.250 ml, 0.262 g, 4.3 mmol) in diethyl ether (4 ml). After being stirred for 2 h, the ethereal solution was washed with 10% aq. $NaHCO_3$ and water, dried ($MgSO_4$) and then concentrated by removal of the solvent by distillation under reduced pressure. The crude product mixture was transferred to a Kugelrohr system. (−)-(*S*)-1-Phenylethanol was recovered by heating at 150 °C under 30 mbar pressure. After column chromatography (reversed phase, LiChroprep RP-18, eluent: acetonitrile), the optical rotation of the (−)-(*S*)-1-phenylethanol thus obtained (0.35 g, 2.9 mmol, 68.7%) was $[\alpha]_D^{20}$ −4.0 (*c* 5 in MeOH); op = 8.8%.

The same reaction conditions but with irradiation for 52 h, gave a mixture of acetophenone (0.5 g, 4.1 mmol) and hydride **4** (5.1 g, 9.6 mmol), after column chromatography (reversed phase, LiChroprep RP-18, eluent: acetonitrile), yielded pure (+)-(*R*)-1-phenylethanol (0.363 g, 2.97 mmol, 72.5%); $[\alpha]_D^{20}$ +3.0 (*c* 5 in MeOH); op = 6.6%.

Recovery of the starting hydrides

In the reduction of acetophenone with organotin hydride **4**, to the residue left in the Kugelrohr after distillation of the 1-phenylethanol, *i.e.* a mixture of methyldi-(−)-menthyltin hydride and acetate, CCl_4 (10 ml) was added (exothermic reaction). After being stirred for 2 h the mixture was concentrated by removal of the solvent by distillation under reduced pressure and then treated with diethyl ether (10 ml) and aq. KOH (20%; 20 ml). The mixture was stirred for 16 h after which the organic layer was separated, washed with water and dried ($MgSO_4$). The solvent was distilled off and the residue, bis[methyldi-(−)-menthyltin] oxide, was dissolved in THF (2.5 ml) and reduced with BH_3 in THF (3.36 M; 3.6 ml)[11] Percolation of the residue through a chromatographic column (silica gel 60) using light petroleum (bp 30–65 °C) as eluent gave recovery of compound **4** (3.1 g, 7.36 mmol, 76%).

Acknowledgements

This work was supported by the Volkswagenwerk-Stiftung (Hannover, Germany), CONICET (Capital Federal, Argentina), CIC (Provincia de Buenos Aires, Argentina), and Universidad Nacional del Sur (Bahía Blanca, Argentina).

References

1 (*a*) W. P. Neumann, *Synthesis*, 1987, 665; (*b*) M. Pereyre, J. F. P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworth, London, 1987; (*c*) *Chemistry of Tin*, ed. P. G. Harrison, Blackie, Glasgow and London, 1989; (*d*) B. Giese, *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, Pergamon Press, Oxford, 1986.
2 (*a*) A. B. Chopa, A. E. Zúñiga and J. C. Podestá, *J. Chem. Res.*, 1989, (*S*), 234; (*b*) J. C. Podestá, N. N. Giagante, A. E. Zúñiga, G. O. Danelon and O. A. Mascaretti, *J. Org. Chem.*, 1994, **59**, 3747.
3 J. Podestá, A. Chopa, L. Koll, C. Vitale and A. Zúñiga, *Main Group Metal Chemistry*, 1991, **14**, 101.
4 J. C. Podestá, A. B. Chopa, G. E. Radivoy and C. A. Vitale, *J. Organomet. Chem.*, 1995, **494**, 11.
5 H. Schumann and B. C. Wassermann, *J. Organomet. Chem.*, 1989, **365**, C1.
6 M. Tanaka and I. Ogata, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1049.
7 (*a*) D. Doddrell, I. Burfitt, W. Kitching, C.-H. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila and R. H. Sarma, *J. Am. Chem. Soc.*, 1974, **96**, 1640; (*b*) T. N. Mitchell, J. C. Podestá, A. D. Ayala and A. B. Chopa, *Mag. Reson. Chem.*, 1988, **26**, 497.
8 H. Schumann, B. C. Wassermann and F. E. Hahn, *Organometallics*, 1992, **11**, 2803.
9 H. G. Kuivila, *Adv. Organomet. Chem.*, 1964, **1**, 47.
10 C. A. Vitale, Dr. in Chem. Thesis, Universidad Nacional del Sur, Argentina, 1995.
11 A. B. Chopa, L. C. Koll, J. C. Podestá and F. G. Thorpe, *Synthesis*, 1983, 722.

Paper 6/01132B
Received 15*th February* 1996
Accepted 14*th May* 1996