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Organotin compounds

XI *. Organotin hydride additions to various methyl dihydronaphthalenecarboxylates

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Abstract

Free radical hydrostannation of methyl 3,4-dihydronaphthalene-1-carboxylate (I), methyl 3,4-dihydronaphthalene-2-carboxylate (III), and methyl 1,4-dihydronaphthalene-2-carboxylate (V) with triorganotin hydrides, R_3SnH (R = Me, n-Bu, Ph) gives the energetically unfavourable *cis* products, 2-triorganostannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (II), 1-triorganostannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (IV), and 3-triorganostannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (VI) in high yields, via a *trans* addition of the tin hydrides. The hydride abstractions by the intermediate 2-, 1-, 3-triorganostannyl-1,2,3,4-tetrahydronapththyl radicals (XI, XII and XIII respectively) take place stereospecifically and exclusively from the less-hindered ring side. The structures of the isomers II, IV, and VI, were established by (a) their transformation into the corresponding chlorodiorganostannyl derivatives VIII, IX, and X, which were shown spectroscopically to have *cis* stereochemistries by intramolecular complexation of the ester group, and (b) their NMR data . Full ^1H, ^{13}C, and ^{119}Sn NMR data are given.

Introduction

Among the methods for the synthesis of functionally substituted organotin compounds, the hydrostannation of olefinic systems is perhaps the simplest and most versatile. The reaction normally proceeds by a well-established free radical mechanism [1,2]. In previous studies on the addition of triorganotin hydrides

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* For part X see ref. 7.
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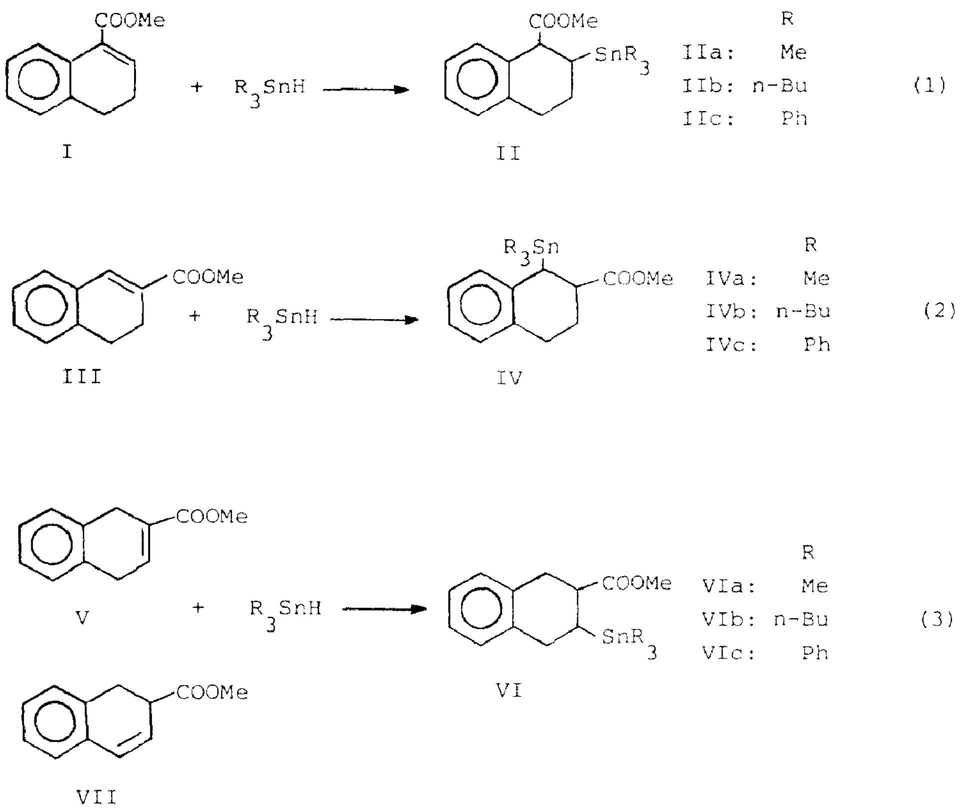


Scheme 1

R_3SnH and diorganotin chlorohydrides R_2SnClH to open-chain olefins [3–6], we were able to show that these reactions take place with a high degree of stereoselectivity. More recently [7] we have shown that in the case of methyl cyclohexene-1-carboxylate and methyl indene-3-carboxylate these reactions occur with exclusive *trans* stereochemistry.

We now wish to communicate the results we have obtained in some studies carried out with the aim of determining the stereochemistry of the hydrostannation of various methyl dihydronaphthalenecarboxylates according to Scheme 1.

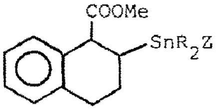
These additions are of interest as model systems for a stereoselective hydrostannation of unsaturated substituted ring systems, including biomolecules, and thus would be a useful contribution to the use of organotin hydrides in organic synthesis.

Results and discussion

All the additions were carried out under free radical conditions. Two methods were used: (a) the mixture of olefin, organotin hydride and azobis(isobutyronitrile) (AIBN) was stirred without solvent under nitrogen (at 80 °C in the case of triphenyl- and tri-n-butyltin hydrides, at 65 °C in the case of trimethyltin hydride) until all the olefin had reacted. (b) The mixture of olefin, excess organotin hydride and AIBN, was irradiated (mercury high pressure lamp) without solvent, under nitrogen and with stirring until all the olefin had reacted (temperature inside the

Table 1

IR and ^{1}H NMR data of *cis*-methyl 2-trialkylstannyl- and 2-chlorodialkylstannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylates



Compound	R	Z	IR [a]	^{1}H NMR, chemical shifts (δ, ppm) [b]	
q			ν(C=O) (cm^{-1})	OMe	Others
IIa	Me	Me	1735	3.64	0.05(s, 9H, $^2J(^{119}Sn-C-H)$, 52.4); 1.43–2.42(cs [c], 3H); 2.62–2.93 (cm [c], 2H); 3.93 (d, 1H, $^3J_{1,2}$ 5.2); 7.04–7.13(cs [c], 4H)
VIIIa	Me	Cl	1658 [d]	3.83	0.41(s, 3H, $^2J(^{119}Sn-C-H)$, 63.6); 0.65 (s, 3H, $^2J(^{119}Sn-C-H)$, 62.3); 2.07–2.32 (cs [c], 3H); 2.75–3.05(cs [c], 2H); 4.13(d, 1H, $^3J_{1,2}$ 5.9); 7.1–7.22(cs [c], 4H)
IIb	n-Bu	n-Bu	1733	3.6	0.57–2.5(cs [c], 30H); 2.55–3.0(cm [c], 2H); 3.8(d, 1H, $^3J_{1,2}$ 5.0); 6.83–7.28(cs [c], 4H)
VIIIb	n-Bu	Cl	1680	3.78	0.71–2.42(cs [c], 21H); 2.63–2.96(cs [c], 2H); 4.06(d, 1H; $^3J_{1,2}$ 5.6); 7.03–7.18(cs [c],4H)
IIc	Ph	Ph	1728 [d]	3.22	1.95–3.03(cs [c], 5H); 4.07(d, 1H, $^3J_{1,2}$ 4.0); 6.7–8.17(cs [c], 19H)
VIIIc	Ph	Cl	1678 [d]	3.87	1.67–3.08(cs [c], 5H); 4.2(d, 1H, $^3J_{1,2}$ 6.0); 6.6–8.0(cs [c], 14H)

[a] IR spectra of pure compounds (film), except when otherwise stated. [b] ^{1}H NMR spectra in $CDCl_3$ solution; chemical shifts with reference to TMS; J values in Hz. [c] cs stands for complex signal and cm for complex multiplet. [d] As KBr pressed disc.

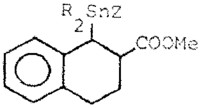
photochemical reactor: ca. 25 °C). The reactions were followed by IR (by observing the disappearance of the Sn–H absorption) and proton NMR spectroscopy (by observing olefin disappearance and product formation). In all cases the optimum times of reaction and hydride/olefin ratios required for a quantitative yield (with respect to olefin) were determined. The product analyses show that, within the limits of ^{1}H NMR spectroscopy (3–5%), only one of the two possible isomers was obtained (as a racemic mixture). It can therefore be concluded that the additions are stereoselective. The main spectroscopic characteristics of the new compounds obtained are summarized in Tables 1–6.

Noteworthy is the fact that the hydrostannation of both methyl 1,4-dihydro-(V) and 1,2-dihydronaphthalene-2-carboxylate (VII) lead to the same adducts (Scheme 1, eq. 3).

The spectroscopic data for adducts II, IV, and VI did not permit an accurate assignment of their stereochemistry because only a single isomer was obtained. In order to obtain more structural information concerning the stereochemistry of these addition reactions, the adducts II, IV and VI were converted into the corresponding halodiorganostannyl derivatives VIIIa–VIIIc, IXa–IXc, and Xa–Xc. This was done because it is known [4–8] that for esters containing a 3-halodiorganostannyl substituent, intramolecular coordination occurs (see Fig. 1). In such compounds the stereochemistry of the addition can sometimes be deduced from the NMR spectra.

Table 2

IR and ^{1}H NMR data of *cis*-methyl 1-trialkylstannyl- and 1-chlorodialkylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates



Compound	R	Z	IR[a]	^{1}H NMR, chemical shifts (δ, ppm)[b]	
			ν(C=O) (cm^{-1})	OMe	Others
IVa	Me	Me	1730	3.75	0.004(s, 9H, $^{2}J(^{119}Sn-C-H)$, 51.9); 1.67–1.84(cs [c], 1H); 2.36–2.48(cs [c], 1H); 2.92 (cm [c], 2H); 3.17(cs [c], 1H); 3.25(d, 1H, $^{3}J_{1,2}$ 2.6); 6.85–7.05(cs [c], 4H)
IXa	Me	Cl	1678	3.81	0.58(s, 3H, $^{2}J(^{119}Sn-C-H)$; 0.69 (s, 3H, $^{2}J(^{119}Sn-C-H)$, 62.3); 1.83–2.33 (cs [c], 2H); 2.6–2.9(cs [c], 2H); 3.1–3.35 (cs [c], 1H); 3.4(d, 1H, $^{3}J_{1,2}$ 6.5); 7.0–7.52(cs [c], 4H)
IVb	n-Bu	n-Bu	1728	3.68	0.85–2.07(cs [c], 27H); 2.18–3.45(cs [c], 6H); 6.47–7.27(cs [c], 4H)
IXb	n-Bu	Cl	1678	3.82	0.79–2.2(cs [c], 20H); 2.57–3.35(cs [c], 3H); 3.38(d, 1H, $^{3}J_{1,2}$ 6.5); 6.98–7.48(cs [c], 4H)
IVc	Ph	Ph	1728 [d]	3.13	1.83–3.0(cs [c], 4H); 3.33–3.78(cm [c], 1H); 3.9(d, 1H, $^{3}J_{1,2}$ 6.0); 6.54–7.56(cs [c], 19H)
IXc	Ph	Cl	1672 [d]	3.83	1.78–2.25(cs [c], 2H); 2.6–2.98(cs [c], 2H); 3.13–3.53(cs [c], 1H); 3.72(d, 1H, $^{3}J_{1,2}$ 6.4); 6.78–8.0(cs [c], 14H)

[a] IR spectra of pure compounds (film), except when otherwise stated. [b] ^{1}H NMR spectra in $CDCl_3$ solution; chemical shifts with reference to TMS; J values in Hz. [c] cs stands for complex signal and cm for complex multiplet. [d] As KBr pressed disc.

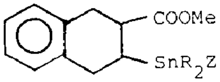
The halodiorganostannyl derivatives (VIII, IX and X) were prepared by treating compounds II, IV, and VI with either trimethyltin chloride (for the trimethylstannyl adducts) or mercury (II) chloride (for the triphenyl- and tri-n-butylstannyl adducts), as shown in Scheme 2.

The reactions were carried out by stirring the mixture of organotin adducts and mercury (II) chloride (R = n-Bu, Ph) or trimethyltin chloride (R = Me), at room temperature in methanol (mercury(II) chloride) or without solvent (trimethyltin chloride), for the time needed in order to obtain a maximum conversion. The main spectroscopic characteristics of the chlorodiorganostannyl derivatives thus obtained are also given in Tables 1–6.

When the IR data for each pair (II/VIII, Table 1, IV/IX, Table 2 and VI/X, Table 3) are compared, the carbonyl stretching frequencies of the chlorodiorganostannyl esters VIII–X are seen to lie without exception at 1658–1680 cm^{-1} (Tables 1–3), i.e., 48–77 cm^{-1} to lower frequency of those of the triorganostannyl esters II, IV, and VI. The ^{1}H NMR ester signals of compounds VIII–X (Tables 1–3) are downfield from the corresponding signals for the triorganostannyl esters II, IV and VI (see for example IIa, OMe 3.64 ppm and VIIIa, OMe 3.83 ppm). These values indicate that in the case of the chlorodiorganostannyl-substituted ester VIII–X there

Table 3

IR and ^{1}H NMR data of cis-methyl 3-trialkylstannyl- and 3-chlorodialkylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates



Compound	R	Z	IR [a]	^{1}H NMR, chemical shifts (δ, ppm) [b]	
			ν(C=O) (cm^{-1})	OMe	Others
VIa	Me	Me	1732	3.66	-0.05(s, 9H, ^2J(^{119}Sn–C–H), 51.8); 1.92–2.11(cm [c], 1H); 2.85–3.16(cs [c], 5H); 7.0–7.1(cs [c], 4H)
Xa	Me	Cl	1676	3.76	0.46(s, 3H, ^2J(^{119}Sn–C–H), 63.2); 0.63 (s, 3H, ^2J(^{119}Sn–C–H), 63.2); 2.19(cm [c], 1H); 2.88–3.15(cs [c], 4H); 3.31(cm [c], 1H); 7.06–7.24(cs [c], 4H)
VIb	n-Bu	n-Bu	1733	3.63	0.2–2.4(cs [c], 29H); 2.58–3.43(cs [c], 4H); 6.72–7.17(cs [c], 4H)
Xb	n-Bu	Cl	1675 [d]	3.71	0.75–2.15(cs [c], 19H); 2.75–3.35(cs [c], 5H); 7.0–7.2(cs [c], 4H)
VIc	Ph	Ph	1728 [d]	3.16	1.93–3.1(cs [c], 6H); 6.35–7.9(cs [c], 19H)
Xc	Ph	Cl	1658 [d]	3.8	2.4–3.63(cs [c], 6H); 6.87–8.0(cs [c], 14H)

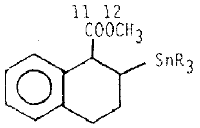
[a] IR spectra of pure compound (film), except when otherwise stated. [b] ^{1}H NMR spectra in $CDCl_3$ solution; chemical shifts with reference to TMS; J values in Hz. [c] cs stands for complex signal and cm for complex multiplet. [d] As KBr pressed disc.

is coordination between the carbonyl group of the ester and the Sn atom, this being known to reduce the carbonyl stretching frequency and to have a deshielding effect on the methoxy group protons [4–9]. This carbonyl coordination to tin must be intramolecular since the carbonyl stretching frequency is nearly the same for the pure compounds as for their solutions. The ^{119}Sn NMR data also support the existence of coordination between the carbonyl of the ester group and the tin atom in the chlorodiorganostannyl-substituted esters VIII–X. Thus the ^{119}Sn NMR signals of esters VIII–X (Tables 4–6) are considerably shifted to high field compared with those for triorganostannyl chlorides RMe_2SnCl [10].

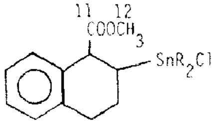
The ^{1}H NMR spectra of the 2-triorganostannyl- and 2-chlorodiorganostannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylates II and VIII (Table 1) show a doublet at 3.8–4.2 ppm corresponding to the proton attached to C(1). The values of the coupling constant ^3J(H–C–C–H) range for 4.0 to 6.0 Hz indicating that this proton is *cis* (axial/equatorial relationship) with respect to the proton attached to C(2) [11]. The ^{1}H NMR spectra of the 1-triorganostannyl- and 1-chlorodiorganostannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates IV and IX (Table 3) also show a doublet at 3.25–3.9 ppm corresponding to the proton attached to C(1): here the values of the coupling constant ^3J(H–C–C–H) range from 2.6–6.55 Hz, also indicating a *cis* relationship between this proton and that attached to C(2) [11]. In the case of the 3-triorganostannyl- and 3-chlorodiorganostannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates, VI and X, the steric relationship between the protons attached to C(2) and C(3) is not easy to assign by ^{1}H NMR because of the

Table 4

^{13}C and ^{119}Sn NMR data for *cis*-methyl 2-trialkylstannyl- and 2-chlorodialkylstannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylates [a,b]



	R
IIa:	Me
IIb:	n-Bu
IIc:	Ph



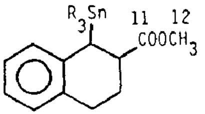
	R
VIIIa:	Me
VIIIb:	n-Bu
VIIIc:	Ph

Compound	R-Sn	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	^{119}Sn
IIa	−9.93 (326.83)	47.84	24.87 (390.37)	29.64	23.97	128.86 $^{+}$	125.22 *	126.57 *	129.40 $^{+}$	134.80	136.59	175.09 (14.0)	51.69	−3.34
VIIIa	−0.63(428.82); −0.65(438.69)	47.78	32.42 (525.15)	29.03	23.54	128.76 $^{+}$	125.57 *	127.21 *	129.62 $^{+}$	131.47	136.47	180.78 (13.9)	53.97	49.35
IIb	8.99(317.90; 13.65; 27.49; 29.22	48.10	24.23 (324.25)	29.97	24.33	129.09 $^{+}$	125.23 *	126.64 *	129.55 $^{+}$	135.29	136.94	175.28 (14.0)	51.78	−20.42
VIIIb	13.58; 13.68 18.84(420.89); 19.20(429.78); 26.64; 26.84; 27.78; 28.10	48.32	32.72 (442.5)	29.37	23.54	128.71 $^{+}$	125.64 *	127.31 *	129.86 $^{+}$	131.89	136.88	181.02 (11.45)	53.97	38.20
IIc	139.35 (492.09)	47.74	27.68 (439.96)	29.95	24.63	129.52 $^{+}$	126.91 *	127.92 *	129.70 $^{+}$	134.47	136.60	175.16 (17.80)	51.81	−116.16
VIIIc	140.08 [c] 141.09 [c]	47.85	34.87 (556.94)	29.54	24.09	129.31 $^{+}$	125.62 *	127.43 *	129.14 $^{+}$	137.44	136.74	181.51 (24.16)	54.64	−98.62

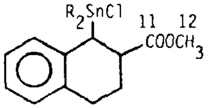
[a] ^{13}C NMR in $CDCl_3$ (internal lock); δ values in ppm; $^{1}J(C-Sn)$ and $^{3}J(Sn-C-C-C{=}O)$ values in Hz; ^{119}Sn NMR in $CDCl_3$; δ values in ppm vs. Me_4Sn. Interchangeable signals are marked + and ★. [b] For ^{13}C NMR data of the basic 1,2,3,4-tetrahydronaphthalene framework see ref. 15. [c] Assignment uncertain.

Table 5

^{13}C and ^{119}Sn NMR data for *cis*-methyl 1-trialkylstannyl- and 1-chlorodialkylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates [a,b]



R
IVa: Me
IVb: n-Bu
IVc: Ph



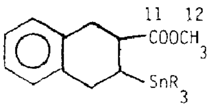
R
IXa: Me
IXb: n-Bu
IXc: Ph

Compound	R-Sn	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	^{119}Sn
IVa	−8.34 (320.44)	34.17 (333.16)	42.81	25.39	28.51	128.61 $^+$	125.23 ★	123.65 ★	126.82 $^+$	140.75	132.48	175.25 (12.72)	51.50	7.58
IXa	0.47(465.4); 0.99(434.88)	37.48 (475.56)	42.29	25.48	27.08	128.75 $^+$	125.66 ★	124.87 ★	129.51 $^+$	135.72	133.82	182.24 (22.88)	53.87	34.22
IVb	10.43(310.26); 13.56; 27.38; 28.88	33.69 (272.12)	43.88	26.10	27.80	128.77 $^+$	125.48 ★	123.69 ★	126.97 $^+$	141.61	132.74	175.35 (10.18)	51.65	−9.1
IXb	13.52; 13.65; 20.22(434.5); 20.41(417.0); 26.55; 26.84; 27.33; 27.8	37.29 (356.7)	42.67	25.97	27.79	128.69 $^+$	125.72 ★	124.76 ★	129.73 $^+$	136.32	133.74	182.39 (17.80)	53.82	22.56
IVc	139.54 (480.1)	37.07 (380.19)	43.20	26.43	28.68	128.60 $^+$	125.84 ★	124.74 ★	128.99 $^+$	139.29	133.85	174.81 (13.99)	51.55	−122.97
IXc	141.45 [c] 142.20 [c]	39.66 (482.6)	42.65	25.91	27.53	128.64 $^+$	125.36 ★	125.69 ★	130.61 $^+$	135.92	133.79	182.89 (27.98)	54.23	−114.94

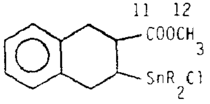
[a] ^{13}C NMR in CDCl$_3$(internal lock); δ values in ppm; ^1J(C–Sn) and ^3J(Sn–C–C–C=O) values in Hz; ^{119}Sn NMR in CDCl$_3$; δ values in ppm vs. Me$_4$Sn. Interchangeable signals are marked + and ★. [b] for ^{13}C NMR data of the basic 1,2,3,4-tetrahydronaphthalene framework see ref. 15. [c] Assignment uncertain.

Table 6

^{13}C and ^{119}Sn NMR data for *cis*-methyl 3-trialkylstannyl- and 3-chlorodialkylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates [a,b]



	R
VIa:	Me
VIb:	n-Bu
VIc:	Ph



	R
Xa:	Me
Xb:	n-Bu
Xc:	Ph

Compound	R-Sn	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	^{119}Sn
VIa	−9.4 (321.71)	33.07	43.32	24.95 (382.74)	31.30	128.52 ★	125.79 +	125.61 +	129.07 ★	134.56	136.27	175.6 [c]	51.62	0.97
Xa	−0.85(420.89) −0.30(424.71)	29.31	41.87	29.47 (516.26)	30.80	127.82 ★	126.35 +	126.06 +	127.90 ★	134.17	137.62	182.19 (26.71)	53.78	58.99
VIb	9.32(314.07); 13.61; 27.48; 29.07	33.63	43.49	24.32 (316.62)	31.72	128.57 ★	125.75 +	125.63 +	129.17 ★	134.72	136.65	175.52 [c]	51.61	−15.81
Xb	13.58; 13.64; 18.89(408.17); 19.09(404.36); 26.76; 26.78; 27.90; 27.93	29.78	42.27	29.37 (378.92)	31.16	127.81 ★	126.49 +	126.10 +	127.95 ★	134.46	138.23	182.44 (22.88)	53.83	47.64
VIc	139.39 (488.12)	32.43	42.88	27.14 (431.07)	31.40	128.31 ★	126.02 +	125.66 +	129.27 ★	134.40	137.34	175.32 [c]	51.64	−112.99
Xc	140.75 (579.84); 141.31(d)	29.80	42.22	31.55 (561.05)	30.69	128.40 ★	126.52 +	126.23 +	127.98 ★	134.05	139.94	182.89 (34.33)	54.30	−85.91

[a] ^{13}C NMR in $CDCl_3$(internal lock); δ values in ppm; $^{1}J(C-Sn)$ and $^{3}J(Sn-C-C-C=O)$ values in Hz; ^{119}Sn NMR in $CDCl_3$; δ values in ppm vs. Me_4Sn. Interchangeable signals are marked + and ★. [b] for ^{13}C NMR data of the basic 1,2,3,4-tetrahydronaphthalene framework see ref. 15. [c] Not observed. [d] Assignment uncertain.

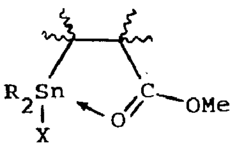
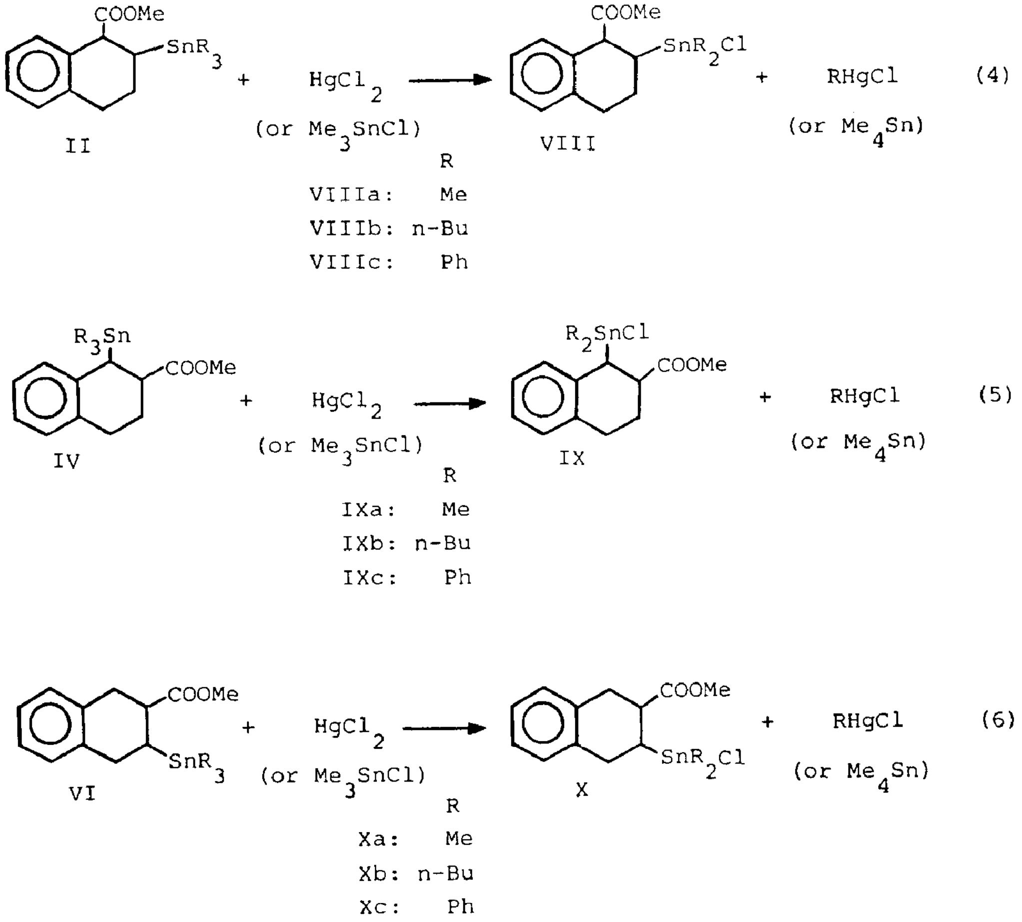


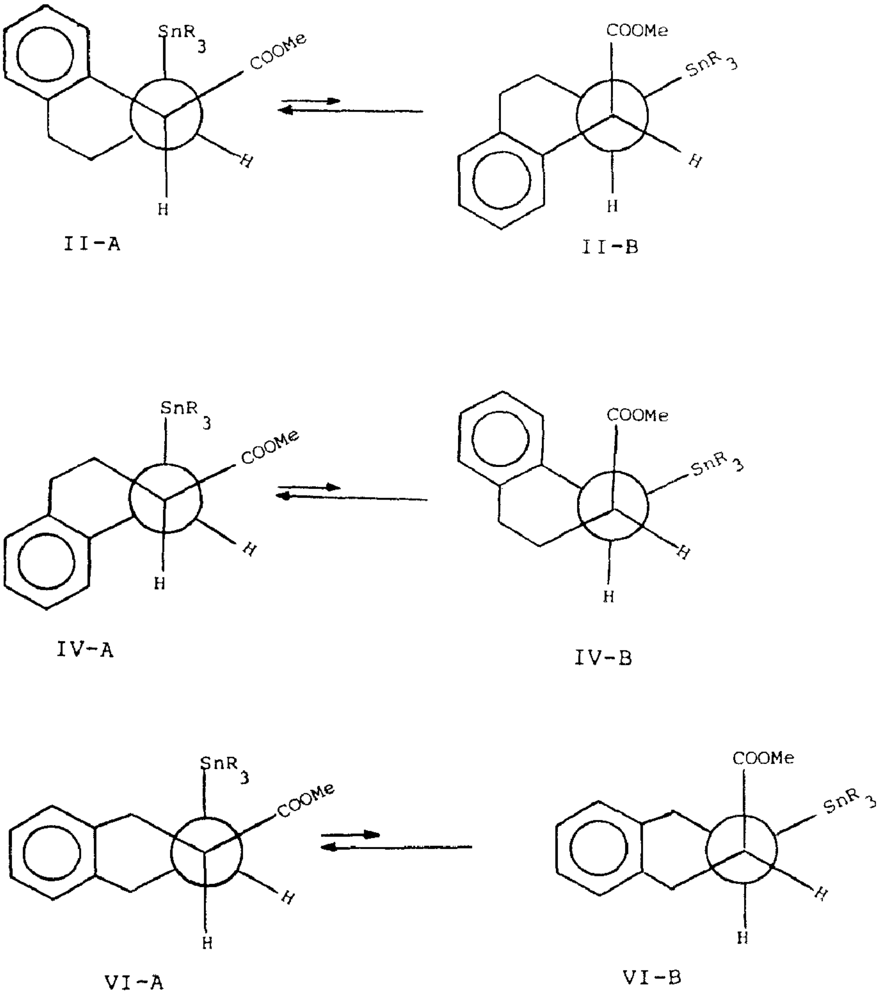
Fig. 1. Intramolecular coordination in 3-halodiorganostannyl substituted methyl propanoates.

complexity of the signals due to these protons. Other relevant features of the proton spectra of these organotin derivatives are as follows: (a) The spectra of the methyltin derivatives VIIIa, IXa, and Xa (Tables 1–3) show splitting of the signals corresponding to the methyl groups, probably due to differences in the chemical enviroment present after intramolecular coordination when the methyl groups become non-equivalent. (b) The coupling constants $^{2}J(^{119}Sn{-}C{-}H)$ in the ^{1}H NMR spectra of derivatives VIIIa, IXa, and Xa have values which range from 62.3–64.2 Hz (Tables 1–3); such values have also been observed in other methyltin derivatives with intramolecular coordination [6,7,9].



Scheme 2

The ^{13}C NMR spectra also provide valuable information on the structures of these compounds. Thus the values of the coupling constant $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}}^{13}\mathrm{C})$ for the C=O group in the methyltin derivatives IIa, ca. 14 Hz, and VIIIa, 13.9 Hz (Table 4) indicate that the dihedral angle between the COOMe group and the organotin substituent must be about 60° [12]. The values of this coupling constant observed for the compounds IVa, 12.7 Hz, and IXa, ca. 23 Hz (Table 5) indicate that whereas in the former compound the dihedral angle between the ester group and the organotin substituent should be of about 60°, in the IXa the dihedral angle may perhaps be reduced to ca. 50°. As for the methyltin derivatives VIa and Xa, although we could not observe the $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}}^{13}\mathrm{C})$ coupling for the C=O group of VIa, the value of 26.7 Hz observed for Xa (Table 6) indicates that in this case the dihedral angle between the COOMe group and the organotin substituent must also be near 40°. It should be noted that ^{13}C NMR spectra also provide evidence of the existence of intramolecular coordination, the splitting of the signals corresponding to the alkyl and phenyl groups attached to tin in compounds VIII–X (arising from



Scheme 3

their non-equivalence due to intramolecular coordination) being clearly observable in all cases (see column R-Sn in Tables 4–6).

A conclusive chemical proof of the existence of intramolecular coordination in the halodiorganostannyl derivatives (VIII–X) was obtained by allowing compounds VIIIa–Xa to react with methylmagnesium bromide: in all cases the only products of reaction were the corresponding triorganostannyl derivatives IIa, IVa, and VIa respectively (eqs. 7–9). These results could be explained by the fact that the intramolecular coordination makes the C=O of the ester group less nucleophilic, thus preventing the addition of the Grignard reagent, which instead alkylates the tin atom.

$$\text{VIIIa} + \text{MeMgBr} \rightarrow \text{IIa} \qquad (7)$$

$$\text{IXa} + \text{MeMgBr} \rightarrow \text{IVa} \qquad (8)$$

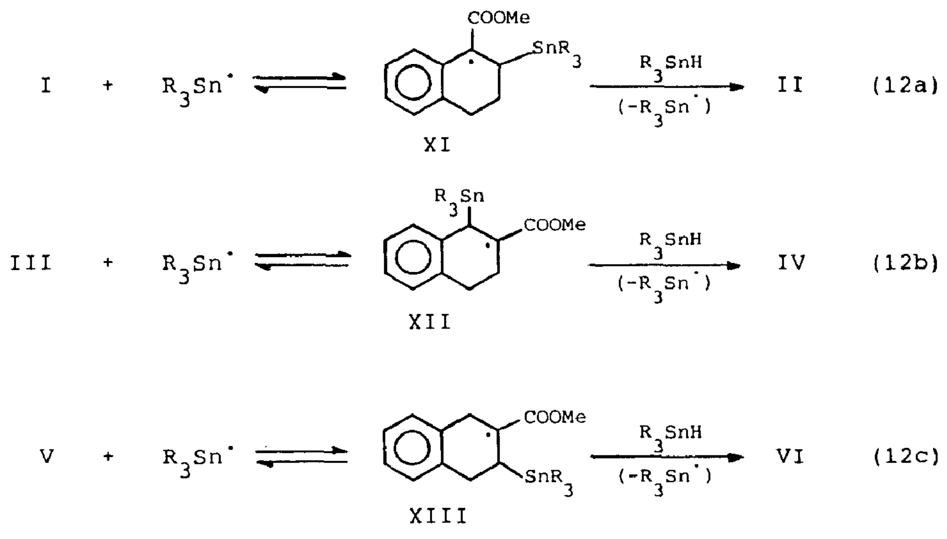
$$\text{Xa} + \text{MeMgBR} \rightarrow \text{VIa} \qquad (9)$$

The existence of intramolecular coordination as well as other features revealed by the spectroscopic data are in accordance with the conclusion that the diastereoisomers formed were those with the (sterically unfavourable) *cis* configuration. The possible conformations of the products are shown in Scheme 3 (only one enantiomer of each conformation is shown).

Dreiding or space-filling models show that the more favourable conformations should be II-A, IV-A, and VI-A (organotin substituent axial and COOMe group equatorial). In these conformations, 1,3-diaxial interactions between the triorganotin substituent and the corresponding axial protons, proton attached to C(4) in II-A, to C(3) in IV-A, and to C(1) in VI-A, should be smaller (A-value for trimethylstannyl

$$\text{Initiator} \longrightarrow \text{Rad}^{\bullet} \qquad (10)$$

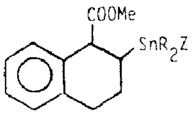
$$R_3SnH + \text{Rad}^{\bullet} \longrightarrow R_3Sn^{\bullet} + \text{RadH} \qquad (11)$$



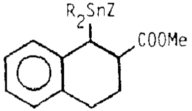
Scheme 4

Table 7

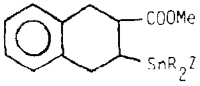
Compounds obtained from hydrostannation of methyl 3,4-dihydronaphthalene-1-carboxylate, methyl 3,4-dihydronaphthalene-2-carboxylate, and methyl 1,4-dihydronaphthalene-2-carboxylate



II: Z = R
VIII: Z = Cl



IV: Z = R
IX: Z = Cl



VI: Z = R
X: Z = Cl

Compound	R	Z	Time [a] (irradiation times)	Temperature (°C) (irradiated)	Substrate/reagent ratio (irradiated reactions)	M.p. (°C) [b] or n_{D}^{c}	Elemental analyses (Found (calc) (%))	
							C	H
IIa	Me	Me	24(10)	65(ca. 25)	1/2(1/2)	47– 49	51.30 (51.03)	6.40 (6.28)
VIIIa	Me	Cl	4	RT	1/1.1	145–147	45.25 (45.02)	5.25 (5.13)
IIb	n-Bu	n-Bu	24(12)	80(ca. 25)	1/1.5(1/1.5)	1.5266 [d]	60.40 (60.14)	8.55 (8.41)
VIIIb	n-Bu	Cl	6	RT	1/1.1	100–102	52.30 (52.49)	6.90 (6.83)
IIc	Ph	Ph	20(6)	80(ca. 25)	1/1.5(1/1.5)	[e]	[e] (66.82)	[e] (5.23)
VIIIc	Ph	Cl	5	RT	1/1.1	[e]	[e] (57.93)	[e] (4.66)
IVa	Me	Me	10(8)	65(ca. 25)	1/2(1/2)	1.5574 [f]	50.95 (51.03)	6.10 (6.28)

IXa	Me	Cl	6	RT	1/1.1	1.5831	45.30 (45.02)	5.20 (5.13)
IVb	n-Bu	n-Bu	24(20)	80(ca. 25)	1/1.5(1/1.5)	1.5315 [g]	59.95 (60.14)	8.30 (8.41)
IXb	n-Bu	Cl	4	RT	1/1.1	1.5441	52.65 (52.49)	6.80 (6.83)
IVc	Ph	Ph	4(4)	80(ca. 25)	1/1.5(1/1.5)	102–104	66.95 (66.82)	5.15 (5.23)
IXc	Ph	Cl	6	RT	1/1.1	108–110	58.10 (57.93)	4.80 (4.66)
VIa	Me	Me	24(6)	65(ca. 25)	1/2(1/2)	1.5515 [g]	51.25 (51.03)	6.15 (6.28)
Xa	Me	Cl	24	RT	1/1.1	1.5712	44.90 (45.02)	5.10 (5.13)
VIb	n-Bu	n-Bu	24(8)	80(ca. 25)	1/1.5(1/1.5)	1.5238 [d]	60.30 (60.14)	8.35 (8.41)
Xb	n-Bu	Cl	6	RT	1/1.1	110–111	52.70 (52.49)	6.75 (6.83)
VIc	Ph	Ph	4(1)	80(ca. 25)	1/1.5(1/1.5)	131–133	66.70 (66.82)	5.20 (5.23)
Xc	Ph	Cl	5	RT	1/1.1	111–113	58.15 (57.93)	4.75 (4.66)

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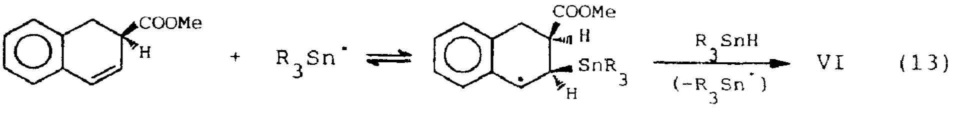
[a] In hours. [b] All compounds recrystallized from ethanol. [c] Refractive indices determined at 20 ° C, except when indicated otherwise. [d] At 24 ° C. [e] Could not be recrystallized. [f] At 22 ° C. [g] At 18 ° C.

group of ca. 0.94 kcal/mol [13]) than the 1,3-diaxial interactions between the COOMe group (A-value ca. 1.27 kcal/mol [14]) and the corresponding axial protons in compounds II-B, IV-B, and VI-B. It should be noted that the same conformational preference, e.g., R_3Sn group axial/COOMe group equatorial, has been found in related (*Z*)-1,2-disubstituted cyclohexene systems [16,17].

The fact that the additions lead only to the *cis* diastereoisomer (as a racemic mixture), strongly suggests that in the last step of the free radical mechanism (Scheme 4, eqs. 12a–12c) the most favourable face of the intermediate radicals (Scheme 4, XI–XIII) for the hydrogen transfer from the organotin hydride is the one opposite (*trans*) to the tin substituent, this being probably due to smaller diaxial interactions.

The formation of radicals XI–XIII, resonance stabilized by the neighbouring ester group, could also account for the fact that substrates I, III, and V undergo hydrostannation more easily (with quantitative yields) than do substrates such us 1-phenylcyclohexene [16a] and 1-hydroxymethylcyclopentene [14].

The reaction of triorganotin hydrides with methyl 1,2-dihydronaphthalene-2-carboxylate (VII) to give the same adducts as those obtained in the additions to methyl 1,4-dihydrohaphthalene-2-carboxylate (V), i.e., *cis*-methyl 3-triorganostannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates (VI), probably proceeds through formation of the resonance stabilized benzylic radical XIV, according to Scheme 5.



VII XIV

Scheme 5

The exclusive formation of the *cis* diastereoisomer could be explained by considering: (a) the known preference for the COOMe group to occupy a pseudo-equatorial position in the starting olefin VII [17], and (b) that the *cis* attack by the triorganotin radical to VII would lead to an intermediate benzylic radical (Scheme 5, XIV) whose stability is enhanced by the neighbouring organotin group. This is so because the entrance of the tin radical in an axial site gives a benzylic radical in which the tin substituent is eclipsed with the half-filled carbon *p* radical, this being the most favourable situation for hyperconjugative and homoconjugative stabilization of the radical as shown by Kochi et al. [18].

Experimental

^1H NMR spectra were obtained with a Varian EM 360L, and ^{13}C and ^{119}Sn NMR spectra with a Bruker AM 300 instrument at Dortmund University (F.R.G.). Infrared spectra were recorded with a Perkin–Elmer 577 spectrophotometer. The refractive indices were measured with a Universal Abbe, Zeiss Jena VEB instrument and the melting points were determined on a Kofler hot stage and are uncorrected. Microanalyses were performed at Dortmund University and at UMYMFOR (Argentina). Sample irradiations were carried out in an irradiator constructed in this Laboratory consisting of four water-cooled mercury lamps (two of 250 W and two of 400 W); the temperature at the sample site was ca. 25 °C. The olefins used were synthesized by known procedures [19,20]. All the solvents and reagents used were analytical-reagent grade. The organotin hydrides were obtained by reduction of the corresponding chlorides, R_3SnCl, with sodium borohydride [21] (R = n-Bu, Ph) and with lithium aluminium hydride [9] (R = Me). The triorganotin chlorides used in the present work were donated by Schering Aktiengesellschaft (F.R.G.). The purification of the organotin adducts and some of their chlorine/alkyl (aryl) exchange derivatives, was carried out by column chromatography (silica gel, Kieselgel 60, 70–230 mesh, Merck).

a. Additions of organotin hydrides to the olefins

The same procedure was used in the preparation of all the organotin compounds. Two experiments are described in detail to illustrate the methods used. The main spectroscopic features of the compounds obtained by hydrostannation of I, III, and V, as well as times of reaction, physical characteristics and elemental analyses (C, H), are listed in Tables 1–7.

Reaction of methyl 3,4-dihydronaphthalene-1-carboxylate (I) with trimethyltin hydride (thermal). Synthesis of cis-methyl 2-trimethylstannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (IIa). Methyl 3,4-dihydronaphthalene-1-carboxylate (3 g, 0.016 mol) was treated for 24 h with trimethyltin hydride (5.27 g, 0.032 mol) under nitrogen at 65 °C with AIBN as a catalyst. (This optimal time of reaction and the use of an adequate excess of organotin hydride were indicated in earlier experiments in which the reaction was monitored by taking samples at intervals and observing the disappearance of the Sn–H absorption by IR, and by checking at the end of the reaction that the ^1H NMR spectrum of the reaction mixture no longer showed the presence of unchanged olefin). The ^1H NMR spectrum showed that under these conditions a quantitative yield of adduct IIa was obtained. The product was purified by column chromatography (silica gel 60). The adduct IIa was eluted with petroleum ether 30–60/benzene (8/1) as an oily colorless liquid; recrystallization from ethanol gave crystals m.p. 47–49 °C.

Reaction of methyl 1,4-dihydronaphthalene-2-carboxylate (V) with 3-tri-n-butyltin hydride (irradiated). Synthesis of cis-methyl 3-tri-n-butylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (VIb). Methyl 1,4-dihydronaphthalene-2-carboxylate (3 g, 0.016 mol) was added to tri-n-butyltin hydride (7 g, 0.024 mol) under nitrogen. Then a catalytic amount of AIBN was added, the reaction vessel was placed in the photochemical reactor (reactor temperature ca. 25 °C) and the mixture stirred for 8 h (optimal reaction conditions determined as above). The ^1H NMR spectrum showed that a quantitative yield of VIb was obtained. The crude product was purified by column chromatography (silica gel 60). The adduct VIb, eluted with petroleum ether 30–60, was an oily yellowish liquid; n_D^{24} 1.5238.

b. Chloro/alkyl(aryl) exchange reactions

The exchanges with trimethyltin chloride were carried out without solvent, and the exchanges with mercury(II) chloride in methanol as solvent. The isolation and purification steps for the latter exchanges vary depending on the nature of R and so one experiment of each type of reaction is described in detail. The main spectroscopic features of the compounds obtained in this section, as well as their physical characteristics, elemental analyses (C, H), and times of reaction, are summarized in Tables 1–7.

Exchange between cis-methyl 2-trimethylstannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (IIa) and trimethyltin chloride. Synthesis of cis-methyl 2-chlorodimethylstannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (VIIIa). Adduct IIa (1.43 g, 0.004 mol) was added to trimethyltin chloride (0.88 g, 0.0044 mol) with stirring under nitrogen and the mixture was left at room temperature for 4 h. The ^{1}H NMR spectrum showed that IIa had been completely converted into VIIIa. The excess of trimethyltin chloride and the tetramethyltin formed, were distilled off under reduced pressure. The solid residue was recrystallized from ethanol; m.p. 145–147 ° C (1.44 g, 96%).

Exchange reaction between cis-methyl 3-tri-n-butylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (VIb) and mercury(II) chloride. Synthesis of cis-methyl 3-chlorodi-n-butylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (Xb). A solution of mercury(II) chloride (0.63 g, 0.00229 mol) in methanol (5 ml) was added with stirring under nitrogen to a solution of VIb (1 g, 0.00208 mol) in methanol (5 ml). The solution was left at room temperature for 6 h and then added to water. Extraction with ether, followed by drying (magnesium sulphate) and removal of the solvent under reduced pressure left a residue whose ^{1}H NMR spectrum showed that complete conversion of VIb in Xb had been achieved. The solid thus obtained was recrystallized three times from ethanol; m.p. 110–111 ° C (0.75 g, 78%).

Exchange reaction between cis-methyl 3-triphenylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (VIc) and mercury (II) chloride. Synthesis of cis-methyl 3-chlorodiphenylstannyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (Xc). A solution of mercury(II) chloride (0.83 g, 0.00306 mol) in methanol (6 ml) was added with stirring under nitrogen to a suspension of VIc (1.5 g, 0.00278 mol) in methanol (9 ml). The mixture was left at room temperature for 5 h and then filtered. The solid thus isolated was extracted with chloroform, and the extract filtered (leaving behind phenylmercury chloride); the chloroform was removed under reduced pressure to give Xc as a white solid, which was recrystallized from ethanol; m.p. 111–113 ° C (1.18 g, 85%).

c. Alkylations with methylmagnesium bromide

The same procedure was used in the alkylation of compounds VIIa, IXa, and Xa with methyl magnesium bromide. One experiment is described in detail to illustrate the method used.

Alkylation of cis-methyl 2-chlorodimethylstannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (VIIIa) with methylmagnesium bromide. Synthesis of cis-methyl 2-trimethylstannyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (IIa). Methylmagnesium bromide (0.97 ml of a 2.77 *M* solution in ether, 0.00268 mol) was added with stirring under nitrogen to a solution of VIIIa (1 g, 0.00268 mol) in ether (20 ml). The reaction mixture was heated under reflux for 6 h. After cooling, distilled water was added (ca. 2 ml), and the solution was acidified with diluted hydrochloric acid. The organic layer was decanted, dried (magnesium sulphate), and the solvent removed under reduced pressure to give IIa (0.83 g, 87%).

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