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Organotin compounds

IX *. Reactions between trialkylstannyl-substituted esters and trimethylsilyl halides: exchange vs. hydrolysis

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Abstract

A study of the reactions between β- and ω-trialkylstannyl-substituted saturated methyl carboxylates (R = Me, n-Bu, Ph) and trimethylsilyl halides (X = Cl, Br, I) is reported. The results indicate that methyl β-(trialkylstannyl)propanoates react with trimethylsilyl halides to give alkyl/halide exchange products; no ester cleavage is observed even using organotin ester/silicon halide ratios of 1/4. The reactions carried out with ω-trialkylstannyl-substituted esters show that the failure of methyl β-(trialkylstannyl)propanoates to give transesterification products is connected with the intramolecular coordination that exists in the methyl β-(halodialkylstannyl)propanoates, alkyl/halide exchange products, which prevents the coordination between the C=O of the ester and the silicon halide. The results obtained also indicate that the alkyl/halide exchange reactions are much faster than the transesterification reactions. Evidence concerning the possibility that these halodealkylation reactions at tin might be a general property of tetralkyltin compounds is presented.

Introduction

In a previous publication [1] we reported that methyl β-(trialkylstannyl)propanoates react with trimethylsilyl halides (X = Cl, I) to give alkyl/halide exchange

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* For part VIII see ref. 1.

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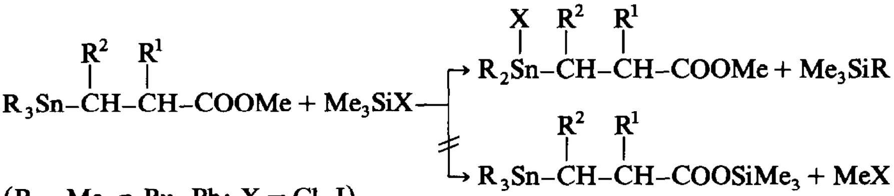
products without ester cleavage according to Scheme 1, even when the silicon halides are in a four-fold excess.



$$R_3Sn\text{-}\overset{R^2}{CH}\text{-}\overset{R^1}{CH}\text{-}COOMe + Me_3SiX \begin{cases} \rightarrow R_2\overset{X}{Sn}\text{-}\overset{R^2}{CH}\text{-}\overset{R^1}{CH}\text{-}COOMe + Me_3SiR \\ \not\rightarrow R_3Sn\text{-}\overset{R^2}{CH}\text{-}\overset{R^1}{CH}\text{-}COOSiMe_3 + MeX \end{cases}$$

(R = Me, n-Bu, Ph; X = Cl, I)

Scheme 1

We now wish to communicate the results we have obtained in some studies carried out aiming to determine the scope and probable mechanism of these reactions.

Results and discussion

In addition to the reactions previously reported [1], we have now performed reactions using a wider range of methyl β-(trialkylstannyl)propanoates and Me_3SiX (where X stands for Cl, Br and I), according to eq. 1.

$$\underset{(I)}{R_3SnCH(R^2)CH(R^1)COOMe} + Me_3SiX \rightarrow \underset{(II)}{R_2Sn(X)CH(R^2)CH(R^1)COOMe} + Me_3SiR$$

$$(R = Me, n\text{-}Bu, Ph;\ X = Cl, Br, I) \qquad (1)$$

These reactions were carried out in CCl_4, under nitrogen atmosphere, at 65 °C with trimethylsilyl chloride and bromide, and at 50 °C with trimethylsilyl iodide, using organotin ester/Me_3SiX molar ratios of 1/1.1 and 1/4. Under these conditions, it was found that all reactions followed the same pattern: the only products were those of alkyl/halide exchange without ester cleavage, even in the case when a four-fold excess of Me_3SiI was used. The systems studied are summarized in Table 1.

Trimethylalkylsilanes, Me_3SiR (R = n-Bu and Ph) obtained in these reactions, were quantitatively identified in each case by ^1H NMR making use of the corresponding standards, synthesized by known procedures [2,3]. This was not possible in the case of trimethylstannyl derivatives owing to the volatility of tetramethylsilane (TMS).

In order to determine whether this is an equilibrium reaction, mixtures of chlorodialkylstannyl esters (IIa) and Me_3SiR were left to react for long periods (120 h) under the same conditions. We could not in any case detect the formation of the corresponding trialkylstannyl esters (I) (eq. 2).

$$\underset{(IIa)}{R_2Sn(Cl)CH(R^2)CH(R^1)COOMe} + Me_3SiR \not\rightarrow \underset{(I)}{R_3SnCH(R^2)CH(R^1)COOMe} + Me_3SiCl$$

$$(R = n\text{-}Bu, Ph;\ R^1 = R^2 = Me) \qquad (2)$$

Table 1

Times of conversion of methyl β-(trialkylstannyl)propanoates at different organotin ester/Me_3SiX ratios [a]

$R_2Sn(X)CH(R^2)CH(R^1)COOMe$					Conversion		ν(C=O) (cm^{-1}) [d]	
No.	R	R^1	R^2	X	A [b] (24 h) (%)	B [c] (% (h))	II [e]	I [f]
1	Ph	H	H	Cl	22	28(24)	1661	1709
2	n-Bu	H	Me	Cl	38	61(72)	1681	1715
3	Me	H	H	Br	26	100(33)	1667	1717
4	n-Bu	H	H	Br	36	100(33)	1667	1718
5	Ph	H	H	Br	40	100(36)	1653	1709
6	Me	Me	H	Br	18	100(68)	1645	1701
7	n-Bu	Me	H	Br	46	100(38)	1664	1715
8	Ph	Me	H	Br	64	100(30)	1653	1695
9	n-Bu	H	Me	Br	51	100(70)	1680	1715
10	n-Bu	Me	Me	Br	76	100(32)	1650	1695
11	Ph	Me	Me	Br	55	100(36)	1647	1680
12	Me	Me	Ph	Br	77	100(26)	1680	1730
13	n-Bu	Ph	Ph	Br	48	100(34)	1667	1730
14	Ph	Ph	Ph	Br	83	100(24)	1645	1695
15	n-Bu	H	H	I	49	100(34)	1676	1718
16	n-Bu	H	Me	I	51	100(60)	1681	1715
17	n-Bu	Me	Me	I	80	100(24)	1669	1695
18	n-Bu	Ph	Ph	I	44	100(26)	1667	1730

[a] Reactions carried out at 65 °C when X = Cl, Br, and at 50 °C when X = I. [b] Organotin ester/Me_3SiX ratio 1/1.1. [c] Organotin ester/Me_3SiX ratio 1/4. [d] IR spectra recorded for pure compounds. [e] Carbonyl stretch of the obtained methyl β-(halodialkylstannyl)propanoates. [f] Carbonyl stretch of the starting methyl β-(trialkylstannyl)propanoates.

These results show that even though these exchange reactions are slow, they are irreversible or at least that the reverse reaction is not detectable by NMR. This irreversibility could be connected with the enhanced stability of type II esters, originating in their intramolecular coordination. It is notable that in all halodialkylstannyl esters (II) coordination exists between the C=O group of the ester and the tin atom, as is shown by the shift of the carbonyl frequency in the IR spectrum to lower frequencies (see Table 1). That the coordination is intramolecular is demonstrated by the fact that there is almost no variation of the C=O frequency between the pure compound and a solution in acetonitrile.

An attempt was also made to study solvent effects on these reactions. In this respect, it should be noted that solvent selection is limited by the fact that trimethylsilyl halides react with common solvents like alcohols, amines, amides and also with dimethylsulfoxide [4,5]. Taking into account the above facts, it was decided to carry out these studies without solvent (excess of Me_3SiCl) and in CCl_4, n-hexane and acetonitrile as solvents. The results obtained are summarized in Table 2, which shows that there is little variation between the reactions carried out in solvents with low dielectric constant, like CCl_4 and n-hexane, whereas the rate of conversion is slower using acetonitrile as solvent (higher dielectric constant).

The results obtained (Tables 1 and 2) together with those previously reported [1], suggest that these reactions do not follow an ionic mechanism because (a) they

Table 2

Solvent effects on exchange reactions [a]

$R_3SnCH(Ph)CH(Ph)COOMe + Me_3SiCl \rightarrow R_2Sn(Cl)CH(Ph)CH(Ph)COOMe + Me_3SiR$

R	Solvent	Conversion (%) (24 h)
n-Bu	–	40
Ph	–	55
n-Bu	CCl_4	54
Ph	CCl_4	58
n-Bu	n-Hexane	40
Ph	n-Hexane	50
n-Bu	Acetonitrile	38
Ph	Acetonitrile	38

[a] Solutions 0.7 *M* in organotin ester; organotin ester/Me_3SiCl ratio 1/1.4, except in reactions 1 and 2 where Me_3SiCl was used as solvent.

should then proceed faster in solvents of higher dielectric constant and (b) the ionic mechanism would favour the cleavage of aromatic groups in all cases.

On the other hand, we have also observed that neither the addition of azobis(isobutyronitrile) nor UV irradiation have a significant effect on the degree of conversion.

Thus, discarding the options of ionic and free radical mechanisms, it is possible to assume that these reactions could follow a 4-center concerted mechanism like the one depicted in Fig. 1.

From the results obtained it is clear that Sn–C bonds are cleaved more readily by trimethylsilyl halides than are the C–O bonds of esters. What is not clear is why, after the alkyl–tin bond is cleaved, the Me_3SiI cannot effect ester cleavage. In our previous report [1], we assumed that this might be explained on the basis of the existence of intramolecular coordination in the β-halodialkylstannyl esters (II), which would prevent the coordination between the C=O and silicon. In order to check the validity of this hypothesis, we performed a series of experiments. Firstly, and with the aim of determining the degree of extension of intramolecular coordination [6*] with increasing length of the carbon chain, we synthesized [7] a series of

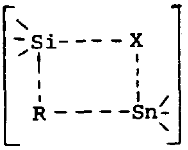


Fig. 1.

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* This and other references marked with asterisks indicate notes occurring in the list of references.

compounds of types III and IV, and from them by halogenation the corresponding halodialkylstannyl esters of types V and VI (eq. 3 and 4):

$$\mathrm{Bu_3Sn(CH_2)_{\mathit{n}}CH(R)COOMe} \qquad \mathrm{[Bu_3Sn(CH_2)_3]_2C(R)COOMe}$$

$$(\mathrm{III}\colon \mathrm{R = H, Ph, COOMe};\ n = 2, 3) \qquad (\mathrm{IV}\colon \mathrm{R = CN, COOMe})$$

$$\mathrm{III} + \mathrm{X_2} \rightarrow \underset{(\mathrm{V})}{\mathrm{Bu_2Sn(X)\text{-}(CH_2)_{\mathit{n}}CH(R)\text{-}COOMe}} + \mathrm{BuX} \tag{3}$$

$$\mathrm{IV} + 2\mathrm{X_2} \rightarrow \underset{\substack{(\mathrm{VI}) \\ (\mathrm{X = Cl_2, I_2})}}{\mathrm{[Bu_2Sn(X)\text{-}(CH_2)_3]_2C(R)COOMe}} + 2\ \mathrm{BuX} \tag{4}$$

In Table 3 are summarized some spectroscopic characteristics of these compounds. The IR spectra of the esters were run both as pure compounds and in acetonitrile solution (10%). Table 3 shows that while in β-halodibutylstannyl esters **15** and **20**, taken as a reference, the IR spectra show a pronounced shift of the C=O stretching frequency to lower frequencies than that of the corresponding tributylstannyl ester (**19**), in general the remaining halodibutylstannyl derivatives do not show such a big variation in the C=O stretching frequency with respect to that of the corresponding starting tributylstannyl esters.

Table 3

Some spectroscopic characteristics of n-butylstannyl-substituted esters

Compound	R	X	n	ν(C=O) ($\mathrm{cm^{-1}}$)		^{1}H NMR[a] δ(OMe) (ppm)
				Pure compound	Solution (acetonitrile)	
n-$Bu_2Sn(X)(CH_2)_nCH(R)COOMe$						
19	H	n-Bu	1	1728	1726	3.53
20	H	Cl	1	1678[b]	1670	3.73
15	H	I	1	1676	1678	3.68
21	H	n-Bu	2	1730	1726	3.50
22	H	Cl	2	1695,1735	1695,1735	3.57
23	H	I	2	1690,1730	1690,1728	3.56
24	H	n-Bu	3	1734	1738	3.47
25	H	Cl	3	1725	1734	3.50
26	H	I	3	1722	1724	3.52
27	Ph	n-Bu	3	1715	1720	3.50
28	Ph	Cl	3	1724	1718	3.52
29	Ph	I	3	1714	1718	3.53
30	COOMe	n-Bu	3	1718,1740	1730,1748[c]	3.62
31	COOMe	Cl	3	1715,1738	1730,1750[c]	3.61
32	COOMe	I	3	1714,1798	1730,1748[c]	3.63
[n-$Bu_2Sn(X)(CH_2)_n]_2C(R)COOMe$						
33	CN	n-Bu	3	1734	1732,1742[c]	3.79
34	CN	Cl	3	1735	1728,1742[c]	3.71
35	CN	I	3	1732	1720,1728[c]	3.83
36	COOMe	n-Bu	3	1720,1740[c]	1725	3.60
37	COOMe	Cl	3	1720,1736[c]	1724	3.57
38	COOMe	I	3	1710,1722[c]	1724	3.57

[a] Chemical shifts relative to TMS; spectra recorded in CCl_4 solution. [b] The value of 1639 $\mathrm{cm^{-1}}$ given in ref. 1 for the pure compound is not correct. [c] Shoulder.

A similar effect is visible in the ^1H NMR spectra. The OMe proton chemical shifts of β-halodibutylstannyl esters **15** and **20** appear at lower fields than that of the corresponding β-tributylstannyl ester (**19**). These differences are less notable with the increasing number of methylene groups between the tin atom and the ester group.

The pronounced shift, ca. 50 cm^{-1}, to lower frequencies in the C=O absorptions of halodibutylstannyl esters **15** and **20** with respect to that of the precursor, tributylstannyl ester **19**, as well as the corresponding shift to lower fields of ^1H NMR chemical shifts of OMe group protons, indicate that in esters **15** and **20** there is coordination between C=O of the ester group and the tin atom. It is known [6,8–10] that C=O → Sn coordination reduces the C=O stretching frequency and that it also has a deshielding effect on the OMe group protons. That the coordination is intramolecular is shown by the fact that the differences between the stretching frequencies of the C=O group in the tributylstannyl ester **19** and its halogen derivatives **15** and **20**, remain even in a polar solvent such as acetonitrile (see Table 3).

The IR spectra of methyl 4-(n-tributylstannyl)butanoate (**21**) and its halogen derivatives **22** (Cl) and **23** (I), show that **22** and **23** have two bands in the C=O stretching frequency range. Whereas one of the bands appears at about the same frequency as that of its precursor **21**, in both compounds the second band appears at about 40 cm^{-1} to lower frequencies than that of **21**. The same results were obtained when the spectra were run in acetonitrile solution. The band which appears at about 1730 cm^{-1} is the one which corresponds to the uncoordinated carbonyl group, and the one at about 1690 cm^{-1} is that of the coordinated carbonyl group.

These results indicate that, although these compounds still show intramolecular coordination, it is weaker than that shown by halogendibutylstannyl esters **15** and **20** which have one methylene group less.

The IR spectra of halogendibutyl esters **25** and **26** show that C=O stretching appears at normal frequencies either in pure state or in solution, and in the ^1H NMR spectra there are only small variations in the OMe proton chemical shifts with respect to that of the precursor, methyl 5-(n-tributylstannyl)pentanoate (**24**). These results clearly indicate that when in the carbon chain there are four methylene groups between the tin atom and the ester group, there is no intramolecular coordination in halodialkylstannyl esters [6]. It should be noted that when the separation by four methylene groups is maintained, the introduction of substituents at C(2) (compounds **27** and **30** and their halogen derivatives **28**, **29**, **31** and **32**), as well as introducing a second chain containing an organotin substituent (compounds **33** and **36**, and their halogen derivatives **34**, **35**, **37** and **38**), leads to organotin esters which also do not show intramolecular coordination.

The above results, together with those from the literature [6,8–10], confirm that in β-(halodialkylstannyl)propanoates the tin atom is pentacoordinated. A remarkable fact is that this intramolecular coordination is little affected by steric effects. When the distance between the tin atom and the ester group is increased by inserting a methylene group (compounds **22** and **23**) there is an equilibrium between tetracoordinated and pentacoordinated structures. Insertion of another methylene group (compounds **25**, **26**, **28**, **29**, **31**, **32**, **34**, **35**, **37** and **38**) causes intramolecular coordination to disappear, and the tin atom remains tetracoordinated as in normal tetraalkyltin compounds.

Table 4

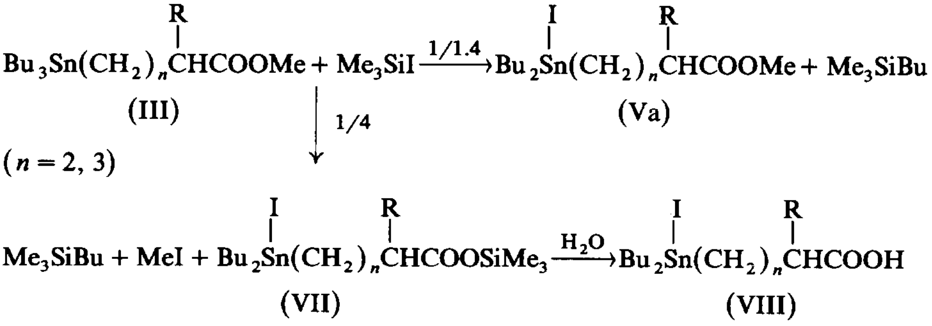
Times of conversion of ω-tributylstannyl-substituted esters at different organotin ester/Me_3SiI ratios

Compound	n	R	Organotin ester/Me_3SiI ratio	
			1/1.4 [a]	1/4
			Exchange [b] (% hours)	Exchange [b] and transesterification [b] (% hours)
n-$Bu_2Sn(CH_2)_nCH(R)COOMe$				
21	2	H	40 (100)	100 (90)
24	3	H	60 (36)	100 (78)
27	3	Ph	100 (120)	100 (125)
30	3	COOMe	100 (168)	100 (240)
$[n$-$Bu_3Sn(CH_2)_n]_2C(R)COOMe$				
33	3	CN	100 (120)	100 (140)
36	3	COOMe	100 (160)	100 (144)

[a] No transesterification was detected. [b] From ^1H NMR spectra.

In order to confirm our hypothesis, namely that the fact that β-trialkylstannyl-substituted methyl esters do not react with Me_3SiI to give transesterification products might be connected with intramolecular coordination, a series of reactions between tributylstannyl esters **21**, **24**, **27**, **30**, **33** and **36**, and Me_3SiI was performed. Reactions were carried out under the same experimental conditions as previously: CCl_4, nitrogen atmosphere, 50 °C and using organotin ester/Me_3SiI molar ratios of 1/1.4 and 1/4. In Table 4, the results obtained are summarized.

The general pattern of these reactions is shown in Scheme 2.



$$\mathrm{Bu_3Sn(CH_2)_n\overset{\overset{R}{|}}{C}HCOOMe + Me_3SiI \xrightarrow{1/1.4} Bu_2\overset{\overset{I}{|}}{S}n(CH_2)_n\overset{\overset{R}{|}}{C}HCOOMe + Me_3SiBu}$$

(III) ($n = 2, 3$) $\quad \downarrow$ 1/4 $\quad$ (Va)

$$\mathrm{Me_3SiBu + MeI + Bu_2\overset{\overset{I}{|}}{S}n(CH_2)_n\overset{\overset{R}{|}}{C}HCOOSiMe_3 \xrightarrow{H_2O} Bu_2\overset{\overset{I}{|}}{S}n(CH_2)_n\overset{\overset{R}{|}}{C}HCOOH}$$

(VII) $\quad$ (VIII)

Scheme 2

Some physical characteristics of the obtained iododibutylstannyl carboxylic acids are summarized in Table 5.

The fact that in the reactions carried out using an organotin ester/Me_3SiI ratio of 1/1.4 only the alkyl/halogen exchange reaction products are obtained clearly indicates that the exchange reactions are much faster than the ester group cleavage reactions. On the other hand, the fact that we have succeeded in the transesterification of these esters (ratio 1/4) demonstrates that the inability of β-(trialkylstannyl) propanoates (type I) to react with an excess of Me_3SiI to give ester cleavage products, derives from the intramolecular coordination existing in their products of

Table 5

Some physical characteristics of the ω-di-n-butyliodostannyl-substituted carboxylic acids obtained from transesterification with Me_3SiI followed by hydrolysis

Acid	*n*	R	n_D [a]	^1H NMR [b] (ppm) δ(COO*H*)	ν(C=O) (cm^{-1}) [c]	Analysis (Found (calcd.) (%))	
						C	H
n-$Bu_2Sn(I)(CH_2)_nCH(R)COOH$							
39	2	H	1.5278 [d]	11.25	1686	32.18 (32.25)	5.70 (5.64)
40	3	H	1.5440	11.04	1678	33.88 (33.87)	5.94 (5.90)
41	3	Ph	1.5663	9.97	1686,1712 [e]	42.38 (42.49)	5.84 (5.82)
42	3	COOH	1.5335 [f]	11.26	1698	33.25 (33.30)	5.32 (5.39)
$[n$-$Bu_2Sn(I)(CH_2)_n]_2C(R)COOH$							
43	3	CN	1.5668	10.80	1692	33.92 (33.86)	5.60 (5.57)
44	3	COOH	1.5659	11.25	1692	33.20 (33.14)	5.50 (5.56)

[a] Refraction indices at 20 °C, except when otherwise stated. [b] ^1H NMR spectra in CCl_4 solution; chemical shifts with reference to TMS. [c] IR spectra of pure compounds (film). [d] At 22 °C. [e] Shoulder. [f] At 21°.

alkyl/halide exchange (type II esters), which prevents the coordination between the C=O group and the silicon by rendering the carbonyl less nucleophilic.

We have also performed reactions between tetra-n-butyltin and trimethylsilicon chloride (eq. 5) under the same conditions as previously, but leaving the mixtures to react for longer periods. After 160 h of reaction, gas chromatographic analysis shows that 9.2% of the exchange product, tri-n-butyltin chloride, is obtained.

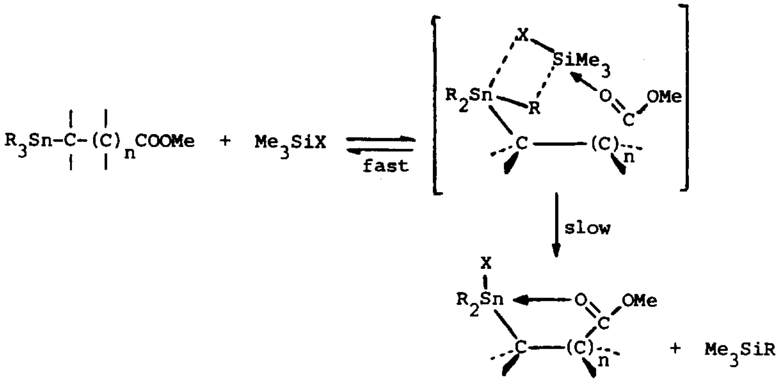
$$Bu_4Sn + Me_3SiCl \rightarrow Bu_3SnCl + Me_3SiBu \qquad (5)$$

Comparing the acceleration in reactivity of the esters relative to tetra-n-butyltin, there are no doubts that the ester moiety plays a fundamental role. Taking into account our results, it is possible to postulate that these reactions could proceed through an intramolecular 4-center concerted mechanism according to Fig. 2. The trimethylsilicon halide coordinated, in a fast previous step, with the ester group will exchange halide for alkyl in a slow rate-determining step with the trialkylstannyl group. Then, either intramolecular coordination will prevent in the case of β-trialkylstannylpropanoates further reaction with an excess of trimethylsilicon halide (iodide) or, as in the case of non-intramolecularly coordinated ω-(halodialkylstannyl)-substituted esters will react further to yield transesterification products.

In the case of tetra-n-butyltin, the coordination which brings the trialkyltin group and the silicon halide closer does not exist, so that the exchange reaction is slower.

Experimental

^1H NMR spectra were obtained with a Varian EM 360L instrument and infrared spectra were recorded with Perkin–Elmer 137B and 599B spectrophotometers.



n = 1, intramolecularly coordinated (as shown)
n > 1, non-intramolecularly coordinated

Fig. 2.

Gas-liquid chromatographic analyses were carried out with a Varian 1400 chromatograph, using a capillary column (25M SIL-52 CB 52, Quarz). The refraction 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, Federal Republic of Germany, and in UMYMFOR, Argentina. All the solvents and reagents used were analytical-reagent grade. Trimethylsilyl iodide and bromide were prepared according to known procedures [11,12], whereas trimethylsilyl chloride was purchased (Fluka). Trimethyl-n-butylsilane and trimethylphenylsilane, used as reference compounds, were obtained from the reactions between trimethylsilyl chloride and the corresponding lithium or Grignard reagents [2,3]. Methyl β-(trialkylstannyl)- and β-(triphenylstannyl)propanoates [10,13–15], as well as methyl β-(chlorodialkylstannyl)- and β-(chlorodiphenylstannyl)-propanoates [9,10,16,17] used as references, were prepared by known procedures. The synthesis of ω-tributylstannyl-substituted esters **24**, **27**, **30**, **33** and **36**, was carried out by hydrostannation of the corresponding olefins with tri-n-butyltin hydride [7]. The halogenation with Cl_2 and I_2 in CCl_4 solution of the above ω-tributylstannyl-substituted esters, led to the corresponding ω-di-n-butylhalostannyl-substituted esters **22**, **23**, **25**, **26**, **28**, **29**, **31**, **32**, **34**, **35**, **37** and **38**, in quantitative yields [7].

a. Alkyl-halogen exchange reactions between β-trialkylstannyl-substituted esters and trimethylsilyl halides

All the reactions were carried out following the same procedure. A typical experiment is described in detail to illustrate the method used.

Exchange reaction between methyl 2-methyl-3-(tri-n-butylstannyl)butanoate and trimethylsilyl iodide. Synthesis of methyl 2-methyl-3-(di-n-butyliodostannyl)butanoate (17). A solution of methyl 2-metyl-3-(tri-n-butylstannyl)butanoate (2.836 g, 0.007 mol) and trimethylsilyl iodide (5.6 g, 3.81 ml, 0.028 mol) in CCl_4 (10 ml), was heated at 50 °C [18*] under nitrogen and with magnetic stirring, until ^1H NMR and IR spectra showed no further change (24 h). Solvent distillation under reduced pressure gave the exchange product **17** in a pure state. Methyl 2-methyl-3-(di-n-butyliodo-

Table 6

Some physical characteristics and elemental analyses of methyl β-(halodialkylstannyl)propanoates obtained from alkyl/halide exchange with Me_3SiX

$R_2Sn(X)CH(R^2)CH(R^1)COOMe$					n_D [a] or m.p. (°C)	Analyses (Found (calcd.) (%))			
Compound	R	R^1	R^2	X		Calculated		Found	
						C	H	C	H
1	Ph	H	H	Cl	1.5830 [b]	48.60	4.33	48.67	4.36
2	n-Bu	H	Me	Cl	1.4983 [b]	42.26	7.37	42.31	7.32
3	Me	H	H	Br	43–45 [c]	22.82	4.15	22.87	4.07
4	n-Bu	H	H	Br	1.6728 [d]	36.04	6.30	36.14	6.36
5	Ph	H	H	Br	1.6081 [e]	43.68	3.90	43.58	3.96
6	Me	Me	H	Br	1.6857	25.49	4.58	25.56	4.50
7	n-Bu	Me	H	Br	1.5098	37.72	6.57	37.79	6.64
8	Ph	Me	H	Br	1.6855	44.98	4.22	44.90	4.17
9	n-Bu	H	Me	Br	1.5139	37.72	6.57	37.81	6.49
10	n-Bu	Me	Me	Br	1.5159	39.29	6.83	39.21	6.92
11	Ph	Me	Me	Br	1.6099	46.20	4.52	46.32	4.48
12	Me	Me	Ph	Br	95–97 [c]	38.47	4.72	38.51	4.70
13	n-Bu	Ph	Ph	Br	1.5701	52.21	6.03	52.45	5.98
14	Ph	Ph	Ph	Br	61–63 [c]	56.80	4.26	56.88	4.32
15	n-Bu	H	H	I	1.5369 [d]	32.25	5.64	32.32	5.68
16	n-Bu	H	Me	I	1.5339 [e]	33.87	5.90	33.92	5.92
18	n-Bu	Ph	Ph	I	1.5949 [d]	48.11	5.55	48.18	5.55

[a] Refraction indices at 20 °C, except when otherwise stated. [b] At 21 °C. [c] Recrystallized from ethanol. [d] At 19 °C. [e] At 22 °C.

stannyl) propanoate (**17**) is a liquid, n_D^{19} 1.5275. PMR (CCl_4, δ, ppm), 3.67 (s), 2.89(m), 1.24(m); IR (film), ν(C=O) 1669 cm^{-1}. Analysis: Found: C, 35.45; H, 6.10. $C_{14}H_{29}IO_2Sn$ calcd.: C, 35.40; H, 6.15%.

The new compounds obtained in these exchange reactions as well as their main characteristics are summarized in Tables 6 and 7. When the exchange products were not completely pure, they were purified by column chromatography (silica gel, Kieselgel 60, 70–230 mesh, Merck).

b. *Reactions between ω-tri-n-butylstannyl-substituted esters and trimethylsilyl iodide*

The reactions were performed following the same procedure in all cases. One experiment is described in detail to illustrate the method used.

Reaction between methyl 2-methoxycarbonyl-5-(tri-n-butylstannyl)pentanoate and trimethylsilyl iodide. Synthesis of 2-carboxy-5-(di-n-butyliodostannyl)pentanoic acid (42). A solution of methyl 2-methoxycarbonyl-5-(tri-n-butylstannyl)pentanoate (1 g, 0.0022 mol) and trimethylsilyl iodide (1.73 g, 1.18 ml, 0.0088 mol) in CCl_4 (3 ml), was heated at 50 °C, under nitrogen and with magnetic stirring, until ^1H NMR and IR spectra showed no further change (240 h). Water was then added (1 ml) and the mixture was extracted with ether and dried with Na_2SO_4. Removal of solvent under reduced pressure gave the pure exchanged dicarboxylic acid **42**. Microanalyses as well as some physical properties of **42** and the acids obtained by this method are summarized in Table 5. All atempts to distil these acids led to decomposition.

c. *Reaction between tetra-n-butyltin and trimethylsilyl chloride*

A solution of tetra-n-butyltin (2.43 g, 2.3 ml, 0.007 mol) and trimethylsilyl chloride (3.042 g, 3.55 ml, 0.028 mol) in CCl_4 (10 ml), was heated at 65 °C, under

Table 7

^{1}H NMR data of methyl β-(halodialkylstannyl)propanoates obtained from the exchanges with Me_3SiX

$R_2Sn(X)CH(R^2)CH(R^1)COOMe$					Chemical shifts (δ, ppm) [a]	
Compound	R	R^1	R^2	X	δ(OMe)	Others
1	Ph	H	H	Cl	3.64	7.34(complex signal, 10H); 2.7(t, 2H, J 7.0); 1.62(t, 2H, J 7.0)
2	n-Bu	H	Me	Cl	3.67	2.60(d, 2H, $J_{2,3}$ 6.0, $J_{2,2}$ 9.0); 1.20(complex signal, 22H)
3	Me	H	H	Br	3.67	2.70(t, 2H, J 7.2); 1.40(t, 2H, J 7.2); 0.7(s, 6H, $J(^{119\text{-}117}Sn\text{-}C\text{-}H)$ 60 and 63)
4	n-Bu	H	H	Br	3.73	2.70(t, 2H, J 7.6); 1.28(complex signal, 20H)
5	Ph	H	H	Br	3.54	7.32(complex signal, 10H); 2.59(t, 2H, J 7.2); 1.60(t, 2H, J 7.2)
6	Me	Me	H	Br	3.67	2.92(m, 1H); 1.34(complex signal, 5H); 0.73(s, 3H); 0.66(s, 3H)
7	n-Bu	Me	H	Br	3.70	2.87(m, 1H); 1.32(complex signal, 23H)
8	Ph	Me	H	Br	3.66	7.32(complex signal, 10H); 2.99(m, 1H); 1.88(d, 2H, $J_{2,3}$ 7.6, $J_{3,3}$ 9.6); 1.30(d, 3H, J 7.4)
9	n-Bu	H	Me	Br	3.72	2.63(d, 2H, $J_{2,3}$ 6.0, $J_{2,2}$ 9.0); 1.77(complex signal, 22H)
10	n-Bu	Me	Me	Br	3.70	2.94(m, 2H); 1.34(complex signal, 24H)
11	Ph	Me	Me	Br	3.77	7.42(complex signal, 10H); 3.10(m, 1H); 2.47(m, 1H); 1.35(d, 3H, J 7.6); 1.30(d, 3H, J 7.6)
12	Me	Me	Ph	Br	3.77	6.83(complex signal, 5H); 3.10(m, 2H); 1.17(d, 3H, J 6.0); 0.73(s, 3H, $J(^{119\text{-}117}Sn\text{-}C\text{-}H)$ 60 and 64); 0.33(s, 3H, $J(^{119\text{-}117}Sn\text{-}C\text{-}H)$ 60 and 64)
13	n-Bu	Ph	Ph	Br	3.80	6.89(complex signal, 10H); 4.29(d, 1H, J 2.6); 3.16(d, 1H, J 2.6); 1.20 (complex signal, 18H)
14	Ph	Ph	Ph	Br	3.73	7.14(complex signal, 20H); 4.2(d, 1H, J 2.6); 3.32(d, 1H, J 2.6)
15	n-Bu	H	H	I	3.69	2.68(t, 2H, J 7.4); 1.4(complex signal, 20H)
16	n-Bu	H	Me	I	3.69	2.63(d, 2H, $J_{2,3}$ 5.8, $J_{2,2}$ 8.0); 1.23(complex signal, 22H)
18	n-Bu	Ph	Ph	I	3.83	6.96(complex signal, 10H); 4.27(d, 1H, J 2.8); 3.28(d, 1H, J 2.8); 1.30 (complex signal, 18H)

[a] ^{1}H NMR spectra measured in CCl_4 solution; chemical shifts with reference to TMS; J values in Hz.

nitrogen and with magnetic stirring during 160 h. After that time, GLC analysis showed that tri-n-butyltin chloride (9.2%) was formed.

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