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Organotin compounds

X *. Organotin hydride addition to methyl cyclohexene-1-carboxylate and methyl indene-3-carboxylate

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Abstract

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

Introduction

Hydrostannation of olefins provides a versatile method for the synthesis of organotin compounds containing a broad variety of functional groups. The reaction

* For part IX see ref. 19.

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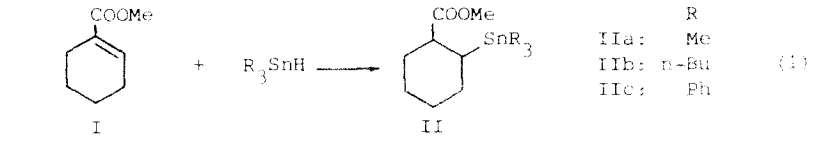
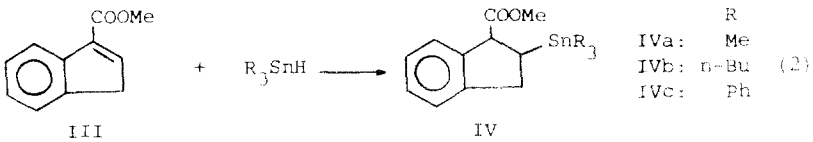
normally proceeds by a well-established free radical mechanism [1,2]. In previous studies [3–6] we were able to show that in almost all cases studied the addition of trialkyltin hydrides R_3SnH and dialkyltin chlorohydrides R_2SnClH to open-chained olefins led to formation of one of the two diastereoisomers expected (as a racemate) when R = n-Bu or Ph, but that a mixture of diastereoisomers, with high predominance of one of them, is formed when R = Me.

In order to determine whether there is any stereoselectivity in the hydrostannation of cyclic olefins, and which factors govern the stereochemistry of the additions, the addition of organotin hydrides to methyl cyclohexene-1- (I) and indene-3-carboxylates (III) (see equations 1 and 2) has now been studied. These additions are of interest as model systems for a stereoselective hydrostannation of unsaturated substituted ring systems, including biomolecules. This would be a useful contribution to use organotin hydrides in organic synthesis, including stereoselective multistep one-pot syntheses (for a recent review see ref. 7).





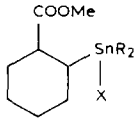
The nature of adducts II and IV formed could give valuable information on the stereochemistry of these addition reactions, and for this knowledge their spectroscopic characteristics is essential. Systematic studies directed towards structure/NMR parameter relationships in cycloalkanes containing trialkylstannyl substituents have been reported [8–14]. However, there are only two reports concerning the stereochemistry of the addition of organotin hydrides to cyclic olefins with alkoxycarbonyl substituents: one deals with the addition of trimethyltin hydride to methyl 3,3-dimethyl cyclobutene-1-carboxylate [15], and the other with the addition of the same hydride to ethyl cyclopentene-1-carboxylate [16].

Results and discussion

All the additions were carried out under free radical conditions. Two methods were used: (a) the mixture of olefin and azobis(isobutyronitrile) (AIBN) was stirred without solvent under nitrogen (at 80 °C in the case of triphenyl- and tri-n-butyl-tin hydrides, and at 65 °C in the case of trimethyltin hydride) until all the olefin had reacted. (b) The mixture of olefin and excess organotin hydride, was irradiated (mercury high pressure lamp) without solvent under nitrogen with stirring until all the olefin had reacted (temperature inside the photochemical reactor: ca. 25 °C). The reactions were followed by IR (by observing the disappearance of the Sn–H absorption) and ^1H NMR spectroscopy (by observing olefin disappearance and product formation). In all cases the optimum times of reaction and hydride/olefin

Table 1

IR and ^{1}H NMR data for methyl 2-trialkylstannyl- and 2-chlorodialkylstannyl-cyclohexanecarboxylates (II and V)

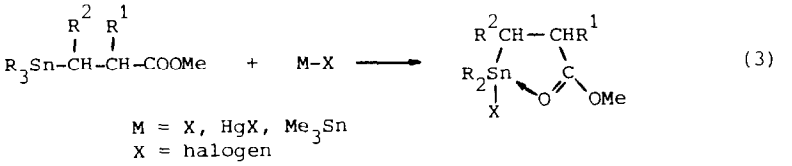


Compound	R	X	IR [a] ν(C=O) (cm^{-1})	^{1}H NMR, chemical shifts (δ, ppm) [b]	
				OMe	Others
IIa	Me	Me	1729	3.63 [c]	0.06(s, 9H; ^2J(^{119}Sn–C–H),61.0) 0.89–2.06(cs [d], 9H); 2.56–2.91 (cs, 1H).
Va	Me	Cl	1681	3.75 [c]	0.56(s, 3H; ^2J(^{119}Sn–C–H), 61); 0.66(s, 3H; ^2J(^{119}Sn–C–H), 60.8); 1.27–2.27(cs, 9H); 2.75–3.17 (cs, 1H).
IIb	n-Bu	n-Bu	1724	3.53	0.53–2.05(cs, 36H); 2.33–2.83 (cs, 1H).
Vb	n-Bu	Cl	1685	3.68	0.48–2.35(cs, 27H); 2.68–3.05 (cs, 1H).
IIc	Ph	Ph	1724	3.27	1.18–2.47(cs, 9H); 2.58–2.97 2.58–2.97(cs, 1H); 6.72–7.88 (cs, 15H).
Vc	Ph	Cl	1667	3.66	0.70–2.56(cs, 9H); 2.63–3.1 (cs, 1H); 7.0–8.33(cs, 10H).

[a] IR spectra of pure compounds (film). [b] ^{1}H NMR spectra in CCl_4 solution except when otherwise stated; chemical shifts with reference to TMS; J values in Hz. [c] In $DCCl_3$. [d] cs stands for complex signal.

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 diastereoisomers was obtained as a racemic mixture. It may be therefore concluded that the additions are stereoselective. The new compounds obtained, as well as their main spectroscopic characteristics, are summarized in Tables 1–4.

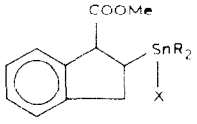
The data did not permit an accurate assignment of the stereochemistry because only a single isomer was found. In order to obtain structural information concerning the stereochemistry of these addition reactions, the adducts II and IV were converted into the halodialkylstannyl derivatives Va–Vc and VIa–VIc. This was done because it is known [4–6,17–19] that for open chain esters containing a β-halodialkyltin substituent, intramolecular coordination (see eq. 3) occurs. In such compounds the stereochemistry of the addition can sometimes be deduced from the ^{1}H NMR spectra.



(3)

Table 2

IR and ^{1}H NMR data for methyl 2-trialkylstannyl- and 2-chlorodialkylstannyl-indane-1-carboxylates (IV and VI)



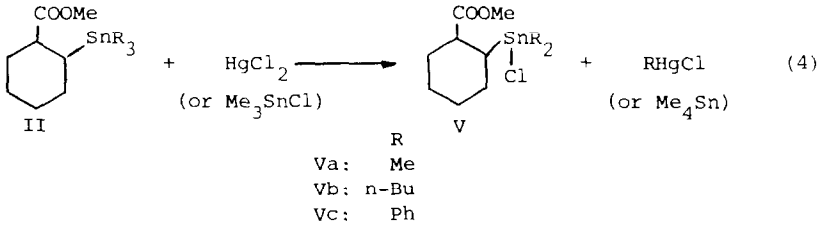
Compound	R	X	IR [a] ν(C=O) (cm^{-1})	^{1}H NMR, chemical shifts (δ, ppm) [b]	
				Ome	Others
IVa	Me	Me	1733	3.61 [c] (s, 3H)	0.06(s, 9H; $^2J(^{119}Sn-C-H)$, 53.0); 2.09(dt, 1H, $J_{1,2}$ 8.4, $J_{2,3}$ 8.0); 3.1(dd, 2H, $J_{3,2}$ 8.0, $J_{3,3}$ 9.5); 4.15(d, 1H, J 8.4); 7.01–7.46 (cs [d],4H)
VIa	Me	Cl	1678	3.88 [c] (s, 3H)	0.26(s, 3H, $^2J(^{119}Sn-C-H)$, 63.8); 0.7(s, 3H, $^2J(^{119}Sn-C-H)$, 64.4); 2.64(dt, 1H, $J_{1,2}$ 8.4, $J_{2,3}$ 8.0); 3.51(dd, 2H, $J_{3,2}$ 8.0, $J_{3,3}$ 6.0); 4.5(d, 1H, J 8.4); 7.04–7.49(cs,4H).
IVb	n-Bu	n-Bu	1725	3.70 (s, 3H)	0.7–2.4(cs, 28H); 3.2(dd, 2H, $J_{3,2}$ 8.0, $J_{3,3}$ 10.0); 4.18(d, 1H, J 8.3); 7.03–7.67(cs, 4H).
VIb	n-Bu	Cl	1680	3.79 (s, 3H)	0.5–2.0(cs, 18H); 2.46(dt, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 7.5); 3.38(dd, 2H, $J_{3,2}$ 7.5, $J_{3,3}$ 5.5); 4.36(d, 1H, J 8.0); 6.83–7.3(cs, 4H).
IVc	Ph	Ph	1725 [e]	3.20 (s, 3H)	2.70(cs, 1 H); 3.08–3.43(cs, under OMe, 2H); 4.13(d, 1H, J 7.0); 6.78–7.89(cs, 19H).
VIc	Ph	Cl	1650	3.88 [c] (s, 3H)	2.99(cs, 1H); 3.65(dd, $J_{3,2}$ 8.0, $J_{3,3}$ (6.0); 4.57(d, 1H, J 8.0); 6.5–8.27(cs, 14H).

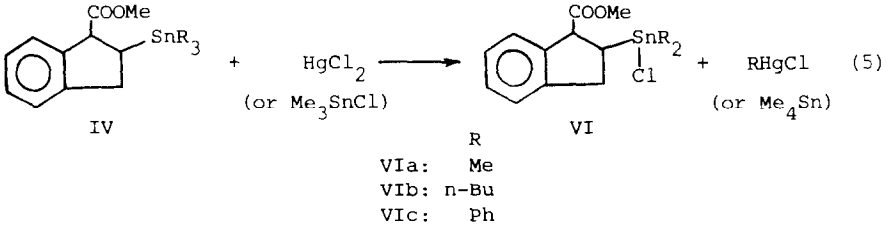
[a] IR spectra of pure compounds (film), except when otherwise stated. [b] ^{1}H NMR spectra in carbon tetrachloride solution, except when otherwise stated; chemical shifts with reference to TMS; J values in Hz. [c] In $CDCl_3$. [d] cs stands for complex signal. [e] As KBr pressed disc.

In the present work the halogen-containing compounds (V and VI) were prepared by treating compounds II and IV with either trimethyltin chloride (for the trimethylstannyl adducts) or mercury(II) chloride (for the triphenyl- and tri-n-butyl-stannyl adducts), as shown in equations 4 and 5.

The reactions were carried out by stirring the mixture of organotin adducts and mercury(II) chloride (R = n-Bu and 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 chlorodialkylstannyl derivatives thus obtained are also given in Tables 1–4.

When the IR data for each pair, II/V (Table 1) and IV/VI (Table 2), are compared the carbonyl stretching frequencies of the chlorodialkylstannyl esters V and VI are seen to be without exception at 1650–1685 cm^{-1} (Tables 1 and 2), i.e., 39–75 cm^{-1} to lower frequency from those of the trialkylstannyl esters II and IV.





The ^{1}H NMR ester signals of compounds V and VI (Tables 1 and 2) are downfield from the corresponding signals for the trialkylstannyl esters II and IV (see for example IIa, OMe 3.50 ppm and Va, OMe 3.70 ppm). These values indicate that in the case of chlorodialkylstannyl-substituted esters V and VI there 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 [4–6,17–19]. This carbonyl coordination to tin must be intramolecular, since the carbonyl stretching frequency remains nearly the same for the pure compound as for a solution. The ^{119}Sn NMR data also support the existence of coordination between the carbonyl of the ester group and the tin atom in β-chlorodialkylstannyl-substituted esters V and VI. Thus the ^{119}Sn NMR signals of esters V and VI (Tables 3 and 4) are considerably shifted to high-field compared with those for trialkylstannyl chlorides $RSnMe_2Cl$ [21].

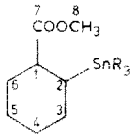
The ^{1}H NMR spectra of the indanyl derivatives (see Table 2), show a doublet at 4.15–4.5 ppm corresponding to the proton attached to C(1). The value of the coupling constants ^{3}J(H–C–C–H) range from 7.0 to 8.4 Hz, indicating that this proton is *cis* with respect to the one attached to C(2) [22]. Other relevant features of the proton spectra of the cyclohexanyl and indanyl organotin adducts are as follows: (a) The spectra of the methyltin derivatives Va and VIa (Tables 1 and 2) show a splitting of the signals corresponding to the methyl groups, probably owing to differences in the chemical environment 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 Va and VIa have values of 61 and 64 Hz (Tables 1 and 2); such values have also been observed in other methyltin derivatives with intramolecular coordination [6,17].

The ^{13}C NMR spectra also provide valuable information on the structures of these compounds. Thus the values of the coupling constants $^{3}J(^{119}Sn–C–C–^{13}C)$ for the C=O group in the methyltin derivatives IIa, 8.9 Hz, and Va, 12.72 Hz, indicate that the dihedral angle between the COOMe group and the organotin substituent

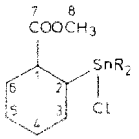
(*Continued on p. 324*)

Table 3

^{13}C and ^{119}Sn NMR data for methyl 2-trialkylstannyl- and 2-chlorodialkyl-stannylcyclohexanecarboxylates [a-c]



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



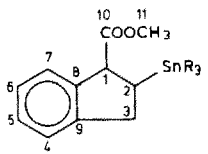
R
Va : Me
Vb : n-Bu
Vc : Ph

Compound	R–Sn	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	^{119}Sn
IIa	−8.69 (317.9)	45.76	28.86 (405.60)	28.91	26.27	25.21	29.18	176.47 (8.90)	51.34	−5.79
Va	−0.72(429.38), 1.01(427.24)	44.43	34.18 (523.88)	26.25	25.65	24.48	28.51	182.05 (12.72)	53.21	52.37
IIb	9.72(311.53), 13.63, 27.59,	45.68	28.13 (338.24)	29.13	27.06	24.92	29.40	176.39	51.29	−21.36
Vb	13.61, 18.48 (412.36), 20.49(411.98), 26.81, 28.01	45.00	34.30 (451.41)	28.08	26.09	24.81	29.06	182.29	53.30	43.82
IIc	140.27 (478.10)	44.81	31.22 (448.87)	28.87	27.59	24.32	29.53	176.19	51.45	−118.17
Vc	141.77(605.26), 142.06(640.86)	44.81	36.10 (567.12)	26.75	25.90	24.71	28.50	182.86	53.76	−90.92

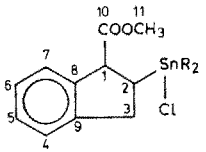
[a] ^{13}C NMR in $CDCl_3$ (internal lock), δ values in ppm; $^1J(C-Sn)$ values in Hz. [b] ^{119}Sn NMR in $CDCl_3$; δ values in ppm vs. Me_4Sn; $^1J(Sn-C)$ values in Hz. [c] For ^{13}C NMR data of the basic cyclohexanyl framework see spectrum of methyl cyclohexanecarboxylate in ref. 20.

Table 4

^{13}C and ^{119}Sn NMR data for methyl 2-trialkylstannyl- and 2-chlorodialkylstannylindane-1-carboxylates [a-c]



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



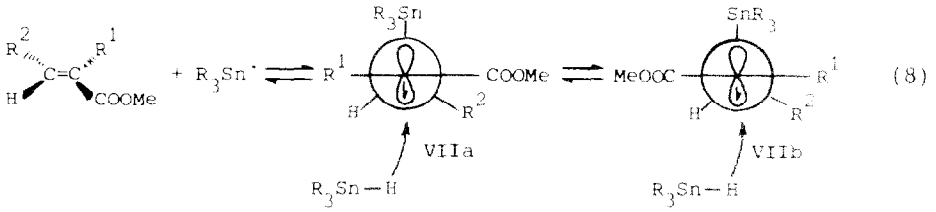
VIa : R = Me
VIb : R = n-Bu
VIc : R = Ph

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)	^{119}Sn
IVa	−9.37 (335.7)	53.47	28.24 (385.29)	36.23	124.45	127.20	126.07	124.06	142.02	144.99	175.06 (22.88)	51.83	−0.47
VIa	−1.36(447.6), 0.34(462.84)	52.87	32.40 (503.44)	34.76	124.65	127.95	126.55	123.93	138.85	147.37	180.67 (33.06)	54.19	60.22
IVb	9.64(326.79), 13.78, 27.58, 29.34	53.91	29.46 (d)	36.88	124.54	127.25	126.07	124.14	142.46	145.40	175.32	51.96	−15.59
VIb	13.41, 13.59, 18.68(433.61), 19.69(441.23), 26.52, 26.65, 27.52, 28.03	53.06	32.34 (d)	35.14	124.78	127.92	126.47	123.79	139.09	143.71	180.77	54.11	48.74
IVc	139.95 (506.08)	53.53	29.64 (439.96)	36.87	124.80	127.54	126.33	124.26	141.31	144.28	175.29	52.06	−106.84
VIc	140.18(d), 141.41(d)	53.00	34.08 (559.48)	35.35	124.85	128.19	126.70	124.51	138.45	143.35	181.12	54.71	−84.21

[a] ^{13}C NMR in $CDCl_3$ (internal lock), δ values in ppm; ^1J(C–Sn) values in Hz. [b] ^{119}Sn NMR in $CDCl_3$; δ values in ppm vs. Me_4Sn; ^1J(Sn–C) values in Hz. [c] For ^{13}C NMR data of the basic indanyl framework see spectrum of indane-1-carboxylic acid in Sadtler Standard Carbon-13 NMR Spectra, spectrum number 5840. [d] Assignments uncertain.

$$\text{Initiator} \longrightarrow \text{Rad}^{\bullet} \qquad (6)$$

$$R_3SnH + Rad^{\bullet} \longrightarrow R_3Sn^{\bullet} + RadH \qquad (7)$$



(8)

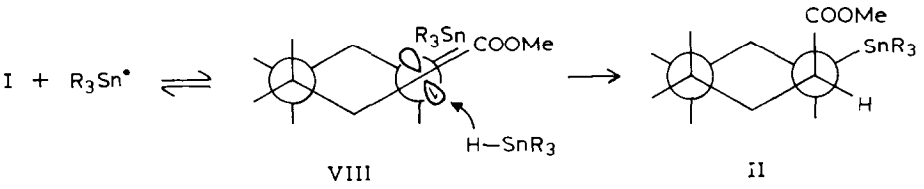
Scheme 1

must be about 60° [9]. As for the corresponding indanyl derivatives, IVa and VIa, the $^3J(^{119}Sn–C–C–^{13}C)$ values of about 23 and 33 Hz, respectively, suggest dihedral angles of about 40°. These values, together with the values of about 8 Hz found for the coupling constants $^3J(H–C–C–H)$, strongly suggest that in the case of the indanyl derivatives, the cyclopentene ring is distorted (twisted) rather than planar. 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 V and VI (arising from their non-equivalence due to intramolecular coordination) being clearly observable in all cases (see column RSn in Tables 3 and 4).

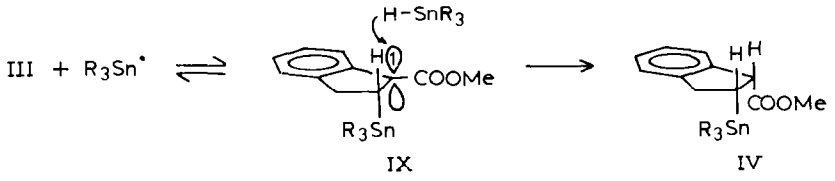
The existence of intramolecular coordination as well as the other features revealed by the spectroscopic data are in accordance with the conclusion that the diastereoisomers formed were exclusively those with the (sterically unfavourable) *cis* configuration. These results strongly suggest that the reactions follow a *trans*-addition stereochemistry.

In order to understand these results, it is important to look at the steric features of the intermediate radicals. With open-chained olefinic systems, we showed [7] that the diastereoisomer composition of the products depends on the equilibrium between the intermediate radicals, VIIa ⇌ VIIb (Scheme 1), and that the hydride abstraction takes place from the less hindered side of the preferred conformations of these radicals, i.e. opposite to the trialkyltin substituent, according to Scheme 1 (only one enantiomer of VIIa, VIIb is shown).

Our results indicate that in the case of the cyclic olefins I and II there is no such equilibrium between intermediate adduct radicals. Dreiding or space-filling models of the six-membered ring radical show that the more favorable conformation, from the steric point of view, for the approach of the bulky organotin hydride to the radical is VIII (Scheme 2). This would lead to hydrogen transfer from the less hindered back-side (with respect to the stannyl substituent), and this would account for the structure of the products (II, Scheme 2). In this respect, it should be noted that the dihedral angle of about 60° between the C=O and the alkyltin substituent (from the values of the $^3J(^{119}Sn–C–C–^{13}C)$ coupling constants), together with intramolecular coordination, are in agreement with both the *cis* relationship between the substituents and with the demonstrated [13,14] preference of trialkyltin substituents in cyclohexanyl systems for equatorial positions.



Scheme 2



Scheme 3

In Scheme 2, one of the possible enantiomers of VIII is shown. In the case of the five-membered ring, molecular models show that the best conformation of the intermediate radical for the approach of the organotin hydride is IX (Scheme 3). The planar conformation postulated for IX is in agreement with the structure of compounds like 3-cyclopentenone, which have an sp^2-hybridized carbon atom next to a C–C double bond [23]. The organotin hydride then approaches the ring plane from the less hindered side, leading to the energetically less favoured isomer IV (again the *cis* adduct) according to Scheme 3 (only one of the possible enantiomers of IV is shown). Although the structure of IV is depicted as planar, the analysis of ^{13}C NMR spectra data indicates it to be somewhat distorted.

The formation of radicals VIII and IX, resonance stabilized by the neighbouring ester group, could also account for the fact that substrates I and II undergo hydrostannation more easily (with quantitative yields) than substrates like 1-phenylcyclohexene [14] and 1-hydroxymethylcyclopentene [16].

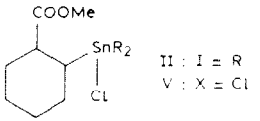
We feel that this concept is of broader importance for the hydrostannation of (substituted) cyclic olefins, and we are at present checking its validity for other ring sizes and other substituents.

Experimental

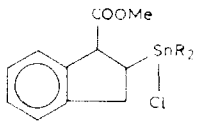
^1H NMR spectra were obtained with a Varian EM 360L, and ^{13}C and ^{119}Sn NMR spectra with a Bruker AM 300 instrument. Infrared spectra were recorded with a Perkin–Elmer 577 spectrophotometer. The refractive indices were measured with a Universal Abbe, Zeiss Jena VEB instrument, and melting points were determined on a Kofler hot stage and are uncorrected. Microanalyses were performed at UMYMFOR (Argentina) and at Dortmund University (F.R.G.). Sample irradiations were carried out in an irradiator constructed in this Laboratory, which consisted 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 standard procedures [24–27]. All the solvents and reagents used were analytical-reagent grade. The organotin hydrides were obtained by reduction of the

Table 5

Compounds obtained from hydrostannation of methyl cyclohexene-1- and indene-3-carboxylates and their corresponding 2-chlorodialkylstannyl derivatives



II : I = R
V : X = Cl



IV : X = R
VI : X = Cl

Compound	R	X	Time [a] (irradiation times)	Temperature (°C)	Substrate/reagent ratio (irradiated reactions)	M.p. (°C) [b] or n_D [c]	Elemental analyses (Found (calcd.) (%))	
							C	H
IIa	Me	Me	300(240)	65	1:2 (1:1.5)	1.5030	43.10	7.30
							(42.32)	(7.27)
Va	Me	Cl	360	RT	1:1.1	65–67	37.40	5.90
							(36.91)	(5.88)
IIb	n-Bu	n-Bu	300(240)	80	1:1.5(1.:2)	1.5005	55.20	9.40
							(55.70)	(9.35)
Vb	n-Bu	Cl	300	RT	1:1.1	52–54	47.39	7.75
							(46.92)	(7.63)
IIc	Ph	Ph	240(120)	80	1:1.5(1:1.5)	83–85	64.45	5.80
							(63.58)	(5.74)
Vc	Ph	Cl	210	RT	1:1.1	95–97	53.88	5.20
							(53.44)	(5.16)
IVa	Me	Me	420(370)	65	1:2 (1:2)	1.4991 [d]	49.78	5.90
							(49.60)	(5.95)
VIa	Me	Cl	90	RT	1:1.1	115–116	43.90	4.82
							(43.44)	(4.77)
IVb	n-Bu	n-Bu	1920(1380)	80	1:2 (1:2)	1.5101	59.49	8.29
							(59.38)	(8.23)
VIb	n-Bu	Cl	300	RT	1:1.1	1.5446 [e]	51.89	6.66
							(51.45)	(6.59)
IVc	Ph	Ph	300(300)	80	1:2 (1:2)	108–110	66.45	4.89
							(66.32)	(4.99)
VIc	Ph	Cl	240	RT	1:1.1	80-83	56.80	4.45
							(57.13)	(4.38)

[a] In minutes. [b] All compounds recrystallized from ethanol. [c] Refractive indices determined at 20 °C, except when indicated otherwise. [d] At 16 °C. [e] At 22 °C.

corresponding chlorides, R_3SnCl, with sodium borohydride [28] (R = n-Bu and Ph) and with lithium aluminium hydride [17] (R = Me). The purification of the organotin adducts and of some of their chlorine/alkyl 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 and III, as well as times of reaction, physical characteristics and elemental analyses are listed in Tables 1–5.

Reaction of methyl cyclohexene-1-carboxylate (I) with trimethyltin hydride (thermal). Synthesis of cis-methyl 2-trimethylstannylcyclohexanecarboxylate (IIa). Methyl cyclohexene-1-carboxylate (2.5 g, 0.0178 mol) was treated for 5 h with trimethyltin hydride (5.88 g, 0.0356 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 involving monitoring of the reaction by taking samples at intervals and observing the disappearance of the Sn-H absorption by IR and by checking at the end 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 carbon tetrachloride/benzene (3/1) as an oily colorless liquid; n_D^{20} 1.5030.

Reaction of methyl indene-3-carboxylate (III) with tri-n-butyltin hydride (irradiated). Synthesis of cis-methyl 2-tri-n-butylstannylindane-1-carboxylate (IVb). Methyl indane-3-carboxylate (1 g, 0.0057 mol) was added to tri-n-butyltin hydride (3.34 g, 0.0114 mol) under nitrogen. The reaction vessel was then placed in the photochemical reactor (the temperature inside the reactor was ca. 25 °C) and the mixture stirred for 23 h (optimal reaction conditions determined as above). The ^1H NMR spectrum showed that a quantitative yield of IVb was obtained. The crude product was purified by column chromatography (silica gel 60). The adduct IVb was eluted with carbon tetrachloride as an oily yellowish liquid; n_D^{20} 1.5001.

b. Chloro / alkyl 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 to 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 1–5.

Exchange between cis-methyl 2-trimethylstannylcyclohexanecarboxylate (IIa) and trimethyltin chloride. Synthesis of cis-methyl 2-chlorodimethylstannylcyclohexanecarboxylate (Va). Adduct IIa (1.26 g, 0.00413 mol) was added to trimethyltin chloride (1 g, 0.005 mol) with stirring under nitrogen and the mixture was left at room temperature for 6 h. The ^1H NMR spectrum showed that IIa had completely been converted into Va. The excess of trimethyltin chloride as well as the tetramethyltin

formed were distilled off under reduced pressure. The solid residue was recrystallized from ethanol; m.p. 65–67 °C (1.26 g, 93.5%).

Exchange between cis-methyl 2-tri-n-butylstannyl indane-1-carboxylate (IVb) and mercury(II) chloride. Synthesis of cis-methyl 2-chlorodi-n-butylstannylindane-1-carboxylate (VIb). A solution of mercury(II) chloride (0.64 g, 0.00236 mol) in methanol (5 ml) was added with stirring under nitrogen to a solution of IVb (1 g, 0.00215 mol) in methanol (10 ml). The solution was left at room temperature for 5 h 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 IVb into IVb had been achieved. The product was purified by column chromatography (silica gel 60), and compound VIb (0.87 g, 93%) was eluted with carbon tetrachloride to yield an oily liquid: n_D^{22} 1.5446.

Exchange reaction between cis-methyl 2-triphenylstannylcyclohexanecarboxylate (IIc) and mercury(II) chloride. Synthesis of cis-methyl 2-chlorodiphenylstannylcyclohexane carboxylate (Vc). A solution of mercury (II) chloride (0.6 g, 0.0022 mol) in methanol (5 ml) was added with stirring under nitrogen to a suspension of IIc (1 g, 0.002 mol) in methanol (10 ml). The mixture was left at room temperature for 3.5 h then the suspension was filtered. The solid thus isolated was extracted with chloroform, and the extract was filtered (leaving behind phenylmercury chloride); the chloroform was removed under reduced pressure to give Vc as a white solid, which was recrystallized from ethanol; m.p. 83–85 °C (0.82 g, 91.5%).

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