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ORGANOMETALLIC COMPOUNDS

LXIII *. SYNTHESIS, OPTICAL STABILITY, STEREO-SELECTIVE AND -SPECIFIC REACTIONS OF CHIRAL TRIORGANOTIN HYDRIDES

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Summary

Optically active triorganotin hydrides have been synthesized by asymmetric reduction of the corresponding halides. These optically stable compounds undergo stereoselective conversions into other optically stable compounds such as tetraorganotin compounds (by reaction with diazomethane or with bifluorenylidene) or hexaorganoditin compounds (by reaction in the presence of palladium) or into optically unstable compounds such as methylneophylphenyltin chloride (by reaction with CCl_4). The H—D exchange between optically active methylneophylphenyltin hydride (deuteride) and triphenyltin deuteride (hydride) occurs with retention of configuration at the metal atom.

Introduction

The first example of optically active organotin compounds in which the tin atom is the only chiral center, optically pure (+)-methyl-1-naphthyl-*p*-anisyl-(3-hydroxy-3-methylbutyl)tin, was synthesized in 1971 [5a]. Other chiral tetraorganotin compounds, of unknown optical purity, have been prepared since [5b]. Whereas the stereochemistry of numerous substitution reactions at silicon or at germanium has been established no stereoselective substitution at tin was known before this work.

Knowing that triorganotin hydrides are configurationally stable within the NMR time-scale [6], we decided to try the synthesis of optically active triorgano-

* For part LXII, see ref. 1. Preliminary communications of this work have appeared previously [1—4]. No reprints are available.

tin hydrides in order to study the stereochemistry of the replacement of H by other ligands.

Synthesis of chiral triorganotin hydrides

(+)-Methylneophylphenyltin hydride (I), (—)-neophylphenyl-t-butyltin hydride (II) and (+)-methyl-1-naphthylphenyltin hydride (III) were prepared [4] by asymmetric reduction of the corresponding racemic halides with one of the chiral reducing agents described by Vigneron and Jacquet [7], $HAl(OC_6H_3\text{-}2,6\text{-}Me_2)_2(O\overset{*}{C}HPh\overset{*}{C}HMeNMe_2)^-Li^+$ (IV).

$(PhMe_2CCH_2)MePhSnCl \xrightarrow{(IV)} (PhMe_2CCH_2)MePhSnH$ (I)

(VII) $[\alpha]_{365}^{30} + 6.4°$ (c 5.57; C_6H_6)
optical purity unknown

$(PhMe_2CCH_2)(Me_3C)PhSnCl \xrightarrow{(IV)} (PhMe_2CCH_2)(Me_3C)PhSnH$ (II)

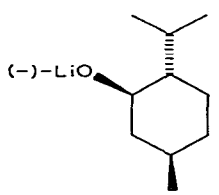
$[\alpha]_{365}^{30} - 3.5°$ (c 6.45; C_6H_6)
optical purity unknown

Me-1-NpPhSnI $\xrightarrow{(IV)}$ Me-1-NpPhSnH (III)

$[\alpha]_{365}^{30} + 2.0°$ (c 4.02; n-C_5H_{12})
optical purity unknown

A similar reaction had been used before in organosilicon chemistry [33]: racemic methoxymethyl-1-naphthylphenylsilicon was converted into (*R*)-(+)-methyl-1-naphthylphenylsilane by the complex $LiAlH_4$/(+)-quinidine.

(—)-I and (—)-II have also been prepared by a method which is analogous to the procedure used by Taddei [8] for the synthesis of optically active tetraorganotin compounds.

(1) 

$(PhMe_2CCH_2)PhRSnCl \xrightarrow[(2)\ LiAlH_4]{} (PhMe_2CCH_2)PhRSnH$

(I) R = Me ; $[\alpha]_D^{30}$ −0.5° (c 7.89 ; C_6H_6)

(II) R = t-Bu ; $[\alpha]_D^{30}$ −0.6° (c 6.95 ; C_6H_6)

Corriu [34] had already prepared a chiral triorganosilane by kinetic resolution:

$RR'SiH_2 \rightarrow RR'SiH(OR^*) \xrightarrow{R''MgX} RR'R''SiH$

TABLE 1

SOLVENT EFFECT ON $[\alpha]^{30}$ OF I

Solvent	c (g/100 ml)	$[\alpha]_D^{30}$	$[\alpha]_{365}^{30}$
CS_2	6.43	+1.6	—
C_6H_6	6.50	+2.2	+7.4
THF	6.49	+3.0	+11.0
CCl_4 [a]	8.53	—	+11.3
Et_2O	6.61	+3.2	+11.8
n-C_5H_{12}	6.38	+3.6	+13.2

[a] See text.

It is thus quite easy to prepare optically active triorganotin hydrides. These key-intermediate compounds can undergo many reactions, and several known transformations lead to optically stable compounds. We studied the stereochemistry of some of them.

Optical stability of chiral triorganotin hydrides

Variation of the concentration of I has little effect on the value of $[\alpha]$ in benzene: $[\alpha]_{365}^{30}$ has a value of 7.3° for *c* 5.9, 7.4° for *c* 10.4, 7.6 for *c* 25.3, and 8.3° for *c* 50.1. In contrast, the solvent effects on $[\alpha]$ are quite marked for I (see Table 1).

A 0.2 *M* solution of I in benzene loses 50% of its optical activity in 17 days at room temperature. At −30°C, $[\alpha]$ remains practically unchanged after 14 months. When a solution of I to which 2 mole % of AIBN has been added is kept at 80°C for 30 min, the recovered triorganotin hydride is racemic. In contrast, a 0.2 *M* benzene solution of I containing 2 mole % of hydroquinone kept at 80°C for 120 min shows an unchanged optical rotation.

The influence of polar solvents on the racemization of I is summarized in Table 2.

With each solvent except HMPT we succeeded in recovering more than 90% of the initial amount of I after the contact time, showing that an eventual change in optical rotation is due to racemization. In HMPT, I is partly transformed into

TABLE 2

SOLVENT EFFECT ON THE RACEMIZATION OF (+)-I AT 23°C

Solvent	Contact time (h)	% racemization
(±)-PhCHMeNH$_2$	2	0
CH_3CN	1	0
DMSO	1	51
HMPT	1	90
MeOH	<1	100
MeOH + 2 mole % Hydroquinone	<1	100

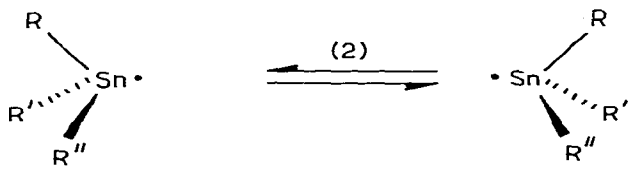
the corresponding racemic hexaorganoditin compound VIII and only 47% I is recovered. Table 2 shows that the racemization of (+)-I occurs more rapidly in methanol (no triorganotin deuteride is formed if CD_3OD is used as the solvent) than in DMSO or in HMPT, although those two solvents are much more nucleophilic towards Me_3SnCl than methanol [9].

Hydride II racemizes ca. twice as slowly as I in benzene. The optical rotation of III (neat) kept for 4 months in the dark did not change within the experimental error, neither that for III kept for 10 min at 50°C or 8 min at 60°C.

Two types of mechanism have to be considered to explain these observations: a radical mechanism, operative in non-polar solvents, and a non-radical mechanism operative in polar solvents such as methanol.

A possible radical mechanism is as follows:

$$In\cdot + RR'R''SnH \xrightarrow{(1)} RR'R''Sn\cdot + InH$$



$$RR'R''Sn\cdot + RR'R''Sn'H \underset{}{\overset{(3)}{\rightleftharpoons}} RR'R''SnH + RR'R''Sn'\cdot$$

$$2\ RR'R''Sn\cdot \xrightarrow{(4)} RR'R''Sn{-}SnR''R'R$$

It has previously been shown that triorganostannyl radicals are non planar [10] and that hydrogen exchange takes place between Me_3SnH and $Me_3Sn\cdot$ at 25°C [11].

A possible non-radical mechanism might proceed via an extension of the coordination number of the metal by a process similar to that postulated for the racemization of triorganotin halides [12]. However we could not get NMR evidence for a strong interaction between I and CD_3OD ($^2J(^{119}Sn{-}CH_3)$ 56.6 Hz in C_6D_6 and 56.8 Hz in CD_3OD, $^1J(^{119}Sn{-}H)$ 1764.8 Hz in C_6D_6 and 1754.6 Hz in CD_3OD), although Ivanov [13] has found that R_3SnH compounds do form labile penta- or hexacovalent complexes with nucleophilic aprotic solvents.

Pentacovalent intermediates ($R_3Sn\overset{A^-}{\underset{H}{<}}$) have been postulated for the hydrolysis, acetolysis and alcoholysis of triorganotin hydrides [14].

Stereoselective substitution reactions at the asymmetric tin atom of chiral triorganotin hydrides

As shown above, triorganotin hydrides are sufficiently optically stable to allow the study of substitution reactions which transform them into other optically stable triorganotin compounds.

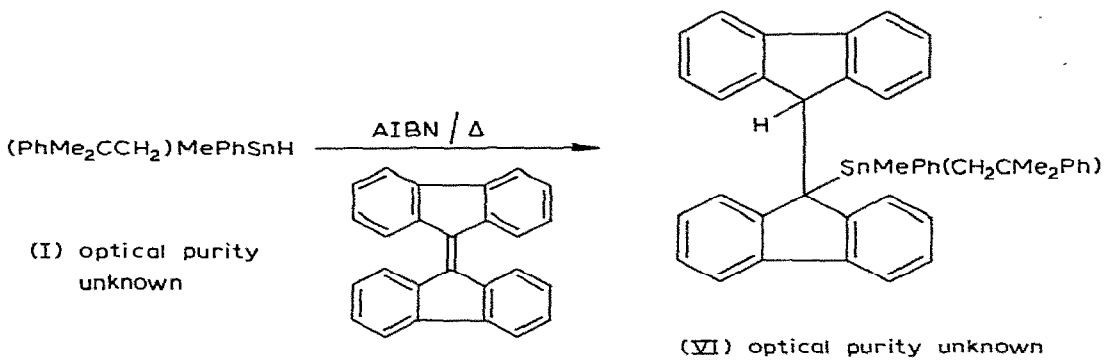
Reaction of (—)-II with diazomethane: insertion of CH_2 into the Sn—H bond

Hydride (—)-II, $[\alpha]_{365}^{30}$ — 0.9° (*c* 12.3; C_6H_6) reacts with CH_2N_2 in the presence of copper in diethyl ether to form optically active methylneophylphenyl-t-butyltin (V) with $[\alpha]_{365}^{30}$ — 1.5° (*c* 3.65; CCl_4) [3].

We note that the insertion of ethyl diazoacetate into the Si—H bond of chiral methyl-1-naphthylphenylsilane proceeds with at least 95% of retention of configuration [15].

Reaction of (+)-I with bifluorenylidene: addition of Sn—H at a C=C double bond

Hydride (+)-I, $[\alpha]_D^{30}$ +1.8° (*c* 20.8; C_6H_6) reacts with bifluorenylidene in the presence of AIBN to form the expected bifluorenylylmethylneophylphenyltin (VI) with $[\alpha]_D^{30}$ + 0.8° (*c* 4.55; CCl_4) [3]; analogously (—)-(I) ($[\alpha]_{365}^{30}$ — 0.7°) is transformed into (—)-VI ($[\alpha]_{365}^{30}$ — 0.4°).



Reaction of (+)-I in the presence of palladium: synthesis of the first example of a chiral hexaorganoditin

In the presence of 10% Pd/C under argon, (+)-I {$[\alpha]_{365}^{30}$ +13.2° (*c* 6.38; n-C_5H_{12})} is exothermically transformed into the corresponding hexaorganoditin compound [$(PhMe_2CCH_2)MePhSn]_2$ (—)-VIII, $[\alpha]_{365}^{30}$ —28.9° (*c* 6.40; C_6H_6) [1]. The same reaction with a mixture of triorganotin and triorganogermanium hydrides yielded only the hexaorganoditin compound.

Reaction of (+)-I with carbon tetrachloride: synthesis of the first example of chiral but optically unstable methylneophylphenyltin chloride (VII)

The reaction of (+)-I, $[\alpha]_{365}^{30}$ +14.0° (*c* 7.28; n-C_5H_{12}), with CCl_4 was followed simultaneously by ORD, NMR and IR [2]. After an induction period which increases with the quantity of air initially dissolved in I, the optical rotation rapidly increases and reaches a maximum when 65—70% of I has been transformed into methylneophylphenyltin chloride (+)-VII as shown by NMR *. After this maximum, the rotation falls, following approximately first-order

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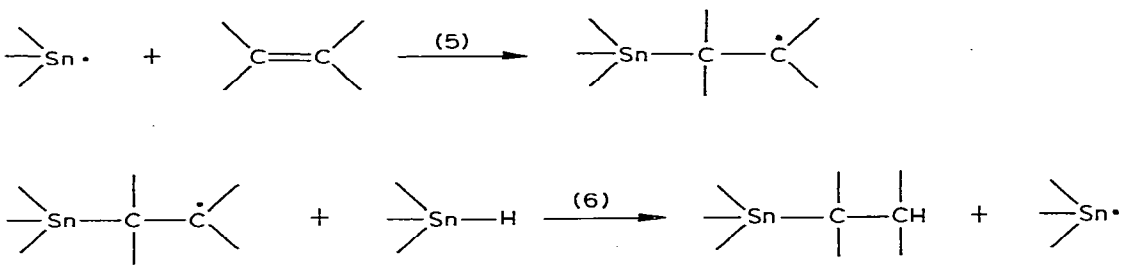
* The sequence: $R_3SnCl \xrightarrow{\text{impure } LiAlH_4} R_3SnH \xrightarrow{\text{impure purification}} R_3SnH \xrightarrow{CCl_4\text{ pure}} R_3SnCl$ can be considered as a new purification method for non-volatile triorganotin halides [28].

kinetics. The reaction is totally inhibited by hydroquinone and is therefore a radical process. It is clear that I is transformed rapidly and stereoselectively into VII, which then racemizes; the lifetime of optically active 0.18 *M* (VII) in CCl_4 is about 10 min.

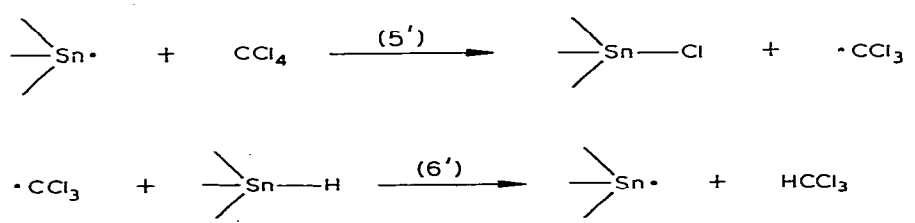
(+)-Methyl-1-naphthylphenylsilane also reacts stereoselectively with CCl_4 (in the presence of AIBN) to give (—)-methyl-1-naphthylphenylsilicon chloride with 80% of retention of configuration [18].

We have thus shown that the addition of I to bifluorenylidene in the presence of AIBN [Scheme a] and the reaction of I with CCl_4 [Scheme b] are stereoselective radical reactions. Steps 5 and 5′ must thus be fast enough compared with the inversion of the triorganostannyl radicals [steps 2 and/or 3] (vide supra).

Scheme a



or Scheme b



Non-stereoselective substitution reactions

The hydrostannation of allyl alcohol with (+)-I at 100°C in the presence of AIBN yields the racemic adduct IX.

$$(+)\text{-I} \xrightarrow{CH_2=CHCH_2OH} \underset{(IX)}{(\pm)\text{-}(PhMe_2CCH_2)MePhSnCH_2CH_2CH_2OH}$$

The reaction of methyl acrylate with methylneophylphenyltin deuteride (+)-I′ at 23°C in the presence of AIBN gives a racemic mixture of the expected adduct XVI and, after the reduction of the ester function, the optically inactive alcohol IX′.

$$(+)\text{-I}' \xrightarrow{CH_2=CHCOOCH_3} \underset{(XVI)}{(\pm)\text{-}[(PhMe_2CCH_2)MePhSnCH_2CHDCOOCH_3]} \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4}$$

$(\pm)$-$(PhMe_2CCH_2)MePhSnCH_2CHDCH_2OH$

(IX')

It is easy to understand that, when step 5 of scheme a is not fast enough compared to the inversion of the triorganostannyl radical, the reaction is not stereoselective.

The reaction of (+)-I with tributylaluminum in cyclohexane [16] yields racemic butylmethylneophylphenyltin (X) and two redistribution products, dibutylmethylneophyltin (XI) and methylneophyldiphenyltin (XII).

(+)-I' reacts with diethylaluminum hydride [32] to give racemic I.

The reaction of (—)-II with dimethylmercury does not yield the expected [17] tetraorganotin, but an optically inactive hexaorganoditin (XIII).

$$(-)\text{-II} \xrightarrow[\text{daylight}]{Me_2Hg} [(PhMe_2CCH_2)(Me_3C)PhSn]_2$$

(XIII)

It should be mentioned that optically inactive XV is obtained when (+)-methylneophylisopropyltrityltin (XIV) reacts with lithium aluminum hydride.

$$(+)\text{-}(PhMe_2CCH_2)Me(Me_2CH)SnCPh_3 \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4} [(PhMe_2CCH_2)Me(Me_2CH)Sn]_2$$

(XIV) (XV)

Stereospecific substitution reactions at the asymmetric tin atom of a chiral triorganotin hydride

H—D exchange between a triorganotin hydride (deuteride) and lithium aluminum deuteride (hydride)

When a mixture of 1 ml of a 0.28 *M* solution of (+)-I in diethylether and of 1 ml of a 0.34 *M* solution of $LiAlD_4$ in the same solvent is kept at 23°C for 5 h the optical activity is reduced by 61.2%, and 47.1% of I is converted to the corresponding deuteride I'.

An analogous experiment with (+)-I' and $LiAlH_4$ gives, for the ratio (% exchange/% inversion), 2.2. after 1 h, 3.0 after 2 h, 3.2 after 5 h and 1.4 after 24 h. The similarity between these results and those obtained by Parker [23] for the reaction of (+)-methyl-1-naphthylphenylsilane with $LiAlD_4$ in diglyme/dioxane (1/1) at 25°C is noteworthy: he obtained ratios of 2.4 after 34 min, 2.7 after 65 min, 2.5 after 90 min and 1.7 after 150 min.

This shows that two parallel reactions are probably operative: one proceeding with retention of configuration and the other with racemization. Lequan [21] came to analogous conclusions for the reaction between (+)-methyl-1-naphthylphenylsilane and $LiAlD_4$ in THF. In contrast to these results the same H—D exchange reaction proceeds with retention of configuration without racemization in diethyl ether [22].

H—D exchange between two triorganotin hydrides

In the absence of Ph_3SnH (I) loses 7% of its optical activity when heated for

9 h at 40°C. When I′ is heated under the same conditions with a large excess of Ph_3SnH, 75% of I′ is converted into I and the initial optical rotation is reduced by 14%. The reaction of I with Ph_3SnH yielded similar but more ambiguous results. The difference of 7% in optical loss between the experiments with and without Ph_3SnH shows that the H—D exchange [32] proceeds with at most 7% racemization and at least 93% retention of configuration.

Analogous but catalyzed H—D exchanges between two triorganosilanes [19] or between two triorganogermanium hydrides [20] also proceed with retention of configuration at the metal atom.

Experimental

Synthesis of (+)-I

A solution of 0.57 g (3.2 mmol) of *N*-methylephedrine, $[\alpha]_D^{20} - 28°$ (*c* 2.61; MeOH) in 15 ml of anhydrous diethyl ether is added dropwise in 1 h to 2.5 ml of a 1.3 *M* [24] ether solution of $LiAlH_4$. This mixture is kept under argon for 30 min, then a solution of 0.78 g (6.4 mmol) of 3,5-dimethylphenol in 5.5 ml of diethyl ether is added during 30 min. The mixture IV, is cooled to —15° C and a solution of 1 g (2.65 mmol) of methylneophylphenyltin chloride (VII) [35] in 1.5 ml of diethyl ether is added. After 2 h at —15°C and 1 h at room temperature, 9 mg of solid hydroquinone are added, and the mixture is then carefully hydrolyzed with 6 ml of a 20% aqueous solution of sodium potassium tartrate. (The optical yield is not affected if the mixture is not hydrolyzed.) The aqueous layer is extracted with diethyl ether as rapidly as possible and the ether extracts are collected and dried over $MgSO_4$. The solvent is evaporated and the residue (2.24 g) is chromatographed on a SiO_2 column and eluted with pe40 *. This gives 493 mg (54.8%) of optically active I (yields up to 80% have been obtained in similar experiments). (R_f 0.44; b.p. 131°C/0.08 Torr; d^{23} 1.2664; n_D^{20} 1.5778; elemental analysis: found: C, 59.23; H, 6.21. $C_{17}H_{22}Sn$ calcd.: C, 59.18; H, 6.38%. ν(Sn—H) 1832 cm^{-1} (broad; film); λ_{max} (ϵ) 258 nm (422) in cyclohexane; ORD: (*c* 5.57 g/100 ml of benzene); λ (nm), $[\alpha]_\lambda^{30}$: 589, +1.89°; 578, +1.97°; 546, +2.24°; 436, +3.94°; 365, +6.39°. The highest $[\alpha]_{365}^{30}$ + 7.40° ± 0.08° for I was obtained in another similar experiment; 70 eV monoisotopic MS: 120 [20, Sn^+]; 135 [14; $MeSn^+$] 197 [32; $PhSn^+$]; 212 [9; $MePhSn^+$]; 213 [12; $MePhSnH^+$]; 227 [1; Me_2PhSn^+]; 253 [2; $PhMe_2CCH_2Sn^+$]; 275 [7; Ph_2SnH^+]; 289 [1; $MePh_2Sn^+$]; 331 [3; $(PhMe_2CCH_2)PhSnH^+$]; 345 [0.5; $MePh(PhMe_2CCH_2)Sn^+$]. 270 MHz ^1H NMR (0.32 *M* in C_6D_6): $\delta(CH_3Sn)$ 0.013; δ(neophylic CH_3) 1.302 and 1.318; δ(neophylic CH_AH_B) 1.479 and 1.547; $\delta(SnH_X)$ 5.443; $|J(H_A—H_B)|$ 12.8 Hz; $|J(H_A—H_X)|$ 4.4 Hz; $|J(H_B—H_X)|$ 0.4 Hz; δ(aromatic protons) 7.011 to 7.456 ppm; $|^1J(Sn—H)|$ 1764.8; 1689.6 Hz; $|^2J(SnCH_3)|$ 56.6; 53.8; 4.2 Hz; $|^3J(CH_3—Sn—H)|$ 2.7 Hz. 22.63 MHz ^{13}C NMR (0.43 m in C_6D_6): $\delta(CH_3Sn)$ —11.503; δ(neophylic CH_3's) 32.365; 32.885; δ(neophylic CH_2) 30.740; δ(neophylic C) 37.824; δ(aromatic C's) 125.495 to 195.750 ppm; $^1J(CH)(CH_3Sn)$ 130.2; $^1J(CH)(CH_3—C)$ 126.5; $^2J(H_3C—Sn—H)$ 10.3 Hz.

* Petroleum ether b.p. 40°C is denoted below by pe40.

The optical yield is not affected if less IV is used *. I′ was prepared analogously (n_D^{20} 1.5751; ν(Sn—D) 1310 cm^{-1} (broad; film); $[\alpha]_{365}$ +5.6° (*c* 5.44; C_6H_6); monoisotopic 70 eV MS: 120 [9; Sn^+]; 121 [1.5; SnH^+]; 122 [1; SnD^+]; 135 [8; $MeSn^+$]; 197 [26; $PhSn^+$]; 212 [10; $MePhSn^+$]; 214 [14; $MePhSnD^+$] 227 [1; Me_2PhSn^+]; 253 [0.5; $PhMe_2CCH_2Sn^+$]; 276 [11; Ph_2SnD^+]; 289 [1.5; $MePh_2Sn^+$]; 332 [15; $(PhMe_2CCH_2)PhSnD^+$]; 345 [1; $(PhMe_2CCH_2)PhMeSn^+$] with a metastable peak at *m/e* 229 (332 → 276). 270 MHz ^1H NMR (0.31 *M* in C_6D_6): δ(CH_3Sn) 0.009; δ(neophylic CH_3's) 1.302 and 1.318; δ(neophylic CH_AH_B) 1.474 and 1.541; $J(H_ACH_B)$ 12.8; δ(aromatic protons) 7.043 to 7.371 ppm; $^2J(SnCH_3)$ 58.0; 55.4 Hz.

Synthesis of (—)-II

The hydride (—)-II was obtained similarly from neophylphenyl-t-butyltin bromide in 65% yield; b.p. 117°C/0.04 Torr; n_D^{20} 1.5628; elemental analysis: found: C, 62.25; H, 7.35. $C_{20}H_{28}Sn$ calcd.: C, 62.06; H, 7.24%. ν(Sn—H) 1820 cm^{-1} (film); ORD: (*c* 6.4; C_6H_6): 589 nm, —1.09°; 578, —1.12°; 546, —1.27°; 436, —2.22°; 365, —3.52°. Monoisotopic 70 eV MS: 120 [8; Sn^+]; 135 [6; $MeSn^+$]; 197 [39; $PhSn^+$]; 212 [17; $MePhSn^+$]; 213 [11; $MePhSnH^+$]; 227 [1; $PhMe_2Sn^+$]; 253 [2; $PhMe_2CCH_2Sn^+$]; 275 [10; Ph_2SnH^+]; 289 [2; $MePh_2Sn^+$]; 331 [3; $(PhMe_2CCH_2)PhSnH^+$]; 345 [1; $(PhMe_2CCH_2)MePhSn^+$]; 387 [0.1; $(PhMe_2CCH_2)PhBuSn^+$] with a metastable peak at *m/e* 228 (331 → 275). 270 MHz 1H NMR (0.26 *M* in C_6D_6): δ[$(H_3C)_3CSn$] 1.104; δ(neophylic CH_3's) 1.353; δ(neophylic CH_2): 1.604; δ(HSn) 5.728; δ(aromatic protons) 6.955 to 7.543 ppm; ^1J(SnH) 1666.6; 1595.1 Hz; $^2J(SnCH_2)$ 45.5 Hz; $^3J(SnCCH_3)$ 70.7; 67.2 Hz. The signals corresponding to the two diastereotopic neophylic methyl groups of II are thus isochronous in ^1H NMR spectroscopy at 270 MHz. They are not in 22.63 MHz ^{13}C NMR (0.7 *M* in C_6D_6): δ(neophylic CH_3's) 32.229; 32.681; δ(t-butylic CH_3's): 30.808; δ(t-butylic C) 29.000; δ(neophylic CH_2) 29.775; δ(neophylic C) 37.340; δ(aromatic C's) 124.783 to 150.166 ppm; ^1J(C—H)(t-butylic CH_3's) 123.3; ^1J(C—H)(neophylic CH_3's) 123.3 Hz.

Synthesis of (+)-III

(+)-III was also prepared analogously from methyl-1-naphthylphenyltin iodide [36] in 71% yield; m.p. 54—56°C; R_f 0.48 (pe40); elemental analysis: found: C, 60.12; H, 4.68. $C_{17}H_{16}Sn$ calcd.: C, 60.23; H, 4.72%. ν(Sn—H): 1835 cm^{-1} (KBr); ORD (*c* 4.02; n-C_5H_{12}): 578 nm: +0.50°; 436, +1.14°; 365, +2.01°. Monoisotopic 70 eV MS: 120 [18; Sn^+]; 121 [2.5; SnH^+]; 135 [4; $MeSn^+$]; 197 [17; $PhSn^+$]; 212 [3; $MePhSn^+$]; 247 [27; $NpSn^+$]; 262 [3; $MeNpSn^+$]; 325 [16; $PhNpSnH^+$]; 339 [3; $MePhNpSn^+$]; 340 [6; $MePhNpSnH^+$] with a metastable peak at *m/e* 311 (340 → 325). 270 MHz ^1H NMR (0.40 *M* in C_6D_6): δ(CH_3Sn) 0.491; δ(SnH) 6.400; δ(aromatic protons) 7.074 to 7.984 ppm; ^1J(SnH) 1871.3; 1788.1; $^2J(SnCH_3)$ 59.2; 56.8; $^2J(H_3C—Sn—H)$ 2.6 Hz; 22.63 MHz ^{13}C NMR (0.39 *M* in C_6D_6): δ(CH_3Sn) 10.853; aromatic C's 136.739 to 206.603 ppm; ^1J(H—C)(CH_3Sn) 118.4 Hz. In the presence of an excess of IV, racemic III, m.p. 52—55°C, is obtained.

* In contrast, with 8 equivalents of IV, the chemical yield is increased to 93% but I is obtained as a racemic mixture.

Synthesis of (—)-I and (—)-II

8.3 ml of a 1.9 *M* solution of n-butyllithium in diethyl ether are added under argon to a solution of 3.01 g (19.8 mmol) of (—)-menthol, $[\alpha]_{546}^{20}$ — 58° (*c* 10.0; EtOH) in 25 ml of ether cooled at 0°C. After 30 min a solution of 5 g (13.2 mmol) of VII in 25 ml of ether is added during 1 h to the solution of menthoxylithium cooled to —50°C. The mixture is kept at —15°C for 2 h and at room temperature overnight, then filtered under argon and added dropwise to a suspension of 0.6 g (15.8 mmol) of $LiAlH_4$ in 45 ml of anhydrous diethyl ether at —50°C. The mixture is kept at —15°C for 2 h and at room temperature overnight. After the addition of 39 mg of solid hydroquinone, the mixture is treated with 25 ml of a 20% aqueous solution of sodium potassium tartrate. The aqueous layer is extracted 3 times with diethyl ether and the ether extracts are collected and dried on $MgSO_4$. The solvent is evaporated and the residue is chromatographed on 300 g of SiO_2 with pe40 progressively enriched with benzene up to a 7/3 ratio pe40/C_6H_6. From the first fraction, 2.41 g (53.6%) of I is obtained with $[\alpha]_{365}^{30}$ — 0.70° (*c* 7.89; C_6H_6). A second fraction (590 mg) contains racemic VIII and two other products, which were not characterized but which gave rather heavy fragment ions (*m/e* ~ 900) in MS.

(—)-II was prepared analogously in 72% yield. Its $[\alpha]_{436}^{40}$ was —1.35° (*c* 6.9; C_6H_6).

Reaction of (—)-II with CH_2N_2

The procedure was similar to that described by Lesbre [25]. The NMR spectrum of V was identical that described in the literature [26].

Reaction of (+)-I with bifluorenylidene

To 5.4 g (16.5 mmol) of bifluorenylidene, 50 mg of AIBN and 5.68 g (16.5 mmol) of (+)-I placed in a 100 ml flask is added enough benzene to homogenize the mixture, which is put for 20 min in an oil bath at 95°C. The mixture is then left for 6 days at 20°C, after which no I can be detected by TLC or NMR. The obtained solid is fixed with benzene on 25 g of microcrystalline cellulose (Merck) which is put upon a dry chromatography column (Ø 5 cm; length 2.85 m; 1620 g of SiO_2) and eluted with a 8/2 mixture of dry pe40/dry toluene. VI is located in the column by its specific reaction with alcoholic $AgNO_3$. The silica is extracted with dry ether. The solvent is evaporated. Yield 11%. Racemic (±)-VI has been obtained from (±)-I in a 45% yield. After three recrystallisations from dry pe60-90, a solid (m.p. 141—144.5°C) is obtained; elemental analysis: found: C, 76.71; H, 5.71. $C_{43}H_{38}Sn$ calcd.: C, 76.88; H, 5.66%. ORD (*c* 4.55; CCl_4): 589 nm: +0.8°; 578: +0.8°; 546: +0.1°; 436: +1.5°. Monoisotopic 70 eV MS: 120 [3; Sn^+]; 135 [1.5; $MeSn^+$]; 197 [9; $PhSn^+$]; 213 [1.5; $MePhSnH^+$]; 227 [4; Me_2PhSn^+]; 289 [21; $MePh_2Sn^+$]; 345 [61; $Me(PhMe_2CCH_2)PhSn^+$]; 407 [0.5; $(PhMe_2CCH_2)Ph_2Sn^+$]; 449 [0.5; $C_{26}H_{17}Sn^+$]; 541 [0.2; $MePhC_{26}H_{17}Sn^+$]. 597 [<0.1; $Me(PhMe_2CCH_2)\ C_{26}H_{17}Sn^+$]; 659 [0.1; $Ph(PhMe_2CCH_2)C_{26}H_{17}Sn^+$]; 673 [<0.1; $M-1$] with a metastable peak at *m/e* 242 (345 → 289). 270 MHz ^1H NMR (0.16 *M* in CCl_4 + 50 µl C_6D_6): δ(CH_3Sn) — 0.357; δ(neophylic CH_3's) 1.081 and 1.102; δ(neophylic CH_AH_B) 1.287 and 1.420; ($J(H_A—H_B)$ 12.8 Hz); δ(H)($C_{26}H_{17}$) 5.087; δ(aromatic protons) 6.609 to 7.540 ppm; $^2J(Sn—CH_3)$

50.6; 48.2 Hz. In C_6D_6 (0.16 *M*), the signals become δ — 0.140; 1.090 and 1.118; 1.500 and 1.610 (13.3 Hz); 5.127, 6.752 to 7.520 ppm and 52.0; 49.6 Hz respectively. 22.63 MHz ^{13}C NMR (0.12 *M* in 2 ml CCl_3 + 500 μl C_6D_6): $\delta(CH_3Sn)$ — 7.733; δ(neophylic CH_3's) 32.267 and 33.697; δ(neophylic CH_2) 31.292; δ(neophylic C) 37.791 (cf. [27]); δ(CH, $C_{26}H_{17}$) 50.692; aromatic C's 119.126 to 149.932 ppm; $^1J(CH)(CH_3Sn)$ 130.9; $^1J(CH)(CH_2)$ 132.4 Hz; ^1J(CH, $C_{26}H_{17}$) 131.6 Hz.

Reaction of (+)-I in the presence of palladium

To 298 mg (0.86 mmol) of I, $[\alpha]^{30}_{365}$ + 13.2° (*c* 6.38; n-C_5H_{12}) are added under argon 10 mg of 10% Pd/C. An exothermic reaction takes place with the evolution of a gas, after which 0.5 ml of benzene is added. The mixture is left at room temperature for a few hours. The catalyst is filtered off and the product is transferred to a preparative SiO_2 TLC plate (400 × 200 × 2 mm). Two elutions with pe40 are followed by a third one with a 8/2 pe40/C_6H_6. Three fractions are obtained. The first (~1 mg) and the third (~6 mg) ones were not identified. The second one is extracted with benzene. 64 mg (22.5%) of VIII are isolated. ORD (*c* 6.4; C_6H_6): 589 nm: —5.79°; 578: —6.07°; 546; —7.12°; 436: —14.55°; 365: —28.9°. Monoisotopic 70 eV MS: 120 [3; Sn^+]; 135 [2; $MeSn^+$]; 197 [17; $PhSn^+$]; 227 [3; Me_2PhSn^+)]; 253 [8; $PhMe_2CCH_2Sn^+$]; 268 [2; Me($PhMe_2$-CCH_2)Sn^+]; 283 [3; Me_2($PhMe_2CCH_2$)Sn^+]; 289 [13; $MePh_2Sn^+$]; 330 [2; Ph($PhMe_2CCH_2$)Sn^+]; 345 [24; MePh($PhMe_2CCH_2$)Sn^+]; 401 [0.5];407 [3; Ph_2($PhMe_2CCH_2$)Sn^+]; [Me_2Ph($PhMe_2CCH_2$)Sn_2^+]; 501 [0.2; $MePh_3Sn_2^+$]; 541 [<0.1; $MePh_2$($PhMe_2CCH_2$(Sn_2H^+)]; 557 [15; Me_2Ph_2($PhMe_2CCH_2$)Sn_2^+]; 613 [0.5; Me_2Ph($PhMe_2CCH_2$)$_2Sn_2^+$]; 675 [1; $MePh_2$($PhMe_2CCH_2$)$_2Sn_2^+$]; 689 [0.2; *M* — 1] with metastable peaks at *m/e* 153 (253 → 197), 242 (345 → 289) and 182 (283 → 227). 270 MHz ^1H NMR (0.07 *M* in CCl_4 + 50 μl C_6D_6): $\delta(CH_3Sn)_1$ (*meso* or *dl*) 0.004; $\delta(CH_3Sn)_2$ (*dl* or *meso*) 0.011; δ(neophylic CH_3's): 1.256 and 1.274 ppm; a complex pattern is observed between δ 1.588 and 1.765 ppm for the CH_2 protons; the aromatic protons absorb between 6.981 and 7.243 ppm; $^2J(SnCH_3)_1$ 47.7; $^2J(SnCH_3)_2$ 47.3; $^2J(SnCH_2)$ 44.8; $^3J[Sn(SnCH_3)_1]$ 15.9; $^3J[Sn(SnCH_3)_2]$ 15.0 Hz. It may be noticed that the 270 MHz ^1H NMR spectrum of VIII in C_6D_6 shows only one CH_3Sn signal at 0.180 ppm, only one $^2J(SnCH_3)$ coupling constant however resolved for ^{119}Sn and ^{117}Sn (48.0 and 45.6 Hz) and only one unresolved $^3J(SnSnCH_3)$ coupling constant (15.5 Hz). The $^2J(SnCH_2)$ coupling constant is equal to 46.8 Hz in C_6D_6.

Reaction of (+)-I with CCl_4

2.5 mmol of (+)-I, $[\alpha]^{30}_{365}$ +14.0° (*c* 7.28; n-C_5H_{12}) are degassed under 0.1 Torr during 45 min and mixed with CCl_4 to give a 0.25 *M* solution. Aliquots of the solution are taken for the IR, NMR and ORD cells. When the reaction is completed, pure VII is obtained in 100% yield: n^{20}_D 1.5860; elemental analysis: found: C, 53.96; H, 5.45; Cl, 9.26. $C_{17}H_{21}SnCl$ calcd.: C, 53.80; H, 5.54; Cl, 9.36%.

We tried to trap the optically unstable VII formed during the reaction of (+)-I with CCl_4 by transforming it into an optically stable tetraorganotin compound, by the following procedure. A solution of 1.5 mmol of (+)-I, $[\alpha]^{30}_{365}$ +

14.0° (*c* 7.28; n-C_5H_{12}) in CCl_4 is prepared as above and placed in an ORD cell; α remains at 0.80° until the 16th minute and increases then rapidly to 1.67, reaching that value in the 20th minute. At the 21st minute, this solution is poured cautiously during 4 min into a solution of 0.1 mol of n-propylmagnesium bromide in diethyl ether at 0°C. The mixture is left for two days at room temperature, then hydrolyzed and chromatographed on SiO_2 (elution with pe40; R_f 0.2). It does not contain any residual of I. Methylneophylphenylpropyltin is obtained in 21% yield; $[\alpha]_\lambda$ 0; n_D^{20} 1.5618; elemental analysis: found: C, 62.27; H, 7.09. $C_{20}H_{28}Sn$ calcd.: C, 62.06; H, 7.24%. Monoisotopic 70 eV MS: 120 [5; Sn^+]; 135 [3; $MeSn^+$]; 197 [12; $PhSn^+$]; 213 [9; $MePhSnH^+$]; 227 [5; Me_2PhSn^+]; 255 [4; $MePhPrSn^+$]; 289 [25; $MePh_2Sn^+$]; 311 [0.5; $Me(PhMe_2CCH_2)PrSn^+$]; 317 [1; Ph_2PrSn^+]; 373 [2; $Ph(PhMe_2CCH_2)PrSn^+$] with a metastable peak at *m/e* 242 (345 → 289). 270 MHz ^1H NMR (0.18 *M* in CCl_4 +50 μl C_6D_6); $\delta(CH_3Sn)$: —0.040; δ(neophylic CH_3's) 1.353 and 1.361; δ(neophylic CH_2) 1.575; δ(propylic CH_3) 0.846; δ(propylic CH_2Sn) complex pattern at high field versus the propylic metal signal; δ(propylic CH_2) complex pattern between the neophylic methylene and methyl signals; δ(aromatic protons) 7.024 to 7.304 ppm; $^2J(SnCH_2CMe_2Ph)$ 53.1 Hz; $^3J(CH_3CH_2)$ 7.3 Hz; $^4J(SnC—C(CH_3)_2Ph)$ 15 Hz. The 270 MHz spectrum of the same compound in C_6D_6 shows signals at δ + 0.047; 1.300 and 1.312; 1.526; 0.871; lower field; lower field; 7.042 to 7.409 ppm respectively with the same coupling constants.

Addition of (+)-I to allyl alcohol

A flask containing 1 g (2.9 mmol) of (+)-I, $[\alpha]_{365}^{30}$ +13.2° (*c* 6.38; n-C_5H_{12}), 170 mg (2.9 mmol) of allyl alcohol, 0.5 ml of benzene and 100 mg of AIBN is placed in an oil bath at 90°C. After 90 min at this temperature, a substantial amount of I is still present. 50 mg of AIBN are added, and the temperature of the oil bath is raised to 110°C and the colourless mixture becomes progressively yellow. After 2 h at 110°C, it is left for one day at room temperature. At this stage, it contains no residual I. IX is isolated by chromatography on silica: elution with benzene eliminates traces of VIII formed: this solvent is then progressively replaced by ethanol. First methylneophenyldiphenyltin (6%) is obtained, then 850 mg of a yellow liquid containing IX. This liquid is treated with carbon black in pe40. After filtration and evaporation of the solvent, 350 mg of colourless IX (30%) are obtained, for which $[\alpha]_\lambda$ 0; n_D^{20} 1.5710; ν(O—H) 3.350 cm^{-1} (film); elemental analysis: found: C, 60.04; H, 6.96. $C_{20}H_{28}OSn$ calcd.: C, 59.60; H, 6.95%. Monoisotopic 70 eV MS: 120 [5; Sn^+]; 135 [4; $MeSn^+$]; 137 [2.5; $SnOH^+$]; 165 [1.5; $SnCH_2CH_2OH^+$]; 179 [2; $Sn(CH_2)_3OH^+$]; 194 [1.5; $MeSn(CH_2)_3OH^+$]; 197 [13; $PhSn^+$]; 209 [0.2; $Me_2Sn(CH_2)_3OH^+$)]; 213 [1.5; $MePhSnH^+$]; 229 [9; $MePhSnOH^+$]; 253 [2; $PhMe_2CCH_2Sn^+$]; 271 [21; $MePhSn)CH_2)_3OH^+$]; 289 [9; $MePh_2Sn^+$]; 311 [1; $Ph(PhMe_2CCH_2)SnH^+$]; 327 [3; $Me(PhMe_2CCH_2)Sn(CH_2)_3OH^+$]; 345 [22; $MePh(PhMe_2CCH_2)Sn^+$]; 389 [3; $Ph(PhMe_2CCH_2)Sn(CH_2)_3OH^+$] with a metastable peak at *m/e* 242 (345 → 289). 270 MHz ^1H NMR (0.22 M in CCl_4 + 100 μl C_6D_6): $\delta(CH_3Sn)$ —0.036; δ(neophylic CH_3's) 1.364 and 1.371; δ(neophylic CH_2) 1.603; δ(hydroxypropylic CH_2Sn) complex pattern centered at 0.658; δ(central hydroxypropylic CH_2) complex pattern between the neophylic methylene and methyl signals; $\delta(CH_2O)$ 3.294; δ(aromatic protons) 7.148 to 7.292 ppm; $^2J(SnCH_3)$ 52.4;

50.0 Hz; ^2J(neophylic CH_2—Sn) 52.8 Hz; $^3J(CH_2CH_2O)$ 6.4 Hz. In benzene, the signals are shifted to δ + 0.047; 1.299 and 1.310; 1.546; 0.684; low field; 3.272 7.043 to 7.400 ppm respectively; $^2J(SnCH_3)$ 51.7; 49.5 Hz; $^3J(CH_2CH_2O$ 6.4 Hz.

Addition of (+)-I' to methyl acrylate

713 mg (2.06 mmol) of (+)-I', $[\alpha]_{365}^{30}$ +10.70° (*c* 5.45; n-C_5H_{12}) and two equivalents of freshly distilled methyl acrylate are mixed with 2 mole% of AIBN. After 18 h at room temperature the reaction is stopped and the mixture is chromatographed on SiO_2. Traces of VIII can be removed with a 8/2 mixture of pe40/C_6H_6. Then, an elution with a 1/1 benzene ethanol mixture yields 76% of ($PhMe_2CCH_2$) MePhSnCH_2CHDCOOMe (XVI), $[\alpha]_\lambda$ 0; ν(C=O) 1730 cm^{-1}; ν(C—O) 1200 cm^{-1} (film). The reduction of the ester function of XVI is achieved by the procedure described in ref. 30. The obtained IX' is purified like IX (vide supra). Its 270 MHz ^{1}H NMR spectrum is similar to that of IX.

Reaction of (+)-I with tributylaluminum

The experiment is carried out in glassware which has been heated overnight at 150°C and then cooled in a stream of argon. 480 mg (1.39 mmol) of (+)-I, $[\alpha]_{365}^{30}$ +13.21° (*c* 6.38; n-C_5H_{12}) are degassed four times and put under argon. 0.5 ml of cyclohexane under argon and 0.35 ml of n-Bu_3Al (275 mg; 139 mmol) are added and the flask is then put for 2.5 h in an oil bath heated at 90°C. After one night at room temperature, TLC shows that I is still present. The flask is heated for 1.5 h at 110°C and the excess of n-Bu_3Al is destroyed by the addition of non-deoxygenated cyclohexane. TLC shows the presence of unreacted I, which cannot easily be separated from X. I is therefore transformed into VII by the addition of CCl_4. The mixture is chromatographed on 100 g of SiO_2 with a 8/2 mixture of pe40/C_6H_6. 9.6 mg (2%) of XI, 71.5 mg (13%). of X and 86.7 mg (15%) of XII are obtained successively. XI is identified by comparison with an authentic sample. Its 270 MHz ^{1}H NMR spectrum (0.33 *M* in CCl_4 containing 50 μl of C_6D_6) is as follows: $\delta(CH_3Sn)$ —0.234; δ(neophylic CH_3's) 1.361; δ(neophylic and two butylic CH_2's) complex pattern at high field versus the neophylic methyl signal; δ(butylic CH_3) 0.846; δ(butylic CH_2Sn) complex pattern between 0.519 and 0.588; δ(aromatic protons) between 7.058 and 7.294 ppm; ^2J(MeSn) 49.5; 46.9 Hz; $^3J(CH_3CH_2)$ 7.1 Hz. XII is identified by NMR [29]; n_D^{20} 1.6015; elemental analysis: found: C, 65.73; H, 6.06. $C_{23}H_{26}Sn$ calcd.: C, 65.61; H, 6.18%. For X (R_f 0.45), $[\alpha]_\lambda$ = 0; n_D^{20} 1.5558; elemental analysis: found: C, 63.70; H, 7.47. $C_{21}H_{30}Sn$ calcd.: C, 62.89; H, 7.49%. Monoisotopic 70 eV MS: 120 [4; Sn^+]; 121 [0.8; SnH^+]; 135 [4; $MeSn^+$]; 145 [0.6]; 197 [13; $PhSn^+$]; 213 [11, $MePhSnH^+$]; 227 [1.5; Me_2PhSn^+]; 269 [4; $MePhBuSn^+$ or $Me(PhMe_2CCH_2)SnH^+$)]; 289 [11; $MePh_2Sn^+$]; 325 [0.5; $MeBu(PhMe_2CCH_2)Sn^+$]; 331 [1; Ph_2BuSn^+ or $Ph(PhMe_2CCH_2)SnH^+$]; 345 [48; $MePh(PhMe_2CCH_2)Sn^+$]; 387 [4; $Ph(PhMe_2CCH_2)BuSn^+$] with metastable peaks at *m/e* 169 (269 → 213) and 242 (345 → 289). 270 MHz ^{1}H NMR spectrum (0.24 *M* in CCl_4 + 50 μl C_6D_6): $\delta(CH_3Sn)$ —0.045; δ(neophylic CH_3's) 1.359 and 1.367; δ(neophylic CH_2) 1.580; δ(butylic CH_3) 0.812 p; δ(butylic CH_2's) complex patterns at high field versus the neophylic methyl signal; δ(butylic CH_2Sn) complex pattern at high field versus the butylic methyl signal;

δ(aromatic protons) 7.033 to 7.296 ppm; $^2J(SnCH_3)$ 50.9; 49.1; ^2J(neophylic CH_2Sn) 52.2; ^3J(butylic CH_3CH_2) 7.0 Hz; in C_6D_6, these signals are shifted to δ + 0.062, 1.308 and 1.318; 1.538; 0.828; lower field; lower field; 7.045 to 7.423 ppm; 51.3; 49.1; 52.2; 7.3 Hz respectively.

Reaction of (+)-I' with diethylaluminum hydride

110 mg (0.32 mmol) of (+)-I', $[\alpha]_{365}^{30}$ +10.70° (*c* 5.45; n-C_5H_{12}) are mixed under argon with 5 equivalents of Et_2AlH in 0.4 ml of benzene. After 10 h in the dark at room temperature, the excess of Et_2AlH is destroyed by the addition of non deoxygenated hexane. After the usual procedure and chromatography on SiO_2 (elution with pe40), 10% of racemic I is obtained. The H—D exchange is complete, as shown by NMR and IR.

Formation of a racemic hexaorganoditin compound from an optical active triorganotin hydride

244 mg (0.6 mmol) of (—)-II, $[\alpha]_{365}^{30}$ —0.95° (*c* = 24.4; C_6H_6) are mixed with 215 mg (0.93 mmol) of diethylmercury in a NMR cell. After 15 h in the dark no reaction has taken place. 20 min in daylight are sufficient for the formation of metallic mercury and the appearance of a yellow colour. After two days, no residual II can be detected by NMR. The mercury (24 mg; 19%) is filtered off. The residue is chromatographed on SiO_2 (elution with pe60—90). 19.1 mg (9.2%) of XIII are obtained, for which $[\alpha]_\lambda$ 0, λ 589 to 365 nm. Monoisotopic 70 eV MS: 120 [4; Sn^+]; 197 [24; $PhSn^+$]; 253 [14; $PhMe_2CCH_2Sn^+$]; 275 [5; Ph_2SnH^+]; 331 [4; $BuPh_2Sn^+$ or $Ph(PhMe_2CCH_2)Sn^+$]; 387 [14; $BuPh(PhMe_2CCH_2)Sn^+$]; 407 [4; $Ph_2(PhMe_2CCH_2)Sn^+$]; 443 [2; $BuPh(PhMe_2CCH_2)SnCH_2CMe_2^+$]; 463 [5; $BuPh(PhMe_2CCH_2)SnC_6H_4^+$]; 527 [0.6; $Ph_2Me_2CCH_2)Sn_2^+$]; 583 [0.4; $(PhMe_2CCH_2)_2PhSn_2^+$]; 641 [0.8; $Bu_2Ph_2(PhMe_2CCH_2)Sn_2^+$ or $BuPh(PhMe_2CCH_2)_2Sn_2H^+$]; 661 [3; $Ph_2(PhMe_2CCH_2)_2Sn_2H^+$]; 675 [3]; 697 [0.1; $Bu_2(PhMe_2CCH_2)_2PhSn_2^+$]; 717 [15; $BuPh_2(PhMe_2CCH_2)_2Sn_2^+$]; 737 [0.2]; 773 [1; *M* — 1] with metastable peaks at *m/e* 283 (387 → 331) and 153 (717 → 331 and/or 253 → 197); 60 MHz ^1H NMR (0.08 *M* in CCl_4): δ(t-butylic CH_3's) 1.14; δ(neophylic CH_3's) 1.32 and 1.34; δ(CH_2) 1.91; δ(aromatic protons) around 7.2 ppm; ^3J(Sn—C—CH_3) 71.2; 68.8 Hz.

Synthesis of (+)-isopropylmethylneophyltrityltin (XIV)

Diastereomeric menthoxytriorganotin compounds are prepared from methylneophyltrityltin bromide and (—)-menthoxylithium by a procedure identical to that described in [8] except that the temperature is kept at —15°C, as in the subsequent reaction of these menthoxytriorganotin compounds with isopropylmagnesium bromide. Hydrolysis and chromatography on silica (elution with a 75/25 mixture of pe60-90/toluene) yields a solid which is recrystallyzed 3 times from MeOH/Et_2O. Yield 26.6% *; m.p. 106—110.5°C; elemental analysis: found: C, 71.99; H, 6.81. $C_{33}H_{38}Sn$ calcd.: C, 71.65; H, 6.88%. ORD (*c* 3.9; CCl_4): 589 nm: +51.2°; 578: +5.41°; 546: +6.54°; 436: +14.85°; 365: +36.0°. Mono-

* The NMR-spectrum of the solution after hydrolysis shows that only 30% of the triorganotin bromide has been converted into XIV.

isotopic 70 eV MS: 120 [3; Sn^+]; 135 [9; $MeSn^+$]; 151 [2.5; Me_2SnH^+]; 178 [1; $MePrSn^+$]; 179 [1; $MePrSnH^+$]; 197 [12; $PhSn^+$]; 213 [14; $MePhSnH^+$]; 253 [4; $PhMe_2CCH_2Sn^+$]; 255 [7; MePh-i-PrSnH$^+$ or $PhMe_2CCH_2SnH_2^+$]; 269 [4; $Me(PhMe_2CCH_2)SnH^+$]; 283 [4]; 311 [39; $Me(PhMe_2CCH_2)$-i-$PrSn^+$]; 421 [Me-i-$Pr(Ph_3C)Sn^+$]; 511 [0.6; $Me(PhMe_2CCH_2)(Ph_3C)Sn^+$]; 539 [0.2; $(PhMe_2CCH_2)(Ph_3C)$-i-$PrSn^+$] with a metastable peak at *m/e* 207 (511 → 325). 270 MHz ^1H NMR (0.18 *M* in CCl_4 + 50 μl C_6D_6): δ(CH_3Sn) −0.234; δ(neophylic CH_3's) 1.279 and 1.300; δ(neophylic CH_AH_B) 1.509 and 1.162 ($^2J(H_ACH_B)$ 12.8 Hz); δ(isopropylic $(CH_3)_A$ and $(CH_3)_B$) 0.862 and 0.968 ($^3J[(H_3C)_A$—CH) 4.6; $^3J[(H_3C)_BCH]$ 5.9 Hz) δ(aromatic protons) 6.827 to 7.197 ppm ($^2J(SnCH_3)$ 46.4; 44.0 Hz); the isopropylic CH absorbs between δ 1.2 and 1.3 ppm, in the neophylic region. Nonequivalence of the three diastereotopic groups of XIV is observed at 270 MHz: the neophylic methyls, the neophylic methylenic protons and the isopropilic methyls. This is also true for the spectrum in benzene. In this case, the signals are shifted to δ −0.040; 1.251 and 1.258; 1.361 and 1.648 ($^2J(H_ACH_B)$ 12.8 Hz); 0.954 and 1.061 (5.9; 6.4 Hz); 6.904 to 7.227 ppm (49.6; 47.4 Hz) respectively.

Formation of a racemic hexaorganoditin compound from an optically active tetraorganotin compound

541 mg (0.98 mmol) of (+)-XIV, $[\alpha]_D^{30}$ + 1.76° (*c* 6.82; CCl_4) in 6 ml of anhydrous diethyl ether are added to 1.2 mmoles of $LiAlH_4$ in 5 ml of the same solvent. After 14 h at room temperature the mixture is hydrolyzed with a 20% aqueous solution of sodium potassium tartrate in the presence of hydroquinone. The residue obtained after the usual treatment is chromatographed on 90 g of SiO_2 with 9/1 n-pentane/benzene. 60 mg (10%) of XV is obtained for which $[\alpha]_\lambda$ 0. Monoisotopic 70 eV MS: 120 [8; Sn^+]; 197 [14; $PhSn^+$]; 253 [10; $PhMe_2CCH_2Sn^+$]; 269 [7; $Me(PhMe_2CCH_2)SnH^+$]; 283 [10; $Me_2PhMe_2CCH_2)Sn^+$]; 311 [18; Me-i-$Pr(PhMe_2CCH_2)Sn^+$]; 347 [2; $Me_2PhSn_2^+$]; 339 [1; Me-i-Pr-$(PhMe_2CCH_2)SnCHMe^+$]; 327 [1; i-$Pr_2Sn_2H^+$]; 373 [1; $PhMe_2CCH_2Sn_2^+$]; 401 [6]; 429 [3; i-$Pr(PhMe_2CCH_2)_2Sn^+$]; 461 [0.5; Me_3-i-$Pr(PhMe_2CCH_2)Sn_2^+$]; 489 [1; Me_2(i-Pr)$_2(PhMe_2CCH_2)Sn_2^+$]; 523 [0.5; Me_2Ph-i-$Pr(PhMe_2CCH_2)Sn_2^+$]; 551 [0.5; i-$Pr(PhMe_2CCH_2)_2Sn_2H_2$]; 579 [18; Me_2-i-$Pr(PhMe_2CCH_2)_2Sn_2^+$]; 607 [0.5; $Me(i\text{-}Pr)_2(PhMe_2CCH_2)_2Sn_2^+$]; 621 [<0.1; *M* − 1] with a metastable peak at *m/e* 167 (579 → 311). 60 MHz ^1H NMR (0.19 *M* in C_6D_6): δ(CH_3Sn) 0.02; δ(neophylic CH_3) 1.40; δ(neophylic CH_2) 1.60; δ(isopropylic CH_3) 1.25; δ(aromatic protons) 7.2 ppm; $^2J(SnCH_3)$ 44.0; 41.6; $^3J(SnSnCH_3)$ 15.2 Hz.

Reaction of (+)-I′ with $LiAlH_4$

A solution of 574 mg of (+)-I′, $[\alpha]_{365}^{30}$ +10.70° (*c* 5.45; n-C_5H_{12}) dissolved in 10 ml of diethyl ether is added dropwise under argon to 8 ml of a 0.265 *M* ether solution of $LiAlH_4$. Aliquots (4 ml) of this mixture are taken at given time intervals, mixed with wet ether, then hydrolyzed. The residue obtained after the usual treatment is chromatographed on SiO_2 with pe40 and analyzed by ORD and NMR. 408 mg (71%) of I + I′ are recovered.

Synthesis of triphenyltin deuteride

The procedure described by van der Kerk [31] was followed but the purifi-

cation method differed from that of the original paper, since chromatography on SiO_2 (elution with a 8/2 mixture of pe40/benzene) was found to be much more efficient than the distillation used by the Dutch team. Yields as high as 94% were obtained of a liquid which was crystalline at low temperatures. R_f 0.49; n_D^{28} 1.6302 (lit. [33] n_D^{28} 1.6318); n_D^{40} 1.6248; elemental analysis: found: C, 61.35; H-D, 4.67. $C_{18}H_{15}DSn$ calcd.: C, 61.42; H-D, 4.83%. ν(Sn—D) 1320 cm^{-1} (film) (lit. [32] 1323 cm^{-1}).

Reaction of (+)-I′ with triphenyltin hydride

123 mg (0.35 mmol) of (+)-I′, $[\alpha]_{365}^{30}$ +5.75° (*c* 5.44; C_6H_6) 624 mg (1.75 mmol) of triphenyltin hydride and 0.2 ml of benzene are mixed in a NMR tube. After 30 min, 16.3% of I is formed, after 60 min, 26.1%; after 90 min, 33.3%; after 150 min, 53.1%; after 180 min, 57.4%; after 330 min, 69.2% and after 525 min, 75.5%. The triphenyltin hydride which is insoluble after the addition of pe40 to the mixture is filtered off. The residual solution is then transferred to a preparative SiO_2 plate (2 × 200 × 400 mm). The elutions are performed in the dark, the first two with pe40 and the third with a 8/2 mixture of pe40/benzene. The R_f of the mixture I + I′ is 0.7; the R_f of the mixture Ph_3SnH + Ph_3SnD is 0.5. The silica is extracted with benzene. 40 mg (32.5%) of a mixture of I and I′ for which $[\alpha]_{365}^{30}$ + 5.00° (*c* 3.78; C_6H_6) are thus obtained. The 70 eV mass and NMR spectra show that this mixture contains 76% of I and 24% of I′. Hexaphenylditin has been isolated from the reaction mixture.

Instruments

The IR spectra were recorded on a Perkin—Elmer 125 Grating double beam spectrometer; the mass spectra were recorded on a Hitachi—Perkin—Elmer RMV-6D or on a MS 902S apparatus; fragment-ions with low intensity (<0.5) have generally not been mentioned.

The 270 MHz ^1H NMR spectra were recorded on a Bruker HDX-270 apparatus, the 60 MHz spectra on a Varian T-60, the 22.63 MHz ^{13}C NMR spectra on a Bruker WH90. TMS was used as internal standard.

The ORD-spectra were recorded on a Perkin—Elmer 141 polarimeter at 589, 578, 546, 436 and 365 nm in a 1 dm cell.

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References

1 M. Gielen and Y. Tondeur, J. Chem. Soc., Chem. Commun., (1978) 81.
2 M. Gielen and Y. Tondeur, Nouv. J. Chim., 2 (1978) 117.
3 M. Gielen and Y. Tondeur, J. Organometal. Chem., 128 (1977) C25.
4 M. Gielen and Y. Tondeur, J. Organometal. Chem., 127 (1977) C75.
5 (a) H. Mokhtar-Jamai, C. Dehouck, S. Boué and M. Gielen, 5th International Conference on Organometallic Chemistry, Moscow, 1971, Abstracts 199, I. 523 and 361, II, 359; M. Gielen and H. Mokhtar-Jamai, Bull. Soc. Chim. Belg., 84 (1975) 197. (b) M. Gielen, Ann. Rep. Inorg. Gen. Synth., (1976) 337 and references cited therein.
6 M. Gielen, S. Simon, Y. Tondeur, M. van de Steen and C. Hoogzand, Bull. Soc. Chim. Belg., 83 (1974) 337; M. Gielen and Y. Tondeur, Bull. Soc. Chim. Belg., 84 (1975) 933.
7 J.P. Vigneron and J. Jacquet, Tetrahedron, 32 (1976) 939.
8 U. Folli, D. Iarossi and F. Taddei, J. Chem. Soc. Perkin II, (1973) 638; see also M. Gielen and S. Simon, Bull. Soc. Chim. Belg., 86 (1977) 589.
9 M. Gielen and J. Nasielski, J. Organometal. Chem., 1 (1963) 173; 7 (1967) 273.
10 G.B. Watts and K.U. Ingold, J. Amer. Chem. Soc., 94 (1972) 491; H.U. Buschhaus, M. Lehnig and W.P. Neumann, J. Chem. Soc., Chem. Commun., (1977) 129.
11 M. Lehnig, Tetrahedron Lett., (1977) 3663.
12 M. Gielen and H. Mokhtar-Jamai, J. Organometal. Chem., 91 (1975) C33; 129 (1977) 325.
13 V.A. Ivanov, V.O. Reikhfel'd and I.E. Saratov, Zh. Obshch, Khim., 45 (1975) 2036; Chem. Abstr., 83 (1975) 205400r.
14 (a) G. Schott and C. Harzdorf, Z. Anorg. Allg. Chem., 307 (1961) 105; (b) R.E. Dessy, T. Hieber and T. Paulik, J. Amer. Chem. Soc., 86 (1964) 28; (c) H.G. Kuivila and P.L. Levins, J. Amer. Chem. Soc., 86 (1964) 23.
15 A.G. Brook, J.M. Duff and D.G. Anderson, J. Amer. Chem. Soc., 92 (1970) 7567.
16 V.B. Schneider and W.P. Neumann, Ann., 707 (1967) 7.
17 V.T. Bychkov, A.I. Burov, V.A. Kuznetsov, I.V. Lomakova and A.A. Klimov, Khim. Elementoorg. Soedin, (1976) 53; Chem. Abstr., 85 (1976) 191792x.
18 H. Sakurai, M. Murakami and M. Kumada, J. Amer. Chem. Soc., 91 (1969) 519.
19 L.H. Sommer, J.E. Lyons and H. Fujimoto, J. Amer. Chem. Soc., 91 (1969) 7051.
20 R.J.P. Corriu and J.J.E. Moreau, J. Organometal. Chem., 40 (1972) 55.
21 F. Meganem, A. Jean and M. Lequan, J. Organometal. Chem., 74 (1974) 43.
22 L.H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, New York, 1965, p. 102—104.
23 G.A. Parker, Ph.D. Thesis, Pennsylvania State University, 1963.
24 H. Felkin, Bull. Soc. Chim.Fr., (1951) 347.
25 M. Lesbre and R. Buisson, Bull. Soc. Chim. Fr., (1957) 1204.
26 M. Gielen and H. Mokhtar-Jamai, Bull. Soc. Chim. Belg., 84 (1975) 1037.
27 D.E. Axelson, S.A. Kandil and C.E. Holloway, Can. J. Chem., 52 (1974) 2968.
28 D.J.D. Peddle and G. Redl, J. Organometal. Chem., 23 (1970) 461.
29 H. Mokhtar-Jamai, Ph.D. Thesis, Brussel, 1975.
30 G.J.M. van der Kerk and J.G. Noltes, J. Appl. Chem., 9 (1959) 176.
31 G.J.M. van der Kerk, J.G. Noltes and J.G.A. Luijten, J. Appl. Chem., 7 (1957) 366.
32 W.P. Neumann and R. Sommer, Angew. Chem., 75 (1963) 788.
33 A. Holt, A.W.P. Jarvie and G.J. Jervis, Tetrahedron Lett., (1968) 4087; see also J. Chem. Soc. Perkin II, (1973) 114.
34 R.J.P. Corriu and J.J.E. Moreau, J. Organometal. Chem., 85 (1975) 19; 120 (1976) 337.
35 G.J.D. Peddle and G. Redl, J. Organometal. Chem., 23 (1970) 461.
36 M. Lequan, F. Meganem and Y. Besace, J. Organometal. Chem., 131 (1977) 231.