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ORGANOMETALLIC COMPOUNDS

XXXV*. PHYSICO-CHEMICAL PROPERTIES OF STERICALLY HINDERED ORGANOTIN COMPOUNDS.

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SUMMARY

The presence of tert-butyl groups on tin very strongly decreases the electrophilicity of trialkyltin halides towards iodide ions and nucleophilic solvents.

The mass spectra of sterically hindered organotin compounds show the expected fragment ions.

INTRODUCTION

Very little is known about sterically hindered organotin compounds. The low melting point of trineophyltin fluoride[2,4] and the Mössbauer parameters of the trineophyltin halides indicate a tetracoordinate structure for these compounds, whereas trimethyltin halides are associated and pentacoordinated in the solid state and even in solution[3]. Tetraneopentyltin reacts with bromine in $CHCl_3$ only very slowly at the reflux temperature of the solvent[4], whereas tetramethyltin reacts instantaneously with bromine even below 0°.

Tetra-tert-butyltin has not yet been synthesized in spite of some unsuccessful attempts[5]; a new approach to this problem has been undertaken in our laboratory[6].

We have tried to gather more precise information about the influence of steric effects on the availability of tin in trialkyltin halides towards nucleophiles, by determining the equilibrium constant for the formation of a pentacoordinate complex from R_3SnBr and either iodide ions or solvent molecules.

RESULTS AND DISCUSSION

Determination of the equilibrium constant for $R_3SnX + I^- \rightleftarrows R_3SnXI^-$

The addition of nucleophiles to triorganotin halides does not seem to be very sensitive to steric effects[3,8], since trimethyl- and triethyltin bromides complex with

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[*] For part 34, see ref. 1. This paper has been presented at the 5th International Conference on Organometallic Chemistry (Moscow, August 1971): Abstracts No. 206 (Vol. 1, p. 541) and 365 (Vol. 2, p. 375).

iodide ions in acetone to rather similar extents; the values of the equilibrium constants K_1 are $K_1(\mathrm{Me}) = 90$, $K_1(\mathrm{Et}) = 168$.

$$R_3SnBr + I^- \overset{K_1(R)}{\rightleftharpoons} (R_3SnBrI)^-$$

TABLE 1

DETERMINATION OF THE EQUILIBRIUM CONSTANT $K_1 = [R_3SnXI^-]/[R_3SnX]\cdot[I^-]$ AT 20° IN ACETONE

All the concentrations have been multiplied by 100.

Compound	$[I^-]_0$	$[R_3SnX]_0$	$[I^-]_{eq}$	$[R_3SnX]_{eq}$	$[R_3SnXI^-]_{eq}$	K_1	*Av.* K_1
i-Pr_3SnCl	1.097	1.146	0.484	0.533	0.613	236	243
	1.097	1.442	0.428	0.773	0.669	202	
	1.097	1.768	0.314	0.985	0.783	252	
	1.140	0.956	0.555	0.371	0.585	284	
i-Pr_3SnBr[a]	1.089	1.78	0.663	1.35	0.427	48	40
	1.089	2.47	0.567	1.95	0.522	46	
	1.089	3.44	0.479	2.83	0.610	45	
	1.106	1.71	0.781	1.38	0.325	31	
	1.106	6.24	0.363	5.64	0.643	32	
i-Bu_3SnBr	1.102	5.43	0.231	4.56	0.871	92	90
	1.102	3.69	0.322	2.91	0.780	84	
	1.102	2.50	0.409	1.81	0.693	93	
	1.081	1.65	0.533	1.10	0.548	94	
	1.081	1.12	0.671	0.71	0.400	86	
t-$BuMe_2SnBr$	1.08	1.20	1.03	1.15	0.05	0.06	0.06
t-$Bu_2MeSnBr$	1.08	1.30	1.08	1.30		$\leqslant 0.01$	$\leqslant 0.01$

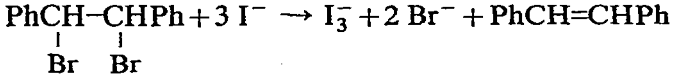
[a] The previously reported results[10] are incorrect owing to the presence of equal amounts of i-Pr_2SnBr_2 and i-Pr_4Sn in the expected i-Pr_3SnBr[13].

TABLE 2

ELECTROPHILICITY OF STERICALLY HINDERED TRIORGANOTIN HALIDES

R_3SnBr	K_1	*Ref.*
Me_3SnBr	90	3, 8, 10
Et_3SnBr	168	10
Bu_3SnBr	123	10
i-Bu_3SnBr	90	17
i-Pr_3SnBr	40	17
Me_2-t-BuSnBr	< 0.06	
Me-t-Bu_2SnBr	≈0	
i-Pr_3SnBr	40	
i-Pr_3SnCl	243	

In order to obtain more information on the influence of steric effects on this type of equilibrium, we took some tert-butyltin halides, and examined the inhibition of the debromination of 1,2-dibromo-1,2-diphenylethane[11] by the addition of sterically crowded trialkyltin halides; from the results[10] the values of K_1 for these compounds were calculated.



$$\underset{\text{Br}}{\text{PhCH}}-\underset{\text{Br}}{\text{CHPh}} + 3\,\text{I}^- \rightarrow \text{I}_3^- + 2\,\text{Br}^- + \text{PhCH{=}CHPh}$$

Table 2 shows that the presence of tert-butyl groups on tin strongly decreases the electrophilicity of trialkyltin halides.

These results are in agreement with those obtained by Mössbauer spectroscopy[16] for the mixed methyl-tert-butyltin bromides: the ratio ρ=quadrupole splitting *QS*/isomeric shift *IS*, which has been described as being related to the

TABLE 3

COUPLING CONSTANTS OF SOME TRIORGANOTIN HALIDES IN DIFFERENT SOLVENTS

Solvent	*Me_3SnBr ΔJ(SnMe) Hz*	*Me_2-t-BuSnBr*		*Me-t-Bu_2SnBr*	
		ΔJ(SnMe) Hz	*ΔJ(Sn-t-Bu) Hz*	*ΔJ(SnMe) Hz*	*ΔJ(Sn-t-Bu) Hz*
CCl_4	0.0[a]	0.0[b]	0.0[c]	0.0[d]	0.0[e]
Dioxane	4.6	1.6	−0.2	0.5	0.4
MeCN	6.2	3.4	−0.2	0.9	1.2
t-BuOH	6.6	1.0	−0.2	0.0	0.5
i-PrOH	9.0	1.6	−0.3	—	0.1
EtOH	9.4	5.6	0.4	0.0	0.0
MeOH	9.5	5.2	0.0	1.0	0.6
DMSO	11.9	12.2	−0.2	5.2	1.8
HMPT	14.4	15.5	−1.6	11.6	0.6

[a] $J(^{117}$SnMe) 55.0 Hz unchanged after a dilution by a factor of 100. [b] 47.6 Hz. [c] $J(^{117}$Sn-t-Bu) 87.4 Hz. [d] 39.6 Hz. [e] 79.4 Hz.

TABLE 4

SUM OF THE % s-CHARACTER OF THE CARBON–TIN BONDS OF TRIORGANOTIN HALIDES IN DIFFERENT SOLVENTS

Solvent	*Me_3SnBr*	*Me_2-t-BuSnBr*	*Me-t-Bu_2SnBr*
CCl_4	79.3 ± 4.5	89.5 ± 4.5	98.4 ± 4.5
Dioxane	86.0	90.9	104.4
MeCN	88.3	92.6	100.6
t-BuOH	88.8	90.3	98.9
i-PrOH	92.3	90.9	
EtOH	92.9	95.1	98.4
MeOH	93.0	94.5	99.5
DMSO	96.5	101.1	102.7
HMPT	100.8	103.6	104.5

coordination number of tin (ref. 7; see however ref. 8 and 9), is equal to 1.65 for Me-t-Bu_2SnBr and to 2.25 for Me_2-t-BuSnBr[18] whereas Me_3SnBr gives a value of 2.41, thus suggesting that steric repulsions can also decrease and even prevent the formation of self-complexed aggregates in the solid state at low temperatures.

NMR investigation of the complexation of Me_n-t-$Bu_{3-n}SnBr$ by nucleophilic solvents

Since the complexation of R_3SnX by nucleophiles changes the tin hybridization, it should affect the $J(Sn{-}C{-}CH_3)$ coupling constant; hence NMR spectroscopy could be expected to be a good probe for detecting the complexing of triorganotin halides with nucleophiles[8,12].

We have recorded the PMR spectra of these mixed methyl-t-butyltin bromides in a series of solvents in order to establish a nucleophilicity scale for the solvents, and at the same time provide an electrophilicity scale for R_3SnX, measured by ΔJ, with CCl_4 taken as reference*, according to

$$\Delta J = J(^{117}SnCCH_3)\,(\text{Solvent}) - J(^{117}SnCCH_3)(CCl_4)$$

The experimental data are given in Table 3.

The known relations between J(Sn–Me), J(Sn–t-Bu) and the % *s*-character of respectively the Sn–Me and the Sn–t-Bu bonds[13,14] allow the evaluation of the sum of the % *s*-characters present in the three hybrid orbitals directed towards the organic substituents. The results are gathered in Table 4 and show (*i*) that the Sn–C bonds become richer in *s*-character as the nucleophile becomes stronger, and (*ii*) the variations of the % *s* in the tin–carbon bonds of sterically hindered triorganotin

TABLE 5

70 eV MASS SPECTRA OF TRIISOPROPYLTIN HALIDES i-Pr_3SnX, TETRAISOPROPYLTIN AND tert-BUTYLTRIISOPROPYLTIN

Fragment	*X=F*	*X=Cl*	*X=Br*	*X=I*	*X=i-Pr*[a]	*X=t-Bu*[b]
i-$Pr_3SnX^{\cdot +}$	4.1	2.8	2.3	2.4	1.0	0.4
i-Pr_2SnX^+	11.9	21.6	24.1	27.0	23.5(a)	4.5
i-$PrSnXH^+$	2.7	3.5	6.3	7.0	30.1(b)	4.6
SnX^+	8.9	13.2	16.2	20.1	11.2(c)	1.6
i-Pr_3Sn^+	1.7	3.3	1.9	1.8	23.5(a)	8.2
i-Pr_2SnH^+	1.0	1.1	1.3	1.8	30.1(b)	11.4
i-Pr-cyclo-$PrSnH^+$	5.0	7.0	7.2	4.1	0	—
i-$PrSnH_2^+$	0.2	1.2	1.3	1.4	21.4	15.7
i-$PrSn^+$	50.3	34.1	27.2	21.6	11.2(c)	12.6
$MeSn^+$	2.7	2.0	1.8	1.8	3.3	6.1
SnH_3^+	0.2	0.1	0.1	0.2	0.9	1.0
SnH^+	7.3	6.7	6.8	6.9	11.5	21.4
Sn^+	4.6	3.3	3.6	3.7	5.3	10.7

There are also minor tin-containing fragment ions: [a] corresponding to i-Pr_2SnEt^+ (0.6), i-$PrSnEt_2^+$ (0.4), i-$PrSnEtH^+$ (0.6), $EtSn^+$ (0.6); [b] corresponding to t-$BuSnH_2^+$ (1.0), $EtSn^+$ (0.3), $MeSnH_2^+$ (0.3).

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* The coupling constant of Me_3SnBr in CCl_4 is not very different from $J(Sn{-}CH_3)$ of Me_3SnBr in cyclohexane (54.6 Hz for a 2 *M* solution, 54.2 Hz for a 0.5 *M* solution), and possibly cyclohexane might be a more suitable reference.

TABLE 6

70 eV MASS SPECTRA OF SOME TERT-BUTYLTIN COMPOUNDS

Fragment ion	*Relative intensity (total = 100)*			
	R = Me *Y = Br*	*R = t-Bu* *Y = Me*	*R = Y = Et*	*R = Y = Pr*
t-BuSnR$_2$Y				
t-BuR$_2$YSn$^{\cdot+}$	5	0.4	0.6	0.2[c]
t-BuRYSn$^+$	0.7	44		
t-BuR$_2$Sn$^+$	6	1	4	2
R$_2$YSn$^+$	23		20[a]	21
t-BuR(CH$_3$)Sn$^+$		3		0.2
t-BuRSnH$^+$		1	20[a]	
t-BuYSnH$^+$		12	20[a]	
R$_2$(CH$_3$)Sn$^+$			0.4	4
R$_2$SnH$^+$	5		29	30
R$_2$Sn$^+$	6			
RYSn$^+$	4			
R(CH$_3$)SnH$^+$		3	0.6	2
RSnH$_2^+$			13	25
RSn$^+$	17	10	13	
t-BuSn$^+$		4		
YSn$^+$	20			
CH$_3$Sn$^+$			1	2
SnH$^+$	4	10	11	9
Sn$^+$	7	9	5	3
			R = Y = Me	*R = Y = Et*
t-Bu$_2$SnRY				
t-Bu$_2$RYSn$^{\cdot+}$	6[b]		3	0.4
t-BuRYSn$^+$	25		30	21
t-Bu$_2$RSn$^+$	3		3	2
t-BuRSnH$^+$	1			10
t-BuRSn$^+$	6		2	
RYSnH$^+$				21
RYSn$^+$	3		35	
Y(CH$_3$)SnH$^+$				1
YSnH$_2^+$				12
YSn$^+$	19		15	12
t-Bu(CH$_3$)SnH$^+$				1
t-BuSn$^+$	1		0.5	
CH$_3$Sn$^+$	19			3
SnH$^+$	6		4	8
Sn$^+$	7		4	4

[a] R$_2$YSn$^+$ and t-BuRSnH$^+$ are indistinguishable if R = Y = Et. [b] There is also a fragment ion at *m/e* 165 (intensity 2). [c] There is also a fragment ion at *m/e* 193 (intensity 0.4).

bromides are much smaller than for trimethyltin bromide. This means that ΔJ only poorly reflects the complexation by nucleophiles for sterically hindered R$_3$SnX molecules.

Mass spectra of tri-iso-propyl- and mixed methyl-tert-butyltin halides

The mass spectra[8,15] of triisopropyltin halides have been recorded, and the

TABLE 7

MASS SPECTRA OF tert-BUTYLMETHYLTIN BROMIDES AT DIFFERENT POTENTIALS

Fragment ion	*Voltage reading on instrument*			
	20[a]	15	12	7.5
t-Bu$_2$MeSnBr				
t-Bu$_2$MeSnBr$^{\cdot+}$	13	16	18	≈30
t-BuMeSnBr$^+$	50	57	63	≈70
t-Bu$_2$MeSn$^+$	8	7	6	
MeSnBr$^+$	3	3	3	
SnBr$^+$	6	4	3	
t-BuMeSnH$^+$	3	2	1	
t-BuMeSn$^+$	7	6	4	
MeSn$^+$	8	3	1	
t-BuMe$_2$SnBr				
t-BuMe$_2$SnBr$^{\cdot+}$	15	22	31	≈60
t-BuMeSnBr$^+$	2	3	3	
Me$_2$SnBr$^+$	40	40	39	≈40
t-BuMe$_2$Sn$^+$	13	15	14	
SnBr$^+$	4	3		
Me$_2$SnH$^+$	8	6	5	
Me$_2$Sn$^+$	8	6	5	
MeSn$^+$	7	2		

[a] It was confirmed that this reading did correspond approximately with a correct value of 20 eV.

results are summarized in Table 5.

All the expected[12] fragments are present, but noteworthy is the formation of an ion with *m/e* 205 which is only present for triisopropyltin halides and not for tetraalkyltins containing the isopropyl group such as i-Pr$_4$Sn or t-Bu-i-Pr$_3$Sn. The formation of this ion may be accounted for as follows:

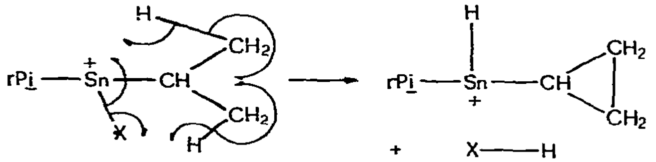

Table 6 shows the mono-isotopic mass spectra of some tert-butyltin compounds. All the expected[15,19] fragment ions are present.

Mass spectra at lower potentials (see Table 7) confirm the sequences for the ease of cleavage of a carbon–tin bond of the molecular ion described before: t-Bu > Me[20] and t-Bu > Br[15].

EXPERIMENTAL

The triorganotin halides have been synthesized following a procedure which has been described elsewhere[13]; their NMR spectra have been recorded on a Varian

A60 (5% solutions, with tetramethylsilane as internal standard). The mass spectra were recorded on a Hitachi–Perkin–Elmer RMU-6D mass spectrometer[15].

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