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SYNTHESIS OF ORGANOTRIALKYLSTANNANES. THE REACTION BETWEEN ORGANIC HALIDES AND HEXAALKYLDISTANNANES IN THE PRESENCE OF PALLADIUM COMPLEXES

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Summary

The aryl halides YC_6H_4X (X = Br or I) have been shown to react with the distannanes $(R_3Sn)_2$ (R = n-Bu or Me) in toluene in the presence of $[Pd(PPh_3)_4]$ or $[PdBr_2(PPh_3)_2]$ to give the compounds $YC_6H_4SnR_3$ for (a) R = n-Bu, Y = H, p-OMe, *o*-Me, *p*-Me, *m*-Cl, *p*-Cl, *m*-CN, *p*-$COCH_3$ and *m*-NO_2, and (b) R = Me, Y = H, *p*-OMe, *p*-Me, *p*-CN, *p*-$COCH_3$, *m*-NO_2 and *p*-NO_2. Benzyl halides $YC_6H_4CH_2X$ (X = Cl or Br) similarly give $YC_6H_4CH_2SnR_3$ for (a) R = n-Bu, Y = H, *m*-OMe, *p*-OMe, *m*-Cl, *m*-CN, and *m*-NO_2, and (b) R = Me, Y = *m*-Cl, *m*-CN, *p*-CN and *m*-NO_2. These reactions are of special value as preparative procedures in cases in which Grignard or organolithium reagents cannot be used. Allyl chloride and bromide were likewise shown to react with $(n\text{-}Bu_3Sn)_2$ to give $CH_2{=}CHCH_2SnBu_3$, but n-BuCl and n-BuBr gave only a trace of $n\text{-}Bu_4Sn$. The mixed dimetallo species $n\text{-}Bu_3SnSiMe_3$ was shown to react with aryl bromides YC_6H_4Br (X = H, *p*-OMe, *p*-Me, or *p*-Cl) to give the arylsilicon compounds $YC_6H_4SiMe_3$, with no aryltin products.

Introduction

It was shown by Atwell and Bokermann in 1973 that some organic halides, RX, react with disilanes in the presence of some transition metal complexes to give R—Si compounds, the reaction being especially effective for allyl halides [1]. Matsumoto, Nagai and their coworkers later found that aryl bromides (and some chlorides) react with hexamethyldisilane in toluene or similar solvents in the presence of $[Pd(PPh_3)_4]$ to give aryl$SiMe_3$ compounds [2,3], thus providing an important new route to such compounds, especially those in which the aryl group bears a reactive functional substituent (e.g. NO_2) and so could not be attached to silicon by methods involving Grignard or organolithium reagents. They later extended the reaction to use of (a) allyl halides [4], (b) the methyl-

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chlorodisilanes $Me_nCl_{6-n}Si_2$, [5], and (c) $[PdCl_2(PPh_3)_2]$ as catalyst [5].

The method was further extended to the reaction of (a) $Me_3SiSiMe_3$ with benzyl halides to give $YC_6H_4CH_2SiMe_3$ compounds, (b) the digermane $Et_3GeGeEt_3$ with aryl halides (which took place more slowly and gave lower yields than that involving $Me_3SiSiMe_3$, and (c) the distannanes $Me_3SnSnMe_3$ and $Bu_3SnSnBu_3$* with aryl halides, which gave the corresponding $XC_6H_4SnR_3$ species but in rather low yield [6]. Since this type of reaction would be especially useful for the preparation of certain organotin compounds, we have now carried out a more thorough study of the reactions of these distannanes with some organic halides, mainly aryl and benzyl halides. The $Bu_3SnSnBu_3$ was included in the study because it is easier to prepare than $Me_3SnSnMe_3$ from the corresponding R_3SnCl, and moreover Bu_3SnCl is more readily available than Me_3SnCl.

Results and discussion

Reactions of aryl halides

The initial experiments were carried out with $Bu_3SnSnBu_3$ and PhBr, with product analyses by GLC. The first important observation was that $[PdBr_2L_2]$, I, (L = PPh_3 throughout) is at least as a good catalyst as PdL_4, II, (see Table 2), and since I is more easily prepared and stored we subsequently used it more often than II. Thus with I as catalyst the effects of varying the temperature, time, and reactant and catalyst ratios were examined for the reactions involving $Bu_3SnSnBu_3$ and PhBr, and the results are shown in Table 1. It will be seen that even at 50°C a substantial proportion of the PhBr disappears, but to give only a little $PhSnBu_3$. There seems little to chose between 105 and 115°C as the reaction temperature, though the highest yield observed was from a reaction at 115°C. Use of a 2/1 ratio of distannane to aryl halide seemed to be the most satisfactory, and led to a significantly lower yield of diphenyl (which is the other main aromatic product) than did use of a 1/1 ratio. Use of 0.003 mmol rather than 0.0065 mmol of I for each 0.5 mmol of PhBr resulted in a lower conversion and yield, but increasing the amount of a catalyst to 0.013 mmol did not further improve the yield. Thus, in most of the subsequent experiments a ratio of 0.0065 mmol of I to 0.5 mmol of organic halide was used, and a reaction temperature of 115°C, with toluene as solvent throughout.

We then examined the effects of varying the aryl halide YX_6H_4X in the reaction with $Bu_3SnSnBu_3$, with the results shown in Table 2. The features are as follows:

(a) Iodobenzene gave a distinctly better yield than bromobenzene, and 94—96% of the PhI was converted into $PhSnBu_3$. (This contrasts with the observations on the reactions involving the disilane $Me_3SiSiMe_3$, in which PhI gave no $PhSiMe_3$, but did form diphenyl, whereas PhBr gave good yields.) With *p*-MeC_6H_4X, while the yield based on the amount of halide consumed was a little greater for X = Br than for X = I, the amount of the aryl halide consumed

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* Throughout the paper Bu represents n-butyl.

TABLE 1

REACTION OF $Bu_3SnSnBu_3$, III, WITH PhBr IN TOLUENE (5 cm^3) IN THE PRESENCE OF $[PdBr_2(PPh_3)_2]$, I

III (mmol)	PhBr (mmol)	Temp. (°C)	Time (h)	I (mmol)	Product yields[a]		PhBr consumed (%)
					PhPh (%)	$PhSnBu_3$ (%)	
1.0	1.0	105	17	0.0065	11	45	100
1.1	1.0	105	17	0.0065	9	51	100
0.75	0.5	115	15	0.0065	14	71	100
1.0	0.5	115	15	0.0065	6	75	100
1.0	0.5	105	17	0.0065	8	66	100
1.5	0.5	115	15	0.0065	4	63	92
1.0	0.5	105	17	0.013	5	58	100
1.0	0.5	105	17	0.003	0	21	56
1.0	0.5	50	15	0.003	0	6	43
1.0	0.5	105	41	0.003	1	20	61

[a] Bu_3SnBr was formed in all cases; yields based on PhBr taken.

TABLE 2

REACTIONS OF ARYL HALIDES RX (0.50 mmol) WITH $Bu_3SnSnBu_3$ (1 mmol) IN TOLUENE (5 cm^3) FOR 15 h AT 115°C IN THE PRESENCE OF $[PdBr_2(PPh_3)_2]$, I (0.0065 mmol) OR $[Pd(PPh_3)_4]$, II (0.0065 mmol)

RX	Catalyst	Product yields (%)[a]		RX consumed (%)
		$RSnBu_3$	R_2	
PhBr	I	75	6	100
PhBr	II	79	8	100
PhI	I	94	2	100
PhI	II	96	3.5	100
PhCl	I	0	0	0[b]
PhCl	II	0	0	0[b]
p-$MeOC_6H_4Br$	I	53	[c]	100
p-$MeOC_6H_4Br$	II	81	[c]	100
p-$MeOC_6H_4I$	I	46	[c]	100
p-$MeOC_6H_4I$	II	53	[c]	100
p-MeC_6H_4Br	I	68	2	74
p-MeC_6H_4Br	II	75	2	94
p-MeC_6H_4I	I	81	1.5	100
p-MeC_6H_4I	II	76	2	100
o-MeC_6H_4Br	I	13	[c]	20
o-MeC_6H_4Br	II	64	[c]	72
p-ClC_6H_4Br	I	59	[c]	95
p-ClC_6H_4Br	II	59	[e]	89
m-ClC_6H_4Br	II	73	[c]	100
p-$H_2NC_6H_4Br$	I	0[d]	[d]	
p-$O_2NC_6H_4F$	I	0	0	0[b]
p-$O_2NC_6H_4Cl$	I	0	0	0[b]
p-$O_2NC_6H_4Br$	I	0	[d]	[d]
p-$O_2NC_6H_4Br$[e]	I	0[d]	[d]	[d]
m-$O_2NC_6H_4Br$	I	35	[c]	100
p-$O_2NC_6H_4I$	I	0[d]	[d]	[d]
p-NCC_6H_4Br	I	57	[c]	94
p-$CH_3COC_6H_4Br$	I	53	[c]	100
p-$CH_3COC_6H_4Br$	II	57	[c]	100

[a] Yields are based on aryl halide taken; Bu_3SnX was formed in all reactions in which $RSnBu_3$ and/or Ar_2 were formed. [b] No reaction took place. [c] Some Ar_2 was formed but the yield was not determined. [d] A substantial amount of Bu_3SnBr was formed, but since no $RSnBu_3$ was produced yields were not determined. [e] 0.2 mmol.

was lower, so that more p-$MeC_6H_4SnBu_3$ was again obtained from the aryl iodide. However, with p-$MeOC_6H_4X$ more p-$MeOC_6H_4SnBu_3$ was obtained for X = Br than for X = I, and the aryl iodides cannot be regarded as always likely to give better results than the bromides. The two aryl chlorides examined, PhCl and p-$O_2NC_6H_4Cl$, underwent no reaction, rather surprisingly in the case of the nitro compound since it reacts with $Me_3SiSiMe_3$ [2,3].
(b) The reaction is satisfactory for a range of Y groups in YC_6H_4X. There is no apparent pattern to the effects of the substituents Y, good yields being obtained for a good number of electron-releasing and electron-withdrawing groups, but no yield for the most strongly electron-releasing group p-NMe_2 or the most strongly withdrawing group p-NO_2. A clearer pattern was revealed in the reactions of $Me_3SnSnMe_3$, as shown below. The reaction is significantly slower with *o*- than with p-MeC_6H_4Br, but a good yield of o-$MeC_6H_4SnBu_3$ can be obtained.

We next turned to the reactions involving $Me_3SnSnMe_3$. With this reagent p-$O_2NC_6H_4SnMe_3$ was formed in 37% yield from p-$O_2NC_6H_4Br$, and this halide and its *meta* isomer gave as good a yield or better when the reaction was carried out at 80°C over a much shorter time, and it is possible that better yields could be obtained from the other halides containing strongly electron withdrawing groups (CN, CH_3CO) if lower temperatures were used. But for the conditions used the yields of the $YC_6H_4SnMe_3$ products in general fell with decreasing electron release or increasing electron withdrawal by Y.

We also briefly examined the reactions of the mixed dimetallo species $Bu_3SnSiMe_3$ (see Table 4) though we appreciate that this compound may possibly disproportionate to some extent to $Bu_3SnSnBu_3$ and $Me_3SiSiMe_3$ in the presence of the palladium complexes. The arylsilicon products $YC_6H_4SiMe_3$ were formed to the exclusion of aryltin compounds $YC_6H_4SnBu_3$. Interestingly, PhI gave neither the phenyltin nor phenylsilicon product, the outcome thus

TABLE 3

REACTIONS OF ARYL HALIDES RX (0.5 mmol) WITH $Me_3SnSnMe_3$ (1 mmol) IN TOLUENE (5 cm^3) IN THE PRESENCE OF $[PdBr_2(PPh_3)_2]$, I (0.0065 mmol) OR $[Pd(PPh_3)_4]$, II (0.0065 mmol)

RX	Temp. (°C)	Time (h)	Catalyst	$RSnMe_3$, yield [a] (%)
PhI	115	15	I	96
p-MeC_6H_4I	115	15	I	86
p-$MeOC_6H_4I$	115	15	II	96
p-ClC_6H_4I	115	15	II	74
p-$Me_2NC_6H_4Br$	115	15	II	0 [b]
p-$Me_2NC_6H_4Br$	110	5	II	0 [b]
p-NCC_6H_4Br	115	15	II	64 [c]
p-NCC_6H_4Br [d]	110	6	II	64 [c]
p-$O_2NC_6H_4Br$	115	15	II	37 [c]
p-$O_2NC_6H_4Br$	80	1	II	37 [c]
m-$O_2NC_6H_4Br$	115	15	II	31 [c]
m-$O_2NC_6H_4Br$ [e]	80	1	II	41 [c]
p-$CH_3COC_6H_4Br$	115	15	II	56

[a] All the RX was consumed in each case, and Me_3SnX was always formed. [b] Me_3SnBr and RR were formed but the yields were not determined. [c] RR was formed but the yield was not determined. [d] 0.80 mmol was used. [e] 1 mmol was used.

TABLE 4

REACTIONS OF $Bu_3SnSiMe_3$ (1 mmol) WITH ARYL HALIDES RX (0.5 mmol) FOR 15 h AT 115°C IN TOLUENE (5 cm^3) IN THE PRESENCE OF $[PdBr_2(PPh_3)_2]$ I (0.0065 mmol) OR $[Pd(PPh_3)_4]$, II (0.0065 mmol)

RX	Catalyst	Product and yield (%) [a]
PhBr	I	$PhSiMe_3$ [b]
p-MeC_6H_4Br	II	p-$MeC_6H_4SiMe_3$, 60
p-ClC_6H_4Br	II	p-$ClC_6H_4SiMe_3$, 34
p-$MeOC_6H_4Br$	II	p-$MeOC_6H_4SiMe_3$, 50
PhI	I	PhPh [b]

[a] In all cases all the RX was consumed; Bu_3SnX and Me_3SiX were formed, but no $RSnBu_3$. [b] A substantial amount was formed but its yield was not determined.

resembling that from the reaction with $Me_3SiSiMe_3$ rather than that with $Bu_3SnSnBu_3$.

To confirm the value of the method as a preparative route to aryltrialkylstannanes the compounds p-$NCC_6H_4SnR_3'$ (R' = Bu or Me) and m- and

TABLE 5

REACTIONS OF BENZYL HALIDES RX (0.50 mmol) WITH $R'_3SnSnR'_3$ (1.0 mmol) IN TOLUENE (5 cm^3) AT 115°C FOR 15 h (UNLESS OTHERWISE INDICATED) IN THE PRESENCE OF $[PdBr_2(PPh_3)_2]$, I (0.0065 mmol OR $[Pd(PPh_3)_4]$, II (0.0065 mmol)

RX	R'	Catalyst	Product yields (%) [a]	
			$RSnR'_3$	RR
$C_6H_5CH_2Br$	Bu	I	76	4
$C_6H_5CH_2Br$		II	57 [b]	2
$C_6H_5CH_2Cl$		I	90 [c]	2
$C_6H_5CH_2Cl$		II	95	2
m-$MeOC_6H_4CH_2Cl$		II	87 [c]	d
p-$MeOC_6H_4CH_2Cl$		II	35 [c]	d
m-$NCC_6H_4CH_2Br$		I	56	d
m-$ClC_6H_4CH_2Br$		I	51	d
m-$ClC_6H_4CH_2Cl$		I	58	d
m-$O_2NC_6H_4CH_2Br$		I	30	d
p-$O_2NC_6H_4CH_2Br$		I	0	d
p-$O_2NC_6H_4CH_2Cl$		II	0	d
p-$NCC_6H_4CH_2Br$		I	0	d
3,5-$Me_2C_6H_3CH_2Br$		I	51	d
m-$NCC_6H_4CH_2Br$		I	56	d
m-$ClC_6H_4CH_2Br$	Me	II	65	
m-$NCC_6H_4CH_2Br$		II	95	
m-$NCC_6H_4CH_2Br$ [e]		II	84	d
m-$NCC_6H_4CH_2Br$ [f]		II	83	
p-$NCC_6H_4CH_2Br$		II	96	
p-$O_2NC_6H_4CH_2Br$ [g]		II	0	d
m-$O_2NC_6H_4CH_2Br$		II	68	d

[a] Yields based on RX taken; all the RX was consumed unless otherwise indicated. R'_3SnX was formed in each case. [b] Only 64% of the RX was consumed. [c] Only 95% of the RX was consumed. [d] RR was formed but the yield was not determined. [e] 0.80 mmol was used; reaction was for 6 h at 110°C. [f] 1.0 mmol was used. [g] No p-$O_2NC_6H_4CH_2SnMe_3$ was obtained from p-$O_2NC_6H_4CH_2Br$ in a reaction involving I as catalyst for 1 h at 65°C or 2 h at 80°C.

p-$O_2NC_6H_4SnMe_3$ were isolated from larger scale reactions carried out in toluene under reflux.

Reaction of benzyl halides

Acceptable to good yields of $YC_6H_4CH_2SnR_3$ compounds (R = Bu or Me) were obtained for a range of benzyl halides, as shown in Table 5. Other features of the results are as follows:

(a) In the two cases in which the comparison was made, $C_6H_5CH_2X$ and p-$MeOC_6H_4CH_2X$, a better yield was obtained for X = Cl than for X = Br, in sharp contrast to the results with aryl halides.

(b) As with the aryl halides there was no consistent pattern in the effects of substituents; while $PhCH_2X$ and p-$NCC_6H_4CH_2Br$, the latter containing a strongly electron withdrawing substituent, both gave high yields, no p-$O_2NC_6H_4CH_2SnR_3$ was obtained for either R = Bu or R = Me. However, the m-$O_2NC_6H_4CH_2SnR_3$ compound was obtained in a 30% yield for R = Bu and a 68% yield for R = Me.

To confirm the value of the method as a preparative route to substituted benzyltrialkylstannanes, the previously unknown m-$O_2NC_6H_4CH_2SnMe_3$ was isolated from a larger scale reaction.

Reactions with other organic halides

The reactions of $Bu_3SnSnBu_3$ with other types of organic halide in the presence of I were briefly examined, with the results shown in Table 6. Allyl bromide gave a fair yield of $CH_2{=}CHCH_2SnBu_3$, and allyl chloride a lower yield. Only very small amounts of Bu_4Sn were formed from BuBr or BuCl. Styryl bromide reacted relatively slowly, to give about a 20% yield of a product of the expected composition $PhC_2H_2SnBu_3$; this was presumably $PhCH{=}CHSnBu_3$.

The use of the reaction in synthesis

The reactions involving aryl and benzyl halides have obvious value as a preparative route to aryl- and benzyl-trialkylstannanes. Because of the simplicity of the procedure, and the ease of isolating the product directly from the reaction mixture by GLC, the reaction would even be useful when the conversion could be carried out via Grignard or organolithium reagents in cases in which only small amounts of products were needed or only small amounts of the organic halide were available. (We should emphasize, however, that as far as we are

TABLE 6

REACTIONS OF VARIOUS ORGANIC HALIDES RX (0.50 mmol) WITH $Bu_3SnSnBu_3$ (1.0 mmol) IN TOLUENE (5 cm^3) FOR 15 h AT 115°C IN THE PRESENCE OF $[PdBr_2(PPh_3)_2]$ (0.0065 mmol)

RX	Yield of $RSnBu_3$ (%)	RX consumed (%)
$CH_2{=}CHCH_2Cl$	32	100
$CH_2CH{=}CH_2Br$	68	100
BuBr	2	100
BuCl	<1	100
$PhCH{=}CHBr$	21	76

aware there is no limit to the scale on which the reactions which can be carried out; sealed tubes need not be used, and we carried out the preparative scale reactions under reflux.) It is most useful, though, in cases in which the use of Grignard or organolithium reagents is ruled out; e.g. for the preparation of compounds containing reactive functional groups such as NO_2, CH_3CO, and (in some cases) CN. Thus we obtained p-$O_2NC_6H_4SnMe_3$ satisfactorily by this new method; this compound has been obtained previously, but by a procedure [requiring p-$(Me_3Sn)_2C_6H_4$] which does not always work satisfactorily [7]. The compound m-$O_2NC_6H_4CH_2SnMe_3$ was made for the first time by the new route, though its *para*-isomer could not be obtained. (We suspect, however, that the *para*-compound could be made this way if time were spent on varying the reaction conditions.) The cyano compounds p-$NCC_6H_4SnBu_3$ and p-$NCC_6H_4SnMe_3$ were also prepared; the latter has been made by treating p-NCC_6H_4Br with Me_3SnNa [8], which we would regard as a more troublesome procedure.

The reaction could also be of value for preparation of some allyl- and substituted allyl-trialkylstannanes.

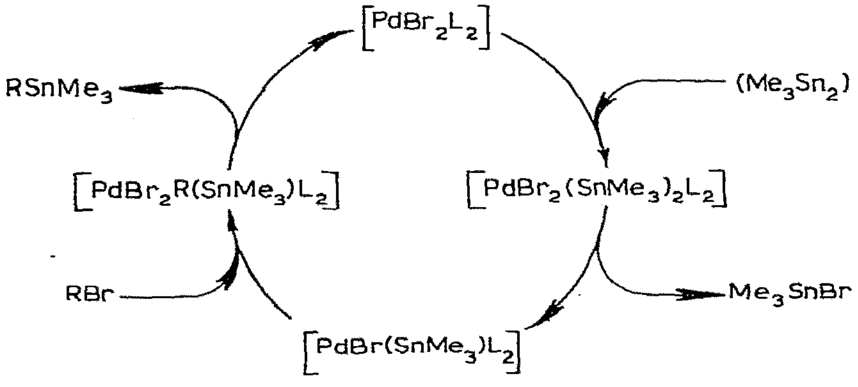
The mechanism of the reaction

Various catalytic cycles can be written for formation of $RSnR'_3$, involving oxidative addition of RX and $R'_3SnSnR'_3$ to $Pt^{(II)}$ complexes and reductive elimination of $RSnR'_3$ and R'_3SnX from the resulting $Pt^{(IV)}$ complexes. One such cycle is shown in Scheme 1 for the catalysis by $[PdBr_2L_2]$, X being taken as Br for simplicity.

When $[PdL_4]$ is used as the catalyst, it can be assumed that it first dissociate into $[PdL_2]$ (possibly complexed with the solvent) which by appropriate oxidative additions and reduction eliminations is converted into $[PdBr_2L_2]$ or one of the other entities shown in the catalytic cycle in Scheme 1. That dissociation of the $[PdL_4]$ is necessary was confirmed by studying the effect of added PPh_3 on the reaction between $Bu_3SnSnBu_3$ (1 mmol) and PhI (0.5 mmol) in the presence of 0.0065 mmol of catalyst. With $[PdBr_2L_2]$ as catalyst, an 89% yield of $PhSnBu_3$ was obtained even in the presence of 0.013 mmol of PPh_3,

SCHEME 1

POSSIBLE CATALYTIC CYCLE FOR FORMATION OF $RSnMe_3$ FROM RBr AND $Me_3SnSnMe_3$ IN THE PRESENCE OF $[PdBr_2(PPh_3)_2]$



whereas no significant reaction occurred when [PdL_4] was used as the catalyst under the same conditions.

It is evident that the reactions between organic halides RX and disilanes or distannes, $(R'_3M)_2$, will be unsatisfactory when there is too great a mismatch between the ease of oxidative addition of the RX and $(R'_3M)_2$. For example, the reaction between PhI and $Me_3SiSiMe_3$ probably fails because the latter oxidatively adds so much less readily than the former that it is effectively excluded from the metal centre. When $Me_3SnSnMe_3$, which is much more reactive in oxidative additions, is used, the reaction with PhI gives good yields.

Experimental

Spectra

Mass spectra were recorded at 70 eV and ^1H NMR spectra at 90 MHz.

Preparation of catalysts

The [$Pd(PPh_3)_4$] and [$PdBr_2(PPh_3)_2$] were prepared by standard procedures [9].

Preparations of $Bu_3SnSnBu_3$, $Me_3SnSnMe_3$ and $Bu_3SnSiMe_3$

(a) (cf. ref. 10) Magnesium powder (0.97 g, 0.04 g-atom) and Bu_3SnCl (24 g, 0.074 mol) were heated together at 100° C for 1 h then a few drops of EtI were added, followed by THF (50 cm^3). The mixture was refluxed for 2 h then set aside at room temperature for 18 h. It was then added to ice water, and the organic material was extracted with ether. The extract was washed with water, dried ($MgSO_4$), and fractionally distilled to give $Bu_3SnSnBu_3$ (14.5 g, 69%), b.p. 135—136° C/0.05 mmHg (lit. [10], 160—162° C/0.3 mmHg).

(b) The $Bu_3SnSiMe_3$ was prepared in 60% yield by a published procedure [11].

(c) The $Me_3SnSnMe_3$ was prepared in 80% yield from Me_3SnBr by the general procedure described by Tamborski et al. [11]; b.p. 48° C/3 mmHg (lit. [12], 181—182° C).

Catalysed reactions of distannanes with organic halides and analysis of products

All the analytical scale reactions were carried out in toluene in sealed thick-wall Pyrex glass ampoules, which were heated in an oven or appropriate bath. The amounts of reactants, solvent, and catalyst and the reaction conditions are specified in the Tables. In addition each tube contained a small amount of an inert hydrocarbon as an internal standard for GLC, as indicated below.

At the end of the reaction the products were analysed by use of a Pye-Unicam G.C.D. Chromatograph fitted with a dual flame ionization detector. The column packing (of ca. 1.6 m × 0.6 cm) was 5 wt-% OV101 on 100—120 mesh acid-washed Chromasorb G. In most cases calibration curves were constructed relating the peak areas of authentic samples of the expected products to that of the internal standard, which was do-, tri-, penta-, or octa-decane; peak areas were measured with an electronic integrator. In some cases, however, it was assumed that the expected product would give a similar detector response to that of a related compound of comparable retention time, experience having shown that this was a satisfactory approximation. Thus, (i) m-$\mathrm{ClC_6H_4SnBu_3}$ was assumed to give the same response as its *para* isomer; (ii) $\mathrm{XC_6H_4SnBu_3}$ with X = m-$\mathrm{O_2N}$, p-NC, or p-$\mathrm{CH_3CO}$, and $\mathrm{PhC_2H_2SnBu_3}$ were assumed to give the same response as p-$\mathrm{MeOC_6H_4SnBu_3}$; (iii) p-$\mathrm{CH_3COC_6H_4SnMe_3}$ was assumed to give the same response as p-$\mathrm{NCC_6H_4SnMe_3}$. and (iv) $\mathrm{XC_6H_4CH_2SnBu_3}$ with X = m-OMe, p-OMe, m-CN, m-Cl, and m-$\mathrm{NO_2}$ were all assumed to give the same response as $\mathrm{C_6H_5CH_2SnBu_3}$; m-$\mathrm{NCC_6H_4CH_2SnMe_3}$ was assumed to give the same response as its p-isomer.

In cases in which authentic samples were not available for determination of retention times the identity of the product was confirmed by a linked GLC-mass spectrometer analysis. The product from PhCH=CHBr and $\mathrm{Bu_3SnSnBu_3}$ was shown in this way to have the composition $\mathrm{PhC_2H_2SnBu_3}$, and it is assumed to be $\mathrm{PhCH{=}CHSnBu_3}$.

Preparative scale reactions

(a) A mixture of $\mathrm{Me_3SnSnMe_3}$ (9.8 g, 0.030 mol), p-$\mathrm{NCC_6H_4Br}$ (4.5 g, 0.025 mol), $[\mathrm{Pd(PPh_3)_4}]$ (0.225 g, 1.95×10^{-4} mol) and toluene (50 cm^3) was heated under reflux in a nitrogen atmosphere for 5 h. The low boiling products, including $\mathrm{Me_3SnBr}$, were taken off under vacuum and n-pentane was added. The n-pentane solution was filtered, the solvent was removed, and the residue was fractionally distilled to give p-$\mathrm{NCC_6H_4SnMe_3}$, (3.8 g, 57%), b.p. 80°C/0.03 mmHg (lit. [8], b.p. 97—99°C/0.5 mmHg); ν(CN) 2224 cm^{-1}; τ(ppm, in $\mathrm{CDCl_3}$), 2.40 (s, 4H, arylH), 9.66 (s with Sn satellites, 9H, $\mathrm{SnMe_3}$) [$^2J(^{119}\mathrm{SnCH})$ 57.6; $^2J(^{117}\mathrm{SnCH})$ 54 Hz]; the mass spectrum showed no parent ion but gave the expected (base) peak at 252 $[M\text{—Me}]^+$ (Found: C, 45.0; H, 4.9; N, 5.2. Calcd. for $\mathrm{C_{10}H_{13}NSn}$: C, 45.2; H, 4.9; N, 5.3%).

(b) A mixture of $\mathrm{Me_3SnSnMe_3}$ (6.6 g, 0.020 mol), m-$\mathrm{O_2NC_6H_4CH_2Br}$ (3.2 g, 0.015 mol), $[\mathrm{Pd(PPh_3)_4}]$ (0.15 g, 1.3×10^{-4} mol), and toluene (50 cm^3) was heated under reflux in a nitrogen atmosphere for 5 h. It was then cooled and filtered, and the filtrate was evaporated to leave an oil. This was taken up in ether, and the solution was washed several times with water then dried $[\mathrm{Mg(SO_4)_4}]$, and the ether was removed to leave an oil (2.8 g, 68%). This was not subjected to any purification procedure (Found: C, 40.7; H, 5.0; N, 4.6. Calcd. for $\mathrm{C_{10}H_{15}NO_2Sn}$: C, 40.0; H, 5.0; 4.7%), but was shown by its spectroscopic characteristics to be the expected m-$\mathrm{O_2NC_6H_4CH_2SnMe_3}$: $\nu(\mathrm{NO_2})$ 1520 and 1350 cm^{-1}; τ(ppm., $\mathrm{CDCl_3}$) 2.20 (m) and 2.60 (m) (together 4 H, both arylH); 7.55 (s with Sn satellites, 2 H, $\mathrm{CH_2}$) [$^2J(^{117,119}\mathrm{SnCH})$, 61 Hz], 9.90 (s with Sn satellites, 9 H, $\mathrm{SnMe_3}$); [$^2J(^{119}\mathrm{SnCH_3})$ 54 Hz, $^2J(^{119}\mathrm{SnCH_3})$ 54 Hz, $^2J(^{119}\mathrm{SnCH_3})$ 52 Hz]; the mass spectral peaks included m/e 301 $[M]^+$ and 286 $[M\text{-Me}]^+$, with base peak at 165 $[\mathrm{Me_3Sn}]^+$.

(c) A procedure similar to that described in (b) gave m-$\mathrm{O_2NC_6H_4SnMe_3}$ (0.96 g, 23%). A sample was purified by preparative GLC and shown to have the expected spectroscopic characteristics: $\nu(\mathrm{NO})_2$, 1520 and 1350 cm^{-1}, τ(ppm, $\mathrm{CDCl_3}$), 1.72—2.5 (m, 4 H, arylH), 9.60 (s with Sn satellites, 9 H, $\mathrm{SnMe_3}$) [$^2J(^{119}\mathrm{SnCH_3})$ 57.5, $^2J(^{117}\mathrm{SnCH_3})$, 52 Hz]; the mass spectrum had the base peak at 272 $[M\text{-Me}]^+$, but there was no parent ion.

(d) A similar procedure to that described under (b), but with final recrystallization from $\mathrm{MeOH/H_2O}$, gave p-$\mathrm{O_2NC_6H_4SnMe_3}$ (1 g, 25%), m.p. 46—47°C (lit.

[7], 52—53°C) (Found: C, 37.5; H, 5.0; N, 4.8. Calcd. for $C_9H_{13}NO_2Sn$: C, 37.8; H, 4.6; N, 4.9%); the 1 R and ^1H NMR spectra were as previously reported [7], and the mass spectrum showed the base peak at 272 $[M—Me]^+$, with no parent ion.

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