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 Sn-O-C-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 C=C, C=C, C=N and C=S bonds were presented. In this and the following paper⁶ the hydrostannation of electrophilic C=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)].

$$-\overset{I}{\underset{I}{\text{Sn-H}}} + O = \overset{I}{\underset{I}{\text{C}}} \rightarrow -\overset{I}{\underset{I}{\text{Sn-O-C-H}}} - \overset{I}{\underset{I}{\text{C}}} - H$$
(1)

$$-\operatorname{Sn-H}_{H} + -\operatorname{Sn-O-C-H}_{H} \longrightarrow -\operatorname{Sn-Sn-H}_{H} + \operatorname{HO-C-H}_{H}$$
(2)

Hydrostannations of C=O bonds which are brought about under free radicalgenerating 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.).

stannations under the influence of zinc chloride were regarded to follow a polar course¹⁰. The catalytic activity of zinc chloride most probably arises from an enhancement of the electrophilic character of the carbon atom of the carbon-oxygen unsaturated bond. Therefore, it is not unreasonable to assume in this case an ionic mechanism similar to the one discussed previously³⁻⁵, viz. a nucleophilic attack of the hydride hydrogen on carbon. In order to substantiate the occurrence of such a nucleophilic attack in the case of C=O bonds the reaction of organotin hydrides with strongly electrophilic carbonyl compounds was studied. The present paper deals with the structure of the products formed in the reaction of trialkyltin hydrides with chloral (trichloroacetaldehyde), pentafluorobenzaldehyde and 2,2,2-trifluoroacetophenone. In the next paper⁶ the mechanism of the addition reaction will be discussed.

RESULTS AND DISCUSSION

The reaction of trialkyltin hydrides with chloral in the absence of solvents proceeds exothermally at room temperature. In general a mixture of products was obtained as appeared from NMR analysis.

Slow addition of the tin hydride to an excess of chloral afforded a mixture of the adducts (I) and (II):

$$R_{3}SnH + O = CH - CCl_{3} \xrightarrow{O^{0}} H$$

$$\longrightarrow R_{3}Sn - O - CH_{2} - CCl_{3} + R_{3}Sn - O - CH_{-}O - CH_{$$

A mixture of the 1:1 adducts (Ib) and (IIIb) was obtained when an equimolecular amount of chloral was slowly added to triethyltin hydride:

$$Et_{3}SnH + 0 = CH - CCl_{3} \xrightarrow{0^{\circ}} Et_{3}Sn - 0 - CH_{2} - CCl_{3} + Et_{3}Sn - 0 - CH_{2} - CHCl_{2}$$
(Ib) (Ib)

In the NMR spectra of the reaction mixtures (see Tables 1 and 2) the signal arising from H_a of (I) was found at approximately 4.1 ppm*, with a ^{117,119}Sn-H coupling of ~29 Hz. According to expectation the signal due to H_a of (II) [δ (H_a) ~5.3 ppm**, J(^{117,119}Sn-H) ~28 Hz] occurred downfield from that of H_a of (I). Since H_b and H_c of (II) are not equivalent these protons appeared as two doublets [at ~4.27 and ~4.45 ppm, J(H_b-H_c) ~12 Hz]. The chemical shifts and coupling constants of H_a and H_b of (IIIb) [δ (H_a) 3.94 ppm, δ (H_b) 5.50 ppm, J(H_a-H_b) 5.8 Hz and J(^{117,119}Sn-H_a) 27.5 Hz] are completely in accord with the proposed structure.

The correctness of these assignments was proven by the following experiments.

^{*} Downfield from tetramethylsilane internal.

^{**} In the NMR spectrum of β -parachloral, a cyclic trimer of chloral which contains similar groups $-O-CH-(CCl_3)-O-$, the chemical shift of this proton has been found to be 5.46 ppm¹¹.

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HYDROSTANNATION OF ELECTROPHILIC	CARBONYL COMPOUNDS	. YIELD OF	1:1 AND	1:2 ADDUCTS
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Tin hydride		Carbonyl compd.	Yield of adducts (%)"			
R	(mmoles)	(mmoles)	1:1	1:2		
R ₃ SnF	I+Cl ₃ CCHO					
Me	10.0	20.0	30	70		
Et	3 9 .7	80.0	10	80		
Bu	20.0	40.0	5	85		
R ₃ SnI	I+C ₆ F ₅ CHO					
Me	20.0	30.0	70	25		
Et	9.9	15.0	75	20		
Bu	9.9	15.0	65	25		
R ₃ SnI	$H + C_6 H_5 C(CF)$	3)0				
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

HYDROGTANIATION OF FIGOTRODHILLC CARBONY	COMPOUNDS.	NMR	DATA OF	COMPOUNDS	(I)-(VI)
HYDROSTANNATION OF ELECTROPHILIC CARBONIL	COmroond3.	1414174	unin oi	00.11 001.00	(*) (**)

Compounds			Chemica	al shift s" (ppm ^b) and	t coupling o	constants (H	z)
_			$\delta(H_{s})$	$\delta(H_{h})$	δ(H _e)	$J(H_a - H_b)$	J(H _b -H _c)	J(Sn-H_)
_	(la)	R=Me	s 4.08					31.0
R ₃ Sn—O—CH ₂ —CCL ₃	(Ib)	R = Et	s 4.15					28.0 ⁴
	(Ic)	R = Bu	s 4.11					27.5
- H	(IIa)	R≕Me	s 5.27	d 4.25	d 4.44		12.0	30.5
R.Sn-0-CH-0-C-CL	(iii)	R = Et	s 5.34	d 4.28	d 4.45		11.5	27.0
CCt ³ H	(IIc)	R=Bu	s 5.32	d 4.28	d 4.45		11.5	26.5
a b	/***	D D	1204			F 0		27.5
R ₃ Sn-O-CH ₂ -CHCl ₂	(1116)	R = Et	d 3.94	t 5.50		5.8		21.5
G	(IVa)	R = Me	ť 4.73					
$R_3Sn - O - CH_2 - C_8F_5$	(ІVЬ)	R=Et	ť 4.77					
	(IVc)	R = Bu	1' 4.74					
ь Н	(Va)	R = Me	ť 6.18	d 4.53	d t' 4.69		11.0	
R35n-0-CH-0-C-C ₆ F5	(Vb)	R=Et	ť 6.20	d t' 4.51	d ť ^{4.69}		10.8	
ĊŢĘĻĮ	(Vc)	R=Bu	ť 6.11	d t' 4.43	d t' 4.69		10.0	
a b	(VIa)	R≠Me	a 4.84			6.8 ^e		26.0
R ₃ Sn-O-CH-CF ₃	(VIb)	R⇒Et	q 4.85			6.8°		24.5
L C-H-	(VIc)	R≈Bu	q 4.78			6.4°		25.0
-0°, 2			-					

^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 C_6F_5 group (J < 2 Hz); q, quartet. ^b Downfield from tetramethylsilane internal. ^c Mean value of coupling constants with ¹¹⁷Sn and ¹¹⁹Sn isotopes. ^d $J(^{117}Sn-H_3)$: 27.4 Hz; $J(^{119}Sn-H_3)$: 28.5 Hz. ^c H-F coupling.

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

$$Et_{3}Sn - O - CH_{2} - CCl_{3} + O = CH - CCl_{3} = Et_{3}Sn - O - CH_{2} - CCl_{3}$$

$$(Ib) \qquad (Ib)$$

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:

$$\begin{array}{cccccc} & & & & & \\ Bu_3Sn-O-CH_{-}O-CH_{2}-CCl_{3} & \xrightarrow{heat} & Bu_3Sn-O-CH_{2}-CCl_{3} & + & Bu_3SnCl & + & \dots \\ & & & & (Ic) & & & (Ic) \end{array}$$

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

Et₃Sn-O-CH₂-CCl₃ + Et₃SnH
$$\stackrel{20^{\circ}}{\longrightarrow}$$
 Et₃Sn-O-CH₂-CHCl₂ + Et₃SnCl
(Ib) (IIb)

With an excess of hydride $Et_3Sn-O-CH_2-CH_2Cl$ 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**:

$$R_{3}SnH + 0 = CH - CCL_{3} \xrightarrow{O^{\circ}} R_{3}Sn - 0 - CH_{2} - CCL_{3}$$

$$(I)$$

$$+ 0CHCCL_{3} \longrightarrow -0CHCCL_{3} \longrightarrow + R_{3}SnH$$

$$CCL_{3}$$

$$R_{3}Sn - 0 - CH_{2} - CCL_{3}$$

$$R_{3}Sn - 0 - CH_{2} - CCL_{3}$$

$$R_{3}Sn - 0 - CH_{2} - CHCL_{2} + R_{3}SnCL$$

$$(II)$$

$$(III)$$

$$(III)$$

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):

$$R_{3}SnH + 0 = CH - C_{6}F_{5} \xrightarrow{20^{\circ}} R_{3}Sn - 0 - CH_{2} - C_{6}F_{5}$$

$$(IVZ)$$

$$+ 0CHC_{6}F_{5} \parallel - 0CHC_{6}F_{5}$$

$$R_{3}Sn - 0 - CH - 0 - CH_{2} - C_{6}F_{5}$$

$$I_{C_{6}}F_{5}$$

$$(Y)$$

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

^{*} 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.

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Additions to 2,2,2-trifluoroacetophenone yielded exclusively the 1:1 adduct (VI). Under the conditions employed this adduct did not react with the ketone:

n

$$\begin{array}{cccc} & & & & & & \\ R_{3}SnH & + & CF_{3}-C-C_{6}H_{5} & \longrightarrow & R_{3}Sn-O-CH & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ C_{6}H_{5} & & & \\ \hline & & & & & \\ (VIa), R=Me; (VIb), R=Et; & & \\ (VIc), R=Bu] & & & (\nabla I) \end{array}$$

In 1965 Cullen and Styan¹³ described the exothermal addition of trimethyltin hydride to hexafluoroacetone yielding a 1:1 and a 1:2 adduct. Although, according to these authors, no conclusive evidence for the structure of the 1:2 adduct could be presented at that time, a structure similar to (II) and (V) was tentatively proposed. Similar results were obtained by Janzen and Willis¹⁴ in the addition of trimethylsilane to hexafluoroacetone. Also in this case a 1:1 and a 1:2 adduct were formed. In contrast to the findigs described above these authors reported that the 1:2 adduct is not formed from the 1:1 adduct. In these reactions the formation of a 1:1 complex, Me₃HSi OC(CF₃)₂ was postulated, which was supposed to rearrange to the 1:1 adduct or to react with a second molecule of the ketone yielding the 1:2 adduct. In the additions involving organotin hydrides described in the present paper such a 1:1

Product compositions, NMR and other physical and analytical data of the reaction mixtures and compounds obtained in this study have been presented in Tables 1, 2 and 3, respectively.

mposition prod. (%)	B.p. [°C(mm)]	n _D ²⁰	Tin analysis (%)		
1:1 1:2			Found	Calcd.	
ССНО					
12	71-72(2.0)	1.5080	36.0	36.19°	
0	79(0.3)	1.5050	33.9	33.50	
.5° 0	95–135(0.5)	1.4923	29.8	29.89 ^b	
F₅ <i>CHO</i>					
15	5960(0.3)	1.4723			
0	86-87(0.1)	1.4748	29.3	29.45	
0	109(0.1)	1.4736	24.3	24.37	
$H_5C(CF_3)O$					
0	62-64(0.3)	. 1.4852	35.0	35.02	
0	80-82(0.1)	1.4878	31.6	31.15	
0	113-115(0.1)	1.4821	25.9	25.51	
	$ \begin{array}{c} mposition \\ mposition \\ rod. (%) \\ \hline 1:2 \\ CCHO \\ 12 \\ 0 \\ .5^{b} \\ 0 \\ F_{5}CHO \\ 15 \\ 0 \\ 0 \\ H_{5}C(CF_{3})O \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \end{array} $	mposition B.p. prod. (%) [°C(mm)] 1:2 [°C(mm)] <t< td=""><td>$\begin{array}{c cccccc} mposition & B.p. & n_D^{20} \\ \hline mposition & [°C(mm)] \\ \hline 1:2 & & & \\ \hline \\$</td><td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td></t<>	$\begin{array}{c cccccc} mposition & B.p. & n_D^{20} \\ \hline mposition & [°C(mm)] \\ \hline 1:2 & & & \\ \hline \\$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

TABLE 3

HYDROSTANNATION OF ELECTROPHILIC CARBONYL COMPOUNDS. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF DISTILLATION PRODUCTS

^a Found: C, 18.9; H, 3.6. Calcd. for this mixture containing 12% (15% by weight) of 1:2 adduct: C, 19.09; H, 3.42%.^b The NMR spectrum as well as elemental analyses pointed to the presence of 35-40% tributyltin chloride. Found: C, 39.6; H, 7.4; Cl (ionic), 3.6. Calcd. for this mixture containing 36.5% (30% by weight) of tributyltin chloride: C, 40.13; H, 7.18; Cl (ionic), 3.27%.

The NMR spectra of the adducts need some comment. Until recently 117,119 Sn-O-C-H coupling has not been reported in the literature. The absence of this coupling in compounds of the type R_n Sn(OCH₃)_{4-n} and R_n Sn(OC₂H₅)_{4-n} was ascribed¹⁵ to the ionic character of the Sn-OC bond. However, as appeared from Table 2 117,119 Sn-O-C-H coupling has been observed in most of the alkoxy-tin 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 Et₃SnOCH₂CH₋- Cl_{3-n} (n=0, 1, 2 and 3) in solution revealed that ^{117,119}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}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}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 Et₃SnOCH₂CH_nCl_{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 benzyloxide 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. C₈H₁₇Cl₃OSn 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. C₁₂H₂₇ClSn 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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