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Preparation of Benzylstannanes by Zinc-Mediated Coupling of Benzyl Bromides with Organotin Derivatives. Physicochemical Characterization and Crystal Structures

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Benzyltrialkyl- (**1**−**13**) and benzyltriphenylstannanes (**16**−**22**) have been easily prepared in a one-pot synthesis *via* coupling reaction of benzyl bromide derivatives ($C_6H_5CH_2Br$ and $XYC_6H_3CH_2Br$, X = H, Y = *o*-, *m*-, *p*-CH_3, *o*-, *m*-, *p*-F, *o*-, *m*-Cl, and *p*-Br; X = *o*-F, Y = *p*-Br) with R_3SnCl compounds (R = Et, Pr, Bu, and Ph) in THF/H_2O (NH_4Cl) medium mediated by zinc powder. Such coupling also occurs with $(Bu_3Sn)_2O$. Dibenzyldibutylstannane (**15**) is prepared by reaction of benzyl bromide with Bu_2SnCl_2 or $(Bu_2SnCl)_2O$, and (2-naphthylmethyl)tributylstannane (**14**) by reaction of 2-(bromomethyl)naphthalene with Bu_3SnCl. ^{13}C- and ^{119}Sn-NMR data are reported for all compounds, and Mössbauer data for benzyltributylstannanes **10** and **11** and benzyltriphenylstannanes **16**−**18** and **20**−**22**. The crystal structures of Ph_3SnBn, with Bn = *o*- (**17**) and *m*-$ClC_6H_4CH_2$ (**18**) and *o*- (**20**) and *m*-FC_6H_4-CH_2 (**21**) have been determined.

Introduction

The considerable development over recent decades in the use of organotin compounds as reagents or intermediates in organic synthesis[1] has prompted the preparation of many new organotin compounds and the development of new rapid and convenient synthetic procedures, some of which are based on the use of water or water−cosolvent media. In particular, water has been successfully used as reaction medium in preparing tribenzyltin chlorides in a one-pot synthesis by reacting at 100 °C benzyl halide derivatives with tin powder[2,3] and trialkyltin chlorides from dialkyltin dichlorides and tin powder at 100 °C.[4] Recently,[5] we have successfully used water−cosolvent media for the direct synthesis under mild conditions of allyl- and allenylstannanes as well as hexaaryldistannanes through a new preparative method based on a Wurtz-type coupling reaction mediated by zinc powder, as shown in eqs 1 and 2, respectively.

$$n\mathrm{RBr} + R'_{4-n}\mathrm{SnX}_n \xrightarrow[\text{r.t., stirring}]{\text{cosolvent/H}_2\text{O (salt)/Zn}} \mathrm{R}'_{4-n}\mathrm{SnR}_n \tag{1}$$

R = allyl or allyl−like group, propargyl;

$\mathrm{R}' = \mathrm{Bu, Ph;\ X = Cl, I, OH;}\ n = 1, 2$

$$2\mathrm{R}'_3\mathrm{SnX} \xrightarrow[\text{r.t., stirring}]{\text{THF/H}_2\text{O (NH}_4\text{Cl)/Zn}} \mathrm{R}'_3\mathrm{Sn{-}SnR}'_3 \tag{2}$$

$\mathrm{R}' = \mathrm{Ph},\ m-$ and $p-\mathrm{Tol;\ X = Cl, I, OH}$

As an extension of this last method, we have prepared several mixed benzylorganostannanes (**1**−**22**) by stirring benzyl bromides with tri- and diorganotin derivatives in a heterogeneous medium such as THF/H_2O (NH_4Cl)/Zn at ambient temperature. Most of the synthesized compounds are new, and ^{13}C- and ^{119}Sn-NMR as well as some Mössbauer data have been collected. The crystal structures of the compounds Ph_3SnBn where Bn = *o*-Cl- (**17**), *m*-Cl- (**18**), *o*-F- (**20**), and *m*-$FC_6H_4CH_2$− (**21**) have been determined.

Results and Discussion

Preparation of Benzylstannanes. Reactions between R_3SnCl (R = Et, Pr, Bu and Ph), $(Bu_3Sn)_2O$, Bu_2SnCl_2 and $(Bu_2SnCl)_2O$ and various benzyl bromide derivatives have been carried out in a three-phase THF/

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Table 1. Preparation of Mixed Benzylstannanes from Tri- and Diorganotin Derivatives and Benzyl Bromides In THF/H_2O/Zn Medium[a]

	reagent						
entry no.	organotin	amt, g	RBr (R)	amt, g	product (no.)	product amt, g (yield, %)	anal.: calcd (found) for C, H, halogen (%)
1	Et_3SnCl	7.4	$C_6H_5CH_2$	10.5	$C_6H_5CH_2SnEt_3$ (**1**)	10.3 (85)	53.48 (53.82), 5.87 (5.70)
2		7.4	*p*-$CH_3C_6H_4CH_2$	12.0	*p*-$CH_3C_6H_4CH_2SnEt_3$ (**2**)	5.6 (58)	54.95 (55.24), 6.26 (6.05)
3	Pr_3SnCl	8.7	$C_6H_5CH_2$	10.5	$C_6H_5CH_2SnPr_3$ (**3**)	7.3 (70)	56.67 (56.61), 8.32 (8.40)
4		8.7	*m*-$CH_3C_6H_4CH_2$	12.0	*m*-$CH_3C_6H_4CH_2SnPr_3$ (**4**)	6.3 (59)	57.82 (57.33), 8.56 (8.64)
5		8.7	*p*-$CH_3C_6H_4CH_2$	12.0	*p*-$CH_3C_6H_4CH_2SnPr_3$ (**5**)	8.0 (74)	57.82 (58.38), 8.56 (8.64)
6	Bu_3SnCl	10.0	$C_6H_5CH_2$	10.5	$C_6H_5CH_2SnBu_3$ (**6**)	10.3 (86)	59.87 (59.73), 8.99 (9.08)
7	$(Bu_3Sn)_2O$	9.2	$C_6H_5CH_2$	10.5	**6**	9.3 (80)	
8	Bu_3SnCl	10.0	*o*-$CH_3C_6H_4CH_2$	12.0	*o*-$CH_3C_6H_4CH_2SnBu_3$ (**7**)	8.5 (70)	60.78 (60.65), 9.18 (9.29)
9		10.0	*m*-$CH_3C_6H_4CH_2$	12.0	*m*-$CH_3C_6H_4CH_2SnBu_3$ (**8**)	8.8 (72)	60.78 (60.89), 9.18 (9.25)
10		10.0	*p*-$CH_3C_6H_4CH_2$	12.0	*p*-$CH_3C_6H_4CH_2SnBu_3$ (**9**)	7.0 (58)	60.78 (61.03), 9.18 (9.09)
11		10.0	*o*-$ClC_6H_4CH_2$	12.6	*o*-$ClC_6H_4CH_2SnBu_3$ (**10**)	11.1 (87)	54.91 (54.77), 8.00 (7.95), 8.53 (8.46)
12		10.0	*m*-$ClC_6H_4CH_2$	12.6	*m*-$ClC_6H_4CH_2SnBu_3$ (**11**)	10.1 (80)	54.91 (55.00), 8.00 (8.08), 8.53 (8.48)
13		10.0	*p*-$BrC_6H_4CH_2$	15.4	*p*-$BrC_6H_4CH_2SnBu_3$ (**12**)	12.4 (88)	49.59 (49.83), 7.23 (7.30), 10.74 (10.68)
14		10.0	*o*-F-, *p*-$BrC_6H_3CH_2$	16.5	*o*-F-, *p*-$BrC_6H_3CH_2SnBu_3$ (**13**)	14.1 (91)	47.73 (46.85), 6.74 (7.03), 3.97 (3.87),[b] 16.73 (16.90)[c]
15		10.0	$C_{10}H_7CH_2$[d]	13.6	$C_{10}H_7CH_2SnBu_3$[e] (**14**)	8.8 (67)	64.36 (64.06), 7.98 (8.00)
16	Bu_2SnCl_2	9.5	$C_6H_5CH_2$	21.4	$(C_6H_5CH_2)_2SnBu_2$ (**15**)	10.4 (81)	63.95 (63.99), 7.32 (7.38)
17	$(Bu_2SnCl)_2O$	8.5	$C_6H_5CH_2$	15.7	**15**	8.1 (63)	
18	Ph_3SnCl	11.8	$C_6H_5CH_2$	10.5	$C_6H_5CH_2SnPh_3$ (**16**)	9.4 (69)	68.07 (67.96), 5.03 (4.97)
19		11.8	*o*-$ClC_6H_4CH_2$	12.6	*o*-$ClC_6H_4CH_2SnPh_3$ (**17**)	13.0 (89)	63.14 (63.02), 4.45 (4.39), 7.45 (7.30)
20		11.8	*m*-$ClC_6H_4CH_2$	12.6	*m*-$ClC_6H_4CH_2SnPh_3$ (**18**)	8.8 (60)	63.14 (63.10), 4.45 (4.49), 7.45 (7.50)
21		11.8	*p*-$BrC_6H_4CH_2$	15.4	*p*-$BrC_6H_4CH_2SnPh_3$ (**19**)	13.9 (75)	57.73 (57.94), 4.07 (4.01), 15.38 (15.03)
22		11.8	*o*-$FC_6H_4CH_2$	11.6	*o*-$FC_6H_4CH_2SnPh_3$ (**20**)	10.3 (73)	65.40 (65.67), 4.61 (4.70), 4.14 (4.30)
23		11.8	*m*-$FC_6H_4CH_2$	11.6	*m*-$FC_6H_4CH_2SnPh_3$ (**21**)	10.0 (71)	65.40 (65.35), 4.61 (4.70), 4.14 (4.19)
24		11.8	*p*-$FC_6H_4CH_2$	11.6	*p*-$FC_6H_4CH_2SnPh_3$ (**22**)	8.2 (58)	65.40 (65.48), 4.61 (4.65), 4.14 (4.09)

[a] Except for entries 7, 16 and 17, all runs have been performed with the following amounts of components: 30.7 mmol of organotin, 61.4 mmol of organic bromide, and 61.4 mmol (4.01 g) of Zn powder (325 mesh, from Aldrich) in the molar ratio 1:2:2, respectively, in 25 mL of THF and 50 mL of H_2O saturated with NH_4Cl; for entry 7, 15.35 mmol of organotin, 61.4 mmol of organic bromide, and 61.4 mmol (4.01 g) of Zn in the molar ratio 1:4:4, respectively; for entry 16, 31.25 mmol of organotin, 125.1 mmol of organic bromide, and 125.1 mmol (8.18 g) of Zn in the molar ratio 1:4:4, respectively; for entry 17, 15.35 mmol of organotin, 92.0 mmol of organic bromide, and 92.0 mmol (6.01 g) of Zn in the molar ratio 1:2:2 respectively. [b] F (%). [c] Br (%). [d] 2-Naphthylmethyl. [e] (2-Naphthylmethyl)trimethylstannane.

H_2O(NH_4Cl saturated)/Zn medium. This direct procedure is very simple and rapid if compared with those dealing with known, customary methods.[6-10] In fact, the products are obtained under mild reaction conditions in air and at ambient temperature. Table 1 shows the experimental data and results for benzylorganostannanes **1**−**22**, most of which have been prepared here for the first time in yields in the range 58−90%.

Many reactions are characterized by high exothermicity and are completed in the short time (5−10 min) required for the addition of the organic bromide to the system THF/H_2O (NH_4Cl)/Zn/organotin compound. Complete disappearance of zinc powder is observed after this time. Through this method there is no need to prepare the organotin lithium or benzyllithium species as, for instance, in the case of benzyltriphenylstannane (**16**), which was prepared previously by reaction of triphenyltin lithium and benzyl chloride[8] in 22% yield (compare with 69% of entry 18), and of (2-naphthylmethyl)-tributylstannane (**14**), obtained by reaction of (2-naphthylmethyl)lithium with chlorotributylstannane[11] in 57% yield (compare with 67% of entry 15). In addition, dibenzyldibutylstannane (**15**) is easily obtained by coupling either Bu_2SnCl_2 (entry 16) or $(Bu_2SnCl)_2O$ (entry 17) with benzyl bromide in the ratio 1:4 and 1:6, respectively. In the case of Bu_2SnCl_2, benzyldibutyltin chloride is formed as an intermediate which can be recovered in 50−75 % yield together with dibenzyldibutyltin when 1:2 and 1:1 molar ratios are employed.

All coupling reactions have been performed using benzyl bromides, which gave better results than the corresponding chlorides. Use of a cosolvent has been limited to THF because workup in the case of cyclohexane and other solvents previously used for allylations[5] produced poor results. The coupling reactions of benzyl bromides and organotin derivatives behave similarly to those of allyl bromides.[5] These between benzyl bromides and R_3SnCl compounds to form benzylstannanes are accompanied by side reactions such as dimerization of R_3Sn and benzyl species and the reduction of the bromides to toluene derivatives.[12]

We believe that the mechanistic aspects of the tin benzylation are analogous to those proposed in the case of allylation.[5] Radical ions pairs $[C_6H_5CH_2Br]^{-\bullet}$ $Zn^{+\bullet}$ are formed by single-electron transfer (SET) from zinc metal to the organic bromide. Subsequently, the radical ions $[C_6H_5CH_2Br]^{-\bullet}$ adsorbed on the metal surface are trapped by R_3SnX molecules to form benzylstannanes. Side reactions, such as coupling and reduction of benzyl species, can be ascribed to the formation of free radicals $[C_6H_5CH_2]^{\bullet}$ adsorbed on the metal surface or freely diffused in solution[13] after desorption. Some chemical evidence[14] suggests the presence also of R_3Sn radical species under these experimental conditions.

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(12) In THF/H_2O (NH_4Cl), zinc powder reacts with benzyl bromide to give both dibenzyl (about 20%) and toluene (80%).

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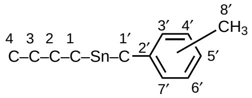
(14) As previously reported,[5] ditin compounds are thought to arise from the trapping of radical ions $[R_3SnCl]^{-\bullet}$ adsorbed on the zinc surface with R_3SnCl molecules. However, also $[R_3Sn]^{\bullet}$ radicals could form ditin compounds. We have ascertained that Bu_3SnCl reacts with several alkyl iodides RI (R = Me, Et, Pr, Bu, Pent) in THF/H_2O (NH_4Cl)/Zn powder to give mixtures of Bu_3SnR and Bu_3SnI. The former may be formed from the coupling of the two reagents, while the latter could arise from the following free-radical halogen abstraction:[15] $RI + Bu_3Sn^{\bullet} \rightarrow Bu_3SnI + R^{\bullet}$.

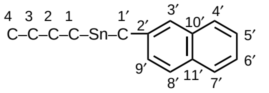
Table 2. Physicochemical Data for Benzyltrialkyl- (1−13), (2-Naphthymethyl)trimethyl- (14), and Dibutyldibenzyl-stannanes (15)[a]

compd no.	bp, °C/mm Hg	^{119}Sn-[b] and ^{13}C-NMR[c] chem shifts, ppm ($^1J(^{119}Sn-^{13}C)$, Hz)															
		Sn	C(4)	C(3)	C(2)	C(1)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(7′)	C(8′)	C(9′)	C(10′)	C(11′)
1	88−90/0.06[d]	−2.8[e]			11.0[f]	0.7 (323)	17.1 (234)	143.2	127.0	128.4	123.2	128.4	127.0				
2	94−96/0.07	−3.9			11.0	0.6 (322)	16.5 (230)	139.8	127.0	129.1	131.9	129.1	127.0	20.9			
3	107−109/0.05	−15.8		19.0	20.5	12.4 (317)	18.4(216)	143.1	127.0	128.3	123.1	128.3	127.0				
4	107−108/0.04	−16.5		19.0	20.5	12.4 (316)	18.3 (-)[g]	142.9	127.8	137.2	124.0	128.2	124.2	21.4			
5	112−116/0.05	−17.7		19.0	20.5	12.4 (314)	17.7 (216)	139.8	126.8	129.0	131.8	129.0	126.8	20.9			
6	130−131/0.04	−12.5	13.4	27.4	29.1	9.2 (316)	18.2 (245)	143.1	126.9	128.2	123.0	128.2	126.9				
7	132−135/0.04	−12.8	13.7	27.5	29.2	9.8 (313)	16.2 (298)	141.4	132.8	129.8	123.1	126.0	127.4	20.2			
8	136−139/0.05	−13.4	13.8	27.6	29.3	9.4 (316)	18.2 (248)	142.9	127.8	137.1	123.9	128.2	124.2	21.4			
9	131−136/0.04	−13.9	13.8	27.6	29.3	9.4 (315)	17.7 (256)	139.8	127.0	129.0	131.8	129.0	127.0	20.9			
10	133−137/0.04	−7.5	13.7	27.5	29.1	10.1 (319)	17.2 (227)	142.0	131.8	129.1	124.2	126.5	128.5				
11	135−137/0.04	−9.4	13.7	27.5	29.2	9.5 (319)	18.2 (228)	143.9	127.1	134.2	123.1	129.3	125.0				
12	175−180/0.2	−11.0	13.7	27.4	29.1	9.4 (319)	17.7 (239)	142.5	128.5	131.1	116.2	131.1	128.5				
13	156−160/0.07	−6.7	13.7	27.4	29.1	9.7 (322)	10.6 (-)[g]	130.2	159.6	118.3	116.0	127.0	130.0				
14	*h*	−11.1[i]	13.7	27.5	29.2	9.5 (315)	18.7 (202)	140.9	127.1	126.7	125.7	123.8	127.6	127.8	123.8	134.3	130.9
15	155−158/0.04	−17.0	13.7	27.3	28.8	9.8 (319)	18.5 (248)	142.5	127.0	128.3	123.2	128.3	127.0				

[a] Carbon identification: for compounds **1**−**13** and **15**:



Carbon identification for compound **14**:

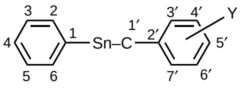


[b] δ values refer to TMT as external standard. [c] δ values refer to TMS as internal standard. [d] Bp 115 °C/4 mmHg; see ref 16. [e] $\delta(^{119}Sn)$ in CCl_4 (saturated solution): −6.0 ppm; see ref 17. [f] $\delta(^{13}C)$ 10.7, 0.5, 16.9, 143.1, 126.8, 128.2, 122.9, 128.2, 126.8; see ref 16. [g] Not determined. [h] Heavy oil. [i] $|^4J(^{119}Sn-C-C-C-^{19}F)| = 14.7$ Hz.

Table 3. Physicochemical Data for Benzyltriphenylstannanes[a]

compd no.	mp, °C	^{119}Sn-[b] and ^{13}C-NMR[c] chem shifts, ppm ($^1J(^{119}Sn-^{13}C)$, Hz)											
		Sn	C(4)	C(3,5)	C(2,6)	C(1)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(7′)
16	90−90.5[d]	−117.1[e]	128.9	128.4	137.0	138.2 (496)	20.0 (333)	140.5	127.8	128.4	123.8	128.4	127.8
17	65.5−66	−115.1	128.8	128.3	136.7	138.1 (503)	19.2 (319)	139.2	132.1	126.6	125.1	129.0	132.1
18	40−40.5	−115.0	129.4	128.4	136.8	137.5 (510)	19.7 (319)	142.8	127.6	133.9	123.8	129.4	125.7
19	64.5−65.5	−117.1	129.8	128.4	136.8	137.6 (-)[f]	19.4 (-)[f]	139.7	129.3	131.2	117.2	131.2	129.3
20	58−58.5	−113.6[g]	128.9	128.5	136.8	138.0 (-)[f]	12.8 (313)	127.3	159.8	114.9	125.4	123.8	128.7
21	96−96.5	−116.0[h]	129.1	128.5	136.9	137.7 (-)[f]	20.1 (322)	143.5	114.4	162.3	129.5	110.7	123.4
22	94.5−95	−116.9[i]	128.7	128.5	137.0	138.0 (-)[f]	18.9 (-)[f]	136.0	129.4	115.1	160.1	115.1	129.4

[a] Carbon identification:



[b] $CDCl_3$ solution, δ values refer to TMT as external standard. [c] $CDCl_3$ solution, δ values refer to TMS as internal standard. [d] Mp 90−91 °C; see ref 8. [e] $\delta(^{119}Sn)$: −118 ppm; see ref 18. [f] Not determined. [g] $|^4J(^{119}Sn-C-C-C-^{19}F)| = 20.2$ Hz. [h] $|^5J(^{119}Sn-C-C-C-C-^{19}F)| = 11.0$ Hz. [i] $|^6J(^{119}Sn-C-C-C-C-C-^{19}F)| = 25.7$ Hz.

Physicochemical Data. Physicochemical data for compounds **1**−**15** and **16**−**22** are listed in Tables 2 and 3, respectively. Among these, only compounds **1** and **16** have been characterized previously.[8,16−18]

The ^{119}Sn-NMR chemical shifts range from −2.7 to −17.7 ppm for compounds **1**−**14** and from −113.6 to −117.1 ppm for **16**−**22**. The single values are strongly dependent upon the nature and the position of the substituents on the benzyl ring as well as upon the other three organic groups bonded to tin. As an example, the $\delta(^{119}Sn)$ values for benzyltributylstannanes **6**−**13** clearly become more negative the lower the electron-withdrawing ability of the substituent (*e.g.*, compare the values of **7**, **10**, and **13**).

As already reported for benzyltrimethylstannanes,[19] the ^{13}C-NMR resonance lines of C(5′) move to upfield with respect to that of the analogue carbon in neopentylbenzene; a similar behavior is observed in benzylstannanes **1**, **3**, **6**, and **16** . This is in line with the pronounced hyperconiugative, electron-releasing ability of the CH_2SnR_3 substituents.[20] Moreover, the $\delta(^{13}C)$ values of the benzyl carbons are consistent with the theoretical substituent-induced chemical shift values. The values of both $^1J(^{119}Sn-^{13}C_{\mathrm{alkyl\ or\ phenyl}})$ and $^1J(^{119}Sn-^{13}C_{\mathrm{benzyl}})$ coupling constants are in the range expected for four-coordinate tin compounds.[19,21] If the former constants show no significant change on varying the nature and the position of the benzyl substituent, the latter exhibit a noticeable increase on the increasing of the electron-donating ability of the substituent. This behavior, albeit observed to a lesser extent, has been described previously for trimethylphenylstannanes.[19] The low $|^4J(^{119}Sn-C-C-C-^{19}F)|$ values for **14** and **20** (14.7 and 20.2 Hz, respectively) exclude any coordinative interaction between the metal and F in the *ortho*-position.[22]

Mössbauer Data. Some of the compounds (**10**, **11**, **16**−**18**, and **20**−**22**) have been examined by Mössbauer

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Table 4. Tin-119 Mössbauer Spectral Data at 80.0 K for Benzyltributylstannanes 10 and 11 and Benzyltriphenylstannanes 16–18 and 20–22

compd	δ,[a] mm s^{-1}	ΔE_Q, mm s^{-1}	Γ, mm s^{-1}	A,[b] mm s^{-1} mmol^{-1}	mp, °C
o-$ClC_6H_4CH_2SnBu_3$ (**10**)	1.60	0.57	0.99		
m-$ClC_6H_4CH_2SnBu_3$ (**11**)	1.62	0.50	1.00		
m-$ClC_6H_4CH_2SnPh_3$ (**18**)	1.52	0.29	0.85	0.323	40–40.5
o-$FC_6H_4CH_2SnPh_3$ (**20**)	1.51	0.29	0.88	0.431	58–58.5
o-$ClC_6H_4CH_2SnPh_3$ (**17**)	1.52	0.27	0.85	0.501	65.5–66
$C_6H_5CH_2SnPh_3$ (**16**)	1.51	0.30	0.87	0.498	90–90.5
p-$FC_6H_4CH_2SnPh_3$ (**22**)	1.53	0.33	0.80	0.563	94.5–95
m-$FC_6H_4CH_2SnPh_3$ (**21**)	1.53	0.28	0.87	0.639	96–96.5

[a] Relative to room temperature, SnO_2. [b] Absorption area.

spectroscopy. The spectra of all the samples present a single, slightly broad line, as expected for tetraorganotin derivatives; however, a fitting to a symmetric doublet gives better χ^2 values and gives much narrower line widths. The results obtained are reported in Table 4. The quadrupole splitting values are obviously very small and, at least in the case of the phenyl derivatives, in good agreement with those calculated by means of the point charge model (0.2 mms^{-1}).[23] The values for the butyl derivatives **10** and **11** are somewhat larger, probably as a consequence of slight deviations from the ideal tetrahedral geometry. Moreover, the Mössbauer spectra of **10** and **11** present also the highest line width, due to structural disorder of the long and bulky butyl groups. The isomer shift values are typical for this type of compound and, within the butyl and phenyl series, almost constant, within experimental error. As already reported,[24] strongly perturbing substituents on the benzyl group do not appreciably affect the *s*-electron density at the tin nucleus. The absorption area (see Table 4) shows a linear positive dependence with the melting points on going from **18** to **21**.

Crystal Structures. Single crystals of the *o*-chloro (**17**), *m*-chloro (**18**), *o*-fluoro (**20**), and *m*-fluoro (**21**) derivatives have been examined by X-ray analysis. The molecular structures of these homologous compounds are schematically shown in Figure 1 and, as an example, in Figure 2 with the atom labeling. The relevant geometrical parameters are given in Table 5.

The coordination about Sn is always consistent with a virtually undistorted tetrahedral geometry, which excludes any bond interaction between Sn and intra- or intermolecular halogen atoms. Except for **17**, all these molecules show the expected staggered orientation of the benzyl bond C(1)-C(2) with respect to the triphenyltin group (σ = C(2)–C(1)–Sn–C(20) = −53 to −68°). In all cases the plane of the benzyl ring forms an angle φ of ca. 80° with the plane through Sn–C(1)–C(2) (or −80° according to the *left*- or the *right*-handed configuration of the usual *propeller-shaped* triphenyltin group), which is in agreement with theoretical predictions when π–π interactions are operating.[25]

The *ortho* substitution of the halogen atom X seems to be controlled by this angle. In fact, between the two possible geometrically nonequivalent *ortho*-positions the one is preferred which leads to the Sn···X nonbonded distance closest to the sum (Σ) of the corresponding van der Waals radii. As an example, for **17** these distances would be 3.7 and 4.28 Å, respectively; the former (ca. 0.25 Å shorter than Σ)[26–28] is the one observed. The orientation of the bond C(1)–C(2) found in this compound, intermediate between staggered and eclipsed

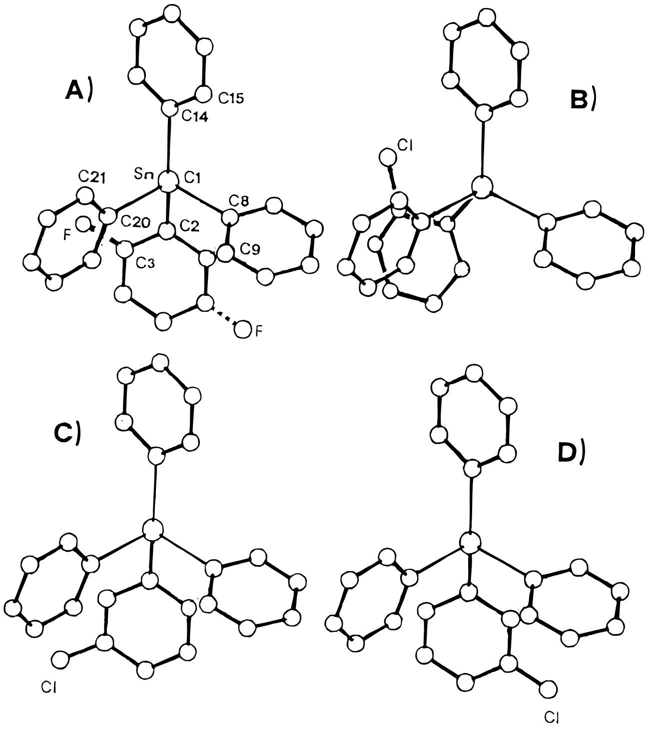

Figure 1. Schematic view of the four molecular structures down the Sn–C(1) axis (Sn overlaps C(1)). **A** refers to the *ortho*- (**20**) and *meta*- (dotted) fluoro (**21**) derivatives; **B** refers to the *ortho*-chloro derivative (**17**). For a given configuration of the Ph_3Sn group, **C** and **D** represent the two stereoisomers of the *meta*-chloro derivative (**18**) present in the crystal.

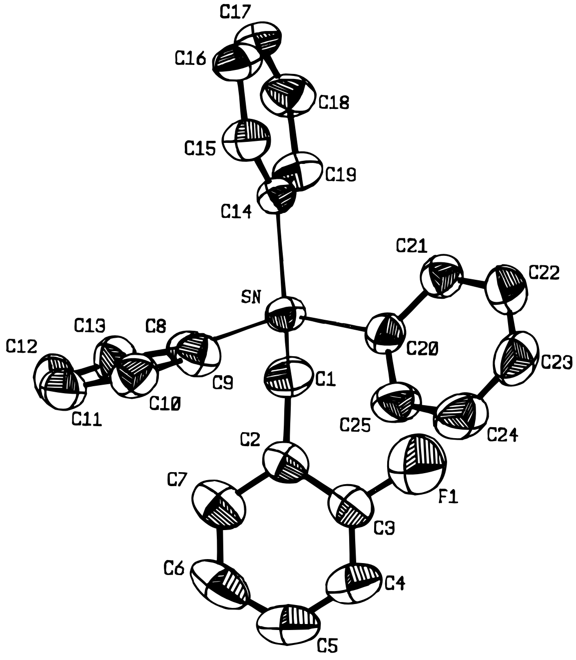

Figure 2. ORTEP view of the *ortho*-fluoro derivative (**20**). The atom labeling is the same for all the examined compounds.

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Table 5. Selected Geometrical Parameters for *o*-$ClC_6H_4CH_2SnPh_3$ (17), *m*-$ClC_6H_4CH_2SnPh_3$ (18), *o*-$FC_6H_4CH_2SnPh_3$ (20), and *m*-$FC_6H_4CH_2SnPh_3$ (21)[a]

	compd				
	17	**18 (C)**	**18 (D)**	**20**	**21**
			Bond Lengths (Å)		
Sn−C(1)	2.150(9)	2.187(4)	2.161(5)	2.166(6)	2.168(9)
Sn−C(8)	2.109(8)	2.140(3)	2.140(3)	2.145(5)	2.159(4)
Sn−C(14)	2.118(9)	2.154(3)	2.148(3)	2.139(5)	2.155(4)
Sn−C(20)	2.102(8)	2.159(3)	2.150(3)	2.143(6)	2.157(5)
X−C(3)	1.660(9)[b]			1.363(8)[c]	
X−C(4)		1.704(3)[b]			1.315(8)[c]
X−C(6)			1.707(3)[b]		
			Bond Angles (deg)		
Sn−C(1)−C(2)	113.4(9)	110.9(4)	115.7(4)	114.4(4)	113.1(5)
C(14)−Sn−C(1)	107.2(5)	109.5(3)	105.3(3)	105.0(3)	109.5(3)
C(14)−Sn−C(8)	107.9(3)	109.3(2)	108.2(2)	110.4(2)	109.2(3)
C(14)−Sn−C(20)	111.0(3)	107.3(3)	110.2(3)	111.0(2)	108.4(3)
C(8)−Sn−C(1)	108.6(4)	110.3(3)	113.9(3)	111.3(2)	113.0(3)
C(8)−Sn−C(20)	106.2(4)	108.6(2)	107.0(2)	106.2(3)	108.2(2)
C(1)−Sn−C(20)	115.7(4)	111.8(2)	112.7(2)	113.0(2)	108.3(3)
			Torsion Angles (deg)		
σ = C(2)−C(1)−Sn−C(20)	−16(1)	−60(1)	−68(1)	−66(1)	−54(1)
φ = C(3)−C(2)−C(1)−Sn	78(1)	94(1)	82(1)	80(1)	79(1)
C(9)−C(8)−Sn−C(1)	−128(1)	−137(1)	−131(1)	−141(1)	−134(1)
C(15)−C(14)−Sn−C(1)	−119(1)	−130(1)	−137(1)	−157(1)	−127(1)
C(21)−C(20)−Sn−C(1)	−145(1)	−126(1)	−115(1)	−106(1)	−129(1)

[a] For labeling, see Figures 1 and 2. [b] X = Cl. [c] X = F.

conformation (σ = 18°), arises from the necessity to maintain the value of ca. 80° for the angle φ and to relieve nonbonded interactions between Cl and phenyl groups bonded to Sn. Actually, Cl is located at distances from C(8) and C(14) of 4.37 and 3.81 Å, respectively; for a staggered conformation they would be <3 and >5 Å, respectively. This does not occur in the case of the *o*-fluoro derivative (**20**) owing to the much smaller steric encumbrance of the fluorine atom.

In the *meta*-derivatives the halogen atoms are so far away from Sn and its phenyl groups that the staggered conformation of the benzyl ring, and the angle φ of ca. 80° as well, are retained. However, in these cases, for a given configuration of the Ph_3Sn group two *meta*-stereoisomers of nearly the same internal conformational energy are theoretically predictable. As a matter of fact, for the *m*-Cl derivative (**18**) we observe the presence in the crystal of both the configurational isomers (and their enantiomers) as individual structural subunits. The crystals of the *m*-F derivative (**21**) here examined contain only one stereoisomer, but the possibility of a second crystalline modification cannot be excluded, even though not observed.

These findings are in some correlation with the Mössbauer data. As reported above, they indicate an almost regular increase of absorption area (see Table 4) on going from **18** to **21**. Interestingly, **18** exhibits the highest crystalline order (two different stereoisomers arranged in the same crystal lattice) and **21** the highest disorder as it derives from a presumably freer libration of the benzyl group. The question arises whether the Mössbauer absorption area can be assumed to be a measure of the degree of order in the crystal.

Table 6. Crystal Data and Details of Intensity Measurements for *o*-$ClC_6H_4CH_2SnPh_3$ (17), *m*-$ClC_6H_4CH_2SnPh_3$ (18), *o*-$FC_6H_4CH_2SnPh_3$ (20), and *m*-$FC_6H_4CH_2SnPh_3$ (21)

	compd			
	17	**18**	**20**	**21**
formula	$C_{25}H_{21}ClSn$	$C_{25}H_{21}ClSn$	$C_{25}H_{21}FSn$	$C_{25}H_{21}FSn$
fw	475.58	475.58	459.13	459.13
a/Å	8.046(1)	14.335(2)	9.829(2)	10.645(2)
b/Å	19.418(2)	16.750(2)	11.262(2)	11.604(2)
c/Å	6.987(1)	10.113(2)	9.476(2)	9.945(1)
α/deg	92.1(1)	95.1(1)	92.2(1)	103.3(1)
β/deg	101.7(1)	110.2(1)	95.0(1)	111.3(1)
γ/deg	98.5(1)	75.3(1)	82.3(1)	102.3(1)
V/Å^3	1054.7	2204.3	1035.2	1052.6
Z	2	4	2	2
d_{calcd}/g cm^{-3}	1.50	1.43	1.47	1.45
F(000)	476	952	460	460
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
cryst dimens/mm	ca. 0.3 × 0.3 × 0.3			
T, K	298			
radiation, λ/Å	graphite-monochromated Mo Kα, 0.7107			
μ/cm^{-1}	12.29	11.76	11.17	11.19
scan speed/deg min^{-1}	2.0 in the 2θ scan mode			
take off angle/deg	3			
2θ range/deg	3.0 ≤ 2θ ≤ 45			
unique reflns	3725	7746	3654	5079
reflns used for refinement[a]	1665	5798	3267	3279
solution method	Patterson			
R^b (on F_o)	0.050	0.032	0.044	0.048
$R_w{}^c$	0.052	0.037	0.053	0.051
GOF^d	1.263	0.820	1.247	1.160
highest map resids	0.53	0.46	0.63	0.95

[a] $F_o{}^2 > 2\sigma(F_o{}^2)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [d] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{ND} - \mathrm{NV})^2]^{1/2}$.

Experimental Section

All manipulations were carried out at room temperature, in air. Solvents, salts, and zinc powder (325 mesh), commercially available, were used as received. All employed organotin derivatives were purified before use by well-known conventional procedures.

Elemental analyses and boiling and melting points for all compounds prepared are listed in Tables 1−3, respectively. Characterization was made by means of ^{119}Sn (33.35 MHz) and ^{13}C (22.49 MHz) nuclear magnetic resonance spectroscopy

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using a Jeol FX90Q Fourier transform NMR spectrometer. Spectra of the triphenyltin derivatives, as $CDCl_3$ solutions, and of neat trialkyltin derivatives were recorded using Me_4Si and Me_4Sn as internal and external standards, respectively.

Mössbauer analysis was carried out in transmission geometry by means of a standard spectrometer using a source of Sn in $BaSnO_3$ matrix and a variable-temperature cryostat. The zero of the velocity scale was the centroid of a high-purity crystalline SnO_2 sample.The velocity scale was determined by a pure iron foil spectrum at room temperature. A standard least-squares minimization routine was used to fit the spectra profiles to Lorentzian lines.

Preparation of Tri- and Dialkylbenzylstannanes (Entries 1−17). In a round-bottomed two-necked flask (200 mL) equipped with a condenser and dropping funnel, the appropriate organotin halide was added to a THF/H_2O (NH_4Cl saturated) mixture and an excess of zinc powder (quantities are given in Table 1). With magnetic stirring, the appropriate benzyl bromide (generally in 1:1 stoichiometric ratio with respect to zinc) was added dropwise at a rate sufficient to maintain a gentle reflux due to the exothermicity of the reaction. The addition lasts about 5−10 min, during which time disappearance of the zinc powder was noted. The heterogeneous mixture was stirred until it had cooled to room temperature (about 30 min). The organic layer was separated and the THF was removed by means of rotary evaporator, leaving a heavy liquid residue. This was distilled under vacuum to afford the pure benzyltin compound. Yields, listed in Table 1, are based on the amounts of the pure distilled products.

Preparation of Triphenylbenzylstannanes (Entries 18−24). The mixing procedure was the same as that described above. The reactions are exothermic, and the zinc powder disappears during the time (5−10 min) of the addition of the benzyl bromide. After removal of THF from the separated organic layer by means of rotary evaporator, a heavy solid−liquid residue was obtained. Initial crystallization from petroleum ether (40−60 °C) or *n*-hexane allowed the separation of the organic dimer and Ph_6Sn_2 when they were formed as byproducts. Pure samples of benzylstannanes were obtained by repeated crystallization from anhydrous ethanol. Yields of the purified products are listed in Table 1.

Crystallographic Analysis. Crystal data, intensity data collection, and processing details are presented in Table 6. The data were obtained with a Philips PW-100 four-circle diffractometer with graphite monochromator. Intensity data were collected at 20 °C using the 2θ scan method. Two reference reflections, monitored periodically, showed no significant variation in intensity. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied to the intensities (Ψ scan). The positions of the Sn and Cl atoms were determined from the three-dimensional Patterson functions. All the remaining atoms, including some of the hydrogen atoms, were located from successive Fourier maps using SHELX-76.[29] Anisotropic thermal parameters were used for all the non-hydrogen atoms. Blocked-cascade least-squares refinements converged to the conventional *R* indexes given in Table 6.

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Supporting Information Available: Tables of X-ray parameters, positional parameters of all atoms, thermal parameters, and complete bond lengths and bond angles (60 pages). Ordering information is given on any current masthead page.

OM9507742

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