

STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXVIII*. STRUCTURE OF PRODUCTS OBTAINED IN THE HYDRO- STANNATION OF STRONGLY ELECTROPHILIC CARBONYL COMPOUNDS**

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SUMMARY

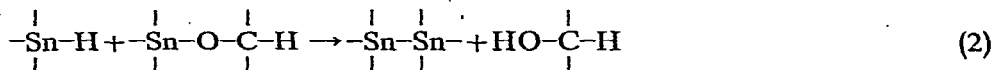
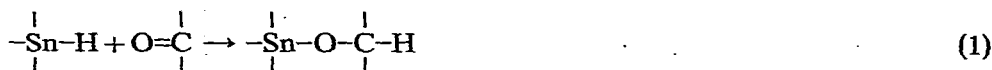
Organotin monohydrides were brought into reaction with strongly electrophilic carbonyl compounds, yielding mainly 1:1 and 1:2 adducts. The identity of these adducts was established by elementary analysis and NMR spectroscopy.

An NMR study of some of the adducts suggests that the absence or presence of $^{117,119}\text{Sn}-\text{O}-\text{C}-\text{H}$ coupling in alkoxytin compounds depends on the rate of exchange of the alkoxy groups bound to tin.

INTRODUCTION

In previous papers (ref. 1-5 and references cited therein) structural and mechanistic details of the hydrostannation of $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$ and $\text{C}=\text{S}$ bonds were presented. In this and the following paper⁶ the hydrostannation of electrophilic $\text{C}=\text{O}$ bonds will be discussed.

In the absence of catalysts the addition of trialkyltin hydrides across the carbon-oxygen double bond of aldehydes and ketones proceeds very slowly. The greater part of the additions reported so far were realized under free radical-generating conditions or under the influence of zinc chloride or methanol. Reactions involving triphenyltin hydride usually led to reduction [hydrostannation (1) followed by hydrostannolysis⁷ (2)].



Hydrostannations of $\text{C}=\text{O}$ bonds which are brought about under free radical-generating conditions evidently proceed by a free radical mechanism⁸⁻¹⁰. Hydro-

* For Part XXVII see ref. 1.

** Taken in part from the Ph.D. thesis of one of us (A.J.L.).

TABLE 1

HYDROSTANNATION OF ELECTROPHILIC CARBONYL COMPOUNDS. YIELD OF 1:1 AND 1:2 ADDUCTS

Tin hydride		Carbonyl compd. (mmoles)	Yield of adducts (%) ^a	
R	(mmoles)		1:1	1:2
<i>R</i> ₃ <i>SnH</i> + <i>Cl</i> ₃ <i>CCHO</i>				
Me	10.0	20.0	30	70
Et	39.7	80.0	10	80
Bu	20.0	40.0	5	85
<i>R</i> ₃ <i>SnH</i> + <i>C</i> ₆ <i>F</i> ₅ <i>CHO</i>				
Me	20.0	30.0	70	25
Et	9.9	15.0	75	20
Bu	9.9	15.0	65	25
<i>R</i> ₃ <i>SnH</i> + <i>C</i> ₆ <i>H</i> ₅ <i>C</i> (<i>CF</i> ₃) <i>O</i>				
Me	20.0	30.0	>90	
Et	9.9	15.2	≥85	
Bu	9.9	15.2	>85	

^a Calcd. from the NMR spectrum of the reaction mixtures.

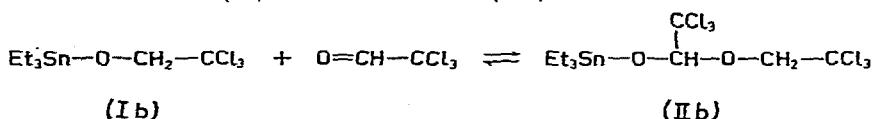
TABLE 2

HYDROSTANNATION OF ELECTROPHILIC CARBONYL COMPOUNDS. NMR DATA OF COMPOUNDS (I)-(VI)

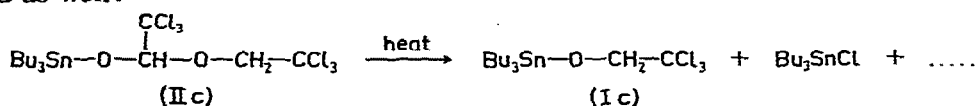
Compounds			Chemical shifts ^a (ppm ^b) and coupling constants (Hz)				
			$\delta(H_a)$	$\delta(H_b)$	$\delta(H_c)$	$J(H_a-H_b)$	$J(H_b-H_c)$
$R_3Sn-O-\overset{a}{CH_2}-\overset{b}{CCl_3}$	(Ia) R=Me	s	4.08				31.0
	(Ib) R=Et	s	4.15				28.0 ^d
	(Ic) R=Bu	s	4.11				27.5
$R_3Sn-O-\overset{a}{CH}-O-\overset{b}{\underset{c}{\overset{H}{ }{C}}}-CCl_3$	(IIa) R=Me	s	5.27	d 4.25	d 4.44	12.0	30.5
	(IIb) R=Et	s	5.34	d 4.28	d 4.45	11.5	27.0
	(IIc) R=Bu	s	5.32	d 4.28	d 4.45	11.5	26.5
$R_3Sn-O-\overset{a}{CH_2}-\overset{b}{CH}Cl_2$	(IIIb) R=Et	d	3.94	t	5.50	5.8	27.5
$R_3Sn-O-\overset{a}{CH_2}-\overset{b}{C_6F_5}$	(IVa) R=Me	t'	4.73				
	(IVb) R=Et	t'	4.77				
	(IVc) R=Bu	t'	4.74				
$R_3Sn-O-\overset{a}{\underset{c}{\overset{H}{ }{C}}}-O-\overset{b}{\underset{c}{\overset{H}{ }{C}}}-C_6F_5$	(Va) R=Me	t'	6.18	d 4.53	d 4.69	11.0	
	(Vb) R=Et	t'	6.20	d 4.51	d 4.69	10.8	
	(Vc) R=Bu	t'	6.11	d 4.43	d 4.69	10.0	
$R_3Sn-O-\overset{a}{\underset{c}{\overset{H}{ }{C}}}-\overset{b}{CF_3}$	(VIa) R=Me	q	4.84			6.8 ^e	26.0
	(VIb) R=Et	q	4.85			6.8 ^e	24.5
	(VIc) R=Bu	q	4.78			6.4 ^e	25.0

^a Only multiplicities due to H-H and H-F coupling are given; s: singlet; d: doublet; t: triplet; t': unresolved triplet due to coupling between hydrogen and *o*-fluorine atoms of the C₆F₅ group (*J* < 2 Hz); q, quartet. ^b Downfield from tetramethylsilane internal. ^c Mean value of coupling constants with ¹¹⁷Sn and ¹¹⁹Sn isotopes. ^d *J*(¹¹⁷Sn-H_a): 27.4 Hz; *J*(¹¹⁹Sn-H_a): 28.5 Hz. ^e H-F coupling.

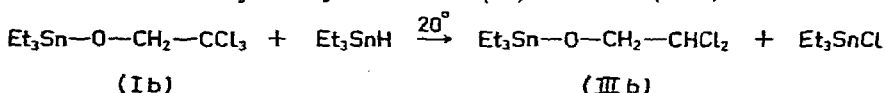
Addition of chloral to (Ib) afforded adduct (IIb)*:



The reversed reaction has also been observed. Distillation of (II) afforded mainly (R = Me) or exclusively (R = Et) (I). In the case of R = Bu (IIc) tributyltin chloride was formed as well:

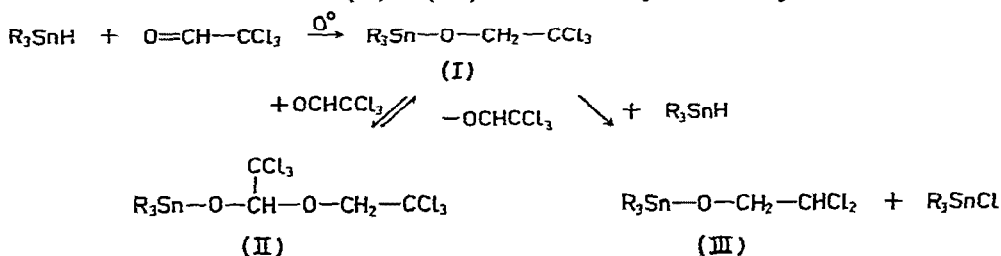


Reaction of triethyltin hydride with (Ib) afforded (IIIb):

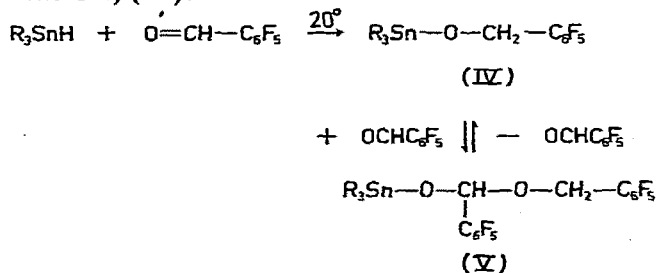


With an excess of hydride $\text{Et}_3\text{Sn}-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$ was formed as well (two triplets in the NMR spectrum at 3.42 and 3.83 ppm with a coupling of 6.1 Hz).

These experiments suggest that in the reaction of trialkyltin hydrides with chloral adduct (I) is the primary adduct. Depending on the mode of addition of the reactants and on their molar ratio (II) or (III) are formed by secondary conversions**:



Similar results were obtained in the hydrostannation of pentafluorobenzaldehyde. Addition of trialkyltin hydrides to an excess of the aldehyde yielded a mixture of the adducts (IV) and (V). The latter compound was also formed upon addition of the aldehyde to adduct (IV). Distillation of (V) yielded mainly (R = Me) or exclusively (R = Et and Bu) (IV):



[(IVa)-(Va), R = Me; (IVb)-(Vb), R = Et; (IVc)-(Vc), R = Bu]

* Similar additions of alkoxytin compounds across the carbon-oxygen double bond of aldehydes and ketones have been reported by Davies and Symes¹².

** As will be outlined in the next paper⁶ part of the 1:2 adduct may be formed by another route.

The NMR spectra of the adducts need some comment. Until recently $^{117,119}\text{Sn-O-C-H}$ coupling has not been reported in the literature. The absence of this coupling in compounds of the type $\text{R}_n\text{Sn}(\text{OCH}_3)_{4-n}$ and $\text{R}_n\text{Sn}(\text{OC}_2\text{H}_5)_{4-n}$ was ascribed¹⁵ to the ionic character of the Sn-OC bond. However, as appeared from Table 2 $^{117,119}\text{Sn-O-C-H}$ coupling has been observed in most of the alkoxytin compounds described in the present study. Since in the latter compounds an electron-withdrawing group is attached to the alkoxy-carbon atom, it is evident that the absence of coupling in non-substituted methoxy- and ethoxytin compounds cannot be ascribed to the ionic character of the Sn-OC bond.

An NMR study of the behaviour of compounds of the type $\text{Et}_3\text{SnOCH}_2\text{CH}_n\text{Cl}_{3-n}$ ($n=0, 1, 2$ and 3) in solution revealed that $^{117,119}\text{Sn-O-C-H}$ coupling is not observed when considerable amounts of impurities are present; so far no coupling has been observed for $n=2$ and 3 , while for $n=1$ coupling has only been observed after careful purification of the component; for $n=0$ coupling has been observed even when small amounts of impurities were present. Upon heating solutions of compound (Ib) ($n=0$) and of compound (IIIb) ($n=1$) from room temperature to 110° the $^{117,119}\text{Sn-O-C-H}$ satellites gradually disappeared. Upon cooling the satellites reappeared. A temperature study of a mixture of equimolar amounts of compound (Ib) and (IIIb) revealed that the coupling in (IIIb) has disappeared at lower temperatures than that of (Ib). From these experiments it must be concluded that the absence of $^{117,119}\text{Sn-O-C-H}$ coupling in alkoxytin compounds is due to exchange of alkoxy groups between different tin atoms. Moreover, the rate of exchange, which is susceptible to catalysis, increases with decreasing chlorine substitution in compounds of the type $\text{Et}_3\text{SnOCH}_2\text{CH}_n\text{Cl}_{3-n}$. This may be due to steric as well as to electronic effects. The observation¹² that coupling is present in tributyltin 2,2,2-trimethylethoxide and tributyltin benzyloxyde strongly suggests that steric factors play an important part.

EXPERIMENTAL

All reactions and subsequent manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. Liquids were handled by the syringe technique. Starting materials were purchased or prepared according to published procedures.

NMR spectra, which were run by Miss L. Veldstra, were recorded using a Varian Associates HR-100A NMR spectrometer. In most of the NMR experiments carbon tetrachloride and tetrachloroethene were used as solvents.

As examples of the procedures followed some experiments have been described below.

Reaction of triethyltin hydride with chloral

Triethyltin hydride (8.21 g, 39.7 mmoles) was added dropwise at 0° to an excess of chloral (11.8 g, 80.0 mmoles). The mixture was left for 20 min at 0° , after which a sample was taken for NMR spectroscopy. The spectrum revealed that adducts (Ib) and (IIb) were present in yields of 5% and 75%, respectively. Distillation afforded 8.5 g (60% yield) of adduct (Ib) with b.p. 79° (0.3 mm), n_D^{20} 1.5050. (Found: Sn, 33.9. $\text{C}_8\text{H}_{17}\text{Cl}_3\text{OSn}$ calcd.: Sn, 33.50%.)

In a second experiment adducts (Ib) and (IIb) were formed in yields of 10% and 80%, respectively. Distillation afforded almost pure adduct (Ib) in 76% yield.

Reaction of tributyltin hydride with chloral

The reaction of tributyltin hydride (5.8 g, 20 mmoles) proceeded in the same way as described above, yielding mainly adduct (IIc) in about 90% yield. The distillation fraction (6.0 g, n_D^{20} 1.4923) passing from 95–135° (0.5 mm) contained 60–65% of adduct (Ic). The NMR spectrum as well as elementary analyses pointed to the presence of 35–40% of tributyltin chloride (compare Table 3).

In a second experiment (2.9 g of tributyltin hydride and 2.95 g of chloral) the resulting reaction mixture was distilled slowly through an efficient Vigreux column. In this way 2.7 g of a mixture boiling at 147° (12 mm) (n_D^{20} 1.4906) was obtained, which contained approximately 25% of adduct (Ic). A redistilled fraction (1.1 g) with b.p. 90–92° (0.2 mm) (n_D^{20} 1.4906), the NMR spectrum of which showed almost exclusively signals characteristic of the tributyltin group, contained mainly tributyltin chloride [reported¹⁶: b.p. 98° (0.45 mm), n_D^{25} 1.4903]. (Found: Cl, 10.2; Sn, 35.9. $C_{12}H_{27}ClSn$ calcd: Cl, 10.89; Sn, 36.46%.)

Reaction of triethyltin hydride with chloral (reversed addition)

To 4.10 g (19.8 mmoles) of triethyltin hydride was added dropwise at 0° 2.95 g (20.0 mmoles) of chloral. The mixture was left at room temperature for 1 h and then distilled. The main fraction [2.4 g, b.p. 96–102° (0.8 mm), n_D^{20} 1.5039] contained, as appeared from NMR spectroscopy and tin analysis, adduct (Ib), adduct (IIIb) and triethyltin chloride in a ratio of 68:17:15. (Found: Sn, 35.9. This mixture calcd.: Sn, 35.8%.)

Reaction of (2,2,2-trichloroethoxy)triethyltin with chloral

In an NMR tube were introduced 0.494 g (1.39 mmoles) of (2,2,2-trichloroethoxy)triethyltin (Ib), 0.210 g (1.42 mmoles) of chloral and 200 μ l of carbon tetrachloride. The NMR spectrum of this mixture revealed that compounds (Ib) and (IIb) were present in a ratio of (Ib):(IIb) = 20:80, while approximately 7% (theoretical value: 20%) of the aldehyde had not reacted. Rise of temperature from 26° to 60° resulted in a small shift in the product ratio in favour of compound (Ib) and the aldehyde. Upon cooling to 26° the mixture retakes its original composition, viz. (Ib):(IIb) = 20:80, presence of ~7% of the aldehyde.

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