Journal of Organometallic Chemistry, 99 (1975) 157—170

GROUP IB ORGANOMETALLIC CHEMISTRY

XV*. ARYLCOPPER COMPOUNDS Ar_nCu_n AS INTERMEDIATES IN ORGANOMETALLIC SYNTHESIS. ONE-STEP SYNTHESIS OF TRIORGANOTIN HALIDES OF THE TYPE Ar_3SnX AND $Ar_{3-n}R_nSnX$

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(Received May 12th, 1975)

Summary

A new method for the one-step preparation of triorganotin halides is described. Triphenyltin halides are synthesized via the reaction of pure phenylcopper with SnX_4 or with Ph_2SnX_2. Me_2NCH_2, Me_2N and OMe-substituted phenylcopper react with Me_2(or Ph_2)$SnBr_2$ to give novel (substituted-phenyl)-diorganotin bromides in high yields. The selective arylation of tin halides by organocopper compounds is based upon the low reactivity of RCu towards the Sn—X bond in triorganotin halides. The selectivity of the arylation by the corresponding phenyllithium derivatives is connected with intra- or inter-molecular Sn—N (or O) coordination and/or of steric factors exerted by substituents *ortho* to the Sn—C(phenyl) bond.

Introduction

Recently we described the interaction of polynuclear organocopper compounds Ar_nCu_n with metal salts MX to give new cluster compounds of the type $[Ar_nCu_nMX]$ [1-3]. In principle these reactions also can result in transmetallation [4]. Such reactions are of particular synthetic interest if the

$$Ar_nCu_n + n\ MX \rightarrow n\ ArM + n\ CuX$$

corresponding Grignard or organolithium reagents give rise to the formation of other end-products. One example, which we report here, is the interaction of arylcopper compounds with tin tetrahalides and with diorganotin dihalides. In

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* For Part XIII see ref. 1. Part XIV (Intramolecular ring-closure reactions of novel arylcopper compounds RCu^I_2) is in preparation.

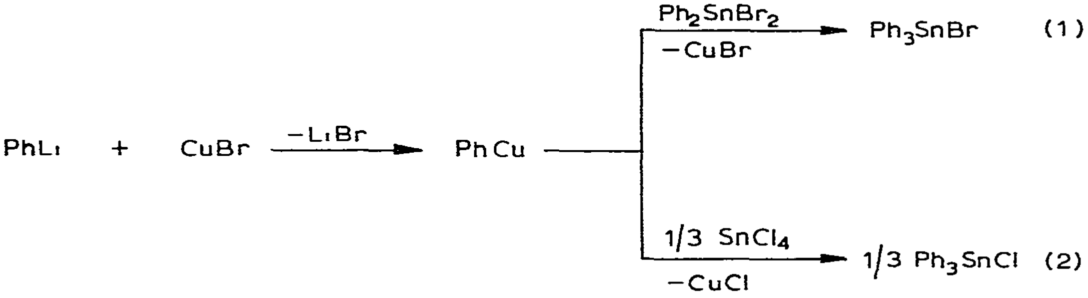
contrast to the reactions involving the corresponding Grignard and lithium reagents [5] these reactions give triorganotin halides in one step.

Some of the triorganotin halides prepared contain an aryl group bearing a built-in ligand in the *ortho* position. The tin atoms in such compounds can be five- or six-coordinate as a result of intramolecular Sn—ligand coordination (vide infra; Ib, Structure A). This aspect will be discussed in a future paper.

Results

Synthesis of triphenyltin halides

The reaction of pure phenylcopper with diphenyltin dibromide in diethyl ether afforded triphenyltin bromide, which was isolated in 86% yield (eqn. 1). Tetraphenyltin could not be detected in the reaction mixture. The reaction of phenylcopper with $SnCl_4$ in diethyl ether gave triphenyltin chloride in almost quantitative yield (eqn. 2). In these reactions the phenylcopper was prepared from the reaction of phenyllithium with cuprous bromide and subsequent removal of lithium halides.



Similarly tetraphenyltin is absent from the products formed by the reaction of $SnBr_4$ with phenylcopper obtained from the reaction of phenylmagnesium bromide with cuprous bromide. However, this organocopper reagent is less well-defined because of the known difficulties of removing magnesium halides from phenylcopper [6]. This makes balancing of the reagents ("PhCu" to $SnCl_4$ ratio) difficult, see Table 1.

Several experiments were carried out to determine the influence of the solvent and the PhLi/CuBr molar ratio on the product composition. Representative examples are summarized in Table 1.

In benzene the reaction proceeds with a lower selectivity, and tetraphenyltin is formed in addition to triphenyltin halide. Furthermore, the reaction of diphenylcopperlithium (obtained from the 1/1 reaction of pure phenylcopper with phenyllithium) with $SnCl_4$ or $SnBr_4$ (Ph/Sn ratio 3/1) gave a greater amount of tetraphenyltin. The overall yield of phenyltin compounds is lower if $SnBr_4$ is used because of the formation of large amounts of insoluble products.

Synthesis of mixed arylalkyltin halides

The reaction of pure phenylcopper with dimethyltin dibromide gave phenyldimethyltin bromide, which was isolated in 70% yield together with a 10% yield of diphenyldimethyltin (eqn. 3). In contrast, the 1/1 reaction of phenyl-

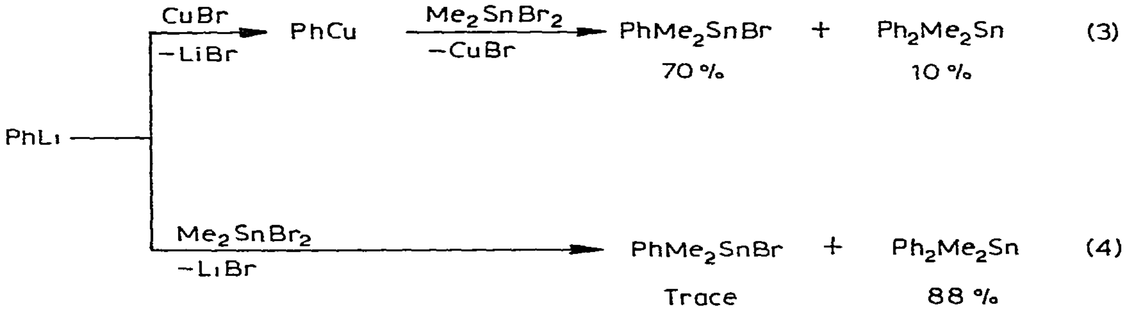
TABLE 1

PHENYLATION OF TIN TETRAHALIDES WITH PHENYLCOPPER

Reagents (mmol)[a]			Solvent[b]	Reaction time[c] (h)	Products[d], yields (%)		Total yield[e] (%)	
RM	CuBr	$SnCl_4$			Ph_3MeSn	Ph_4Sn	Sn	Ph
PhLi								
9.0	10.0	3.0	Et_2O[f]	2	92.4	0	92.4	92.4
9.0	10.0	3.0	C_6H_6[f]	2	48.4	23.5	71.9	80
10.0	5.0	3.0	Et_2O	2 3/4	28.2	50.3	78.5	85.8
10.0	5.0	3.0[g]	Et_2O	2 3/4	23.6	23.5	47.1	49.4
PhMgBr								
9.0	10.0	3.0	C_6H_6[f,h]	3	66.7[i]	0	92.2	84.8

[a] A slight excess of CuBr was used to improve the yield of PhCu. [b] Solvent used in the reaction of PhCu with SnX_4. [c] Reaction time used for the reaction of PhCu with SnX_4. [d] Products obtained after methylation of the reaction mixture, i.e. the yield of Ph_3MeSn corresponds with that of Ph_3SnX formed in the phenylation reaction. [e] Total yield (%) of Sn (calcd. on SnX_4) and Ph (calcd. on PhLi) respectively. [f] Phenylcopper purified by extraction with ether before use in the phenylation reaction. [g] $SnBr_4$. [h] Tetraphenyltin was formed when Et_2O was used for the reaction: PhCu/$SnCl_4$ 3/1, Ph_3MeSn (59%) and Ph_4Sn (37%); Ph_2CuLi/$SnCl_4$ 3/2, Ph_3MeSn (13%) and Ph_4Sn (75%). [i] Along with Ph_3MeSn, a 26.2% yield of Ph_2Me_2Sn was isolated, indicating that a Ph/Sn ratio < 3 was used.

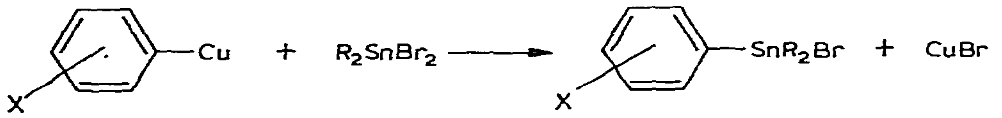
lithium with dimethyltin dibromide afforded diphenyldimethyltin as the major product (88% yield), and only a trace of phenyldimethyltin bromide (eqn. 4).



The reactions of 2-Me_2NCH_2- [7], 2-Me_2N- and di- and trimethoxy [2] substituted phenylcopper compounds with dimethyltin dibromide gave exclusively the mixed (substituted-phenyl)dimethyltin bromides (eqn. 5) (see Table 2).

In these reactions the dimethyltin dibromide solution was added to the organocopper suspension or solution. Only in the case of 2-methoxyphenylcopper did the reaction proceed in a less selective manner, as indicated by the isolation of the tetraorganotin compound $(2\text{-}MeOC_6H_4)_2SnMe_2$ (VIII) in 65% yield. In contrast, the 3/1 complex formed from the organocopper and cuprous bromide [8] afforded, in addition to a 12% yield of VIII, the triorganotin halide $(2\text{-}MeOC_6H_4)SnMe_2Br$ (IVb) in 80% yield.

The identities of the new triorganotin halides, which are all white solids, were established by elemental analysis (see Table 3), and by NMR (Table 4), IR and mass spectroscopy. Some of the compounds (IIb and IIIb in particular) appear to decompose upon exposure to the atmosphere.



(5)

(Ia-VIa) (Ib-VIIb)

(Ib, $R = Me, X = 2\text{-}Me_2NCH_2$
IIb, $R = Me, X = 2\text{-}Me_2N$
IIIb, $R = Me, X = 4\text{-}Me_2N$
IVb, $R = Me, X = 2\text{-}MeO$
Vb, $R = Me, X = 2,6\text{-}(MeO)_2$
VIb, $R = Me, X = 2,4,6\text{-}(MeO)_3$
VIIb, $R = Ph, X = 2\text{-}Me_2NCH_2$)

TABLE 2

PRODUCTS ISOLATED FROM THE REACTIONS OF SUBSTITUTED-PHENYLCOPPER AND -LITHIUM COMPOUNDS WITH DIORGANOTIN DIHALIDES

$X_nC_6H_{4-n}M/R_{4-n}SnX_n$ (mol ratio)	Order of addition[a]	Products (yield, %)[b]
X = 2-Me₂NCH₂		
$R'Cu/Ph_2SnBr_2$ (1/1)	A	$R'Ph_2SnBr$ (53)[c]
$R'Cu/Me_2SnBr_2$ (1/1)	A	$R'Me_2SnBr$ (81)[d]
$R'Cu/Me_2SnBr_2$ (2/1)	A	$R'Me_2SnBr$[e] + [$R'Cu\cdot CuBr$]
$R'Li/Me_2SnBr_2$ (1/1)	A	$R'_2Me_2Sn + Me_2SnBr_2 \rightarrow R'_2MeSnBr + Me_3SnBr$[f]
$R'Li/Me_2SnBr_2$ (1/1)	B	$R'Me_2SnBr$ (50)[g]
$R'Cu/Me_3SnCl$ (1/1)	A	$R'Me_3Sn$[h]
X = 2-Me₂N		
$R'Cu/Me_2SnBr_2$ (1/1)	A	$R'Me_2SnBr$ (96)
$R'Li/Me_2SnBr_2$ (1/1)	B	Mixture of products: $R'Me_2SnBr$ is not present
X = 4-Me₂N		
$R'Cu/Me_2SnBr_2$ (1/1)	A	$R'Me_2SnBr$ (80)
$R'Li/Me_2SnBr_2$ (1/1)	B	$R'Me_2SnBr$ (72)
X = 2,6-(MeO)₂		
$R'Cu/Me_2SnBr_2$ (1/1)	A	$R'Me_2SnBr$ (90)
$R'Li/Me_2SnBr_2$ (1/1)	A	$R'Me_2SnBr$ (87)
X = 2,4,6-(MeO)₃		
$R'Cu/Me_2SnBr_2$ (1/1)	A	$R'Me_2SnBr$ (68)
$R'Li/Me_2SnBr_2$ (1/1)	B	$R'Me_2SnBr$ (95)
X = 2-MeO		
$R'Cu/Me_2SnBr_2$ (1/2)	A	R'_2Me_2Sn (65)
3 $R'Cu\cdot CuBr/Me_2SnBr_2$ (1/1)[i]	A	$R'Me_2SnBr$ (80) + R'_2Me_2Sn (12)

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[a] A, tin compound added to the organo-copper (-lithium) suspension (solution); B, reverse addition. [b] No attempts were made to obtain optimal yields. [c] Organocopper prepared in situ: estimated yield of the organocopper present in solution is 70% (based on the starting amount of R'Li). [d] In situ prepared R'Cu afforded $R'Me_2SnBr$ in 57% yield (see c). [e] Reaction time 2½ h; quantitative yield of $R'Cu\cdot CuBr$; 80% yield of pure $R'Me_2SnBr$; no R'_2Me_2Sn could be detected. [f] See text. [g] See experimental. [h] 70% yield after 48 h; unchanged Me_3SnCl was still present in the reaction mixture. [i] R'/Sn ratio.

TABLE 3

PHYSICAL DATA FOR THE TRIORGANOTIN HALIDES Ib-VIIb

Compound	M.p. (°C)	Analysis found (calcd.) (%)				
		C	H	N	X	Sn
2-$Me_2NCH_2C_6H_4SnMe_2Br$[a] (Ib)	136-137	36.6 (36.41)	5.2 (5.00)	3.8 (3.86)	21.8 (22.02)	31.8 (32.71)
2-$Me_2NC_6H_4SnMe_2Br$ (IIb)	125-131	33.9 (34.43)	4.6 (4.62)	3.9 (4.02)	22.6 (22.91)	33.7 (34.02)
4-$Me_2NC_6H_4SnMe_2Br$ (IIIb)	73-74 (dec.)	32.5 (34.43)	4.7 (4.62)	3.8 (4.02)	22.6 (22.91)	33.6 (34.02)
2,6-$(MeO)_2C_6H_3SnMe_2Br$ (Vb)	65-77	31.1 (31.60)	3.9 (4.12)		23.9 (23.26)	32.6 (32.70)
2,4,6-$(MeO)_3C_6H_2SnMe_2Br$ (VIb)	96-101	33.0 (33.28)	4.3 (4.33)		19.9 (20.19)	30.3 (29.98)
2-$Me_2NCH_2C_6H_4SnPh_2Br$[b] (VIIb)	231-238	51.8 (51.79)	4.5 (4.55)	2.9 (2.88)	16.2 (16.41)	24.0 (24.37)

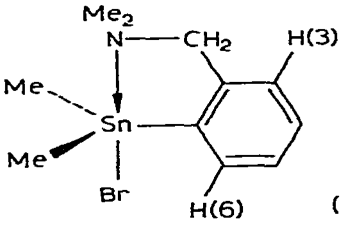
[a] Mol. wt. found: C_6H_6, 364 (osmometry). Calcd.: 363. [b] Mol. wt. found: C_6H_6, 490; $HCCl_3$, 480 (ebulliometry). Calcd.: 487.

NMR spectroscopy

The proton chemical shifts of the various tin compounds are listed in Table 4. The assignment of the resonances due to the CH_3—Sn and the CH_3—X (X = N or O) or benzylic protons is obvious. The resonances at the lowest field in the aromatic region, for which in all cases ^{119,117}Sn—C—C—H couplings (about 50-75 Hz) were observed, were assigned to the proton *ortho* to the Sn—C bond [H(6)]. The multiplet resonance at the high field side of the aromatic region was assigned to the proton H(3), i.e. the proton *ortho* to the heteroatom-containing substituent. In some cases ^{119,117}Sn—C—C—C—H coupling with a value of about 20-30 Hz, was also observed.

The large chemical shift difference found for the various protons when changing the solvent from CCl_4 or $CDCl_3$ to C_6D_6 is interesting. For example for Ib is the $\Delta^{CCl_4}_{C_6D_6}$ +0.77 (NCH_3), +0.68 (NCH_2), +0.12 ($SnCH_3$), —0.55 [H(6)] and +0.18 [H(3)], while for Vb the $\Delta^{CDCl_3}_{C_6D_6}$ equals +0.50 (OCH_3), 0 ($SnCH_3$), +0.23 [H(3,5)] and +0.13 [H(4)].

Ib exists as a monomer both in C_6H_6 and in $CHCl_3$ (see Table 3). A probable structure for Ib* (and similarly for VIIb) is structure A, in which the tin atom is five-coordinate as a result of intramolecular Sn—N bond formation, and in which the more electronegative ligands occupy axial positions.



(Ib, structure A)

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* An X-ray structure determination of VIIb is underway.

TABLE 4

NMR DATA[a] OF THE RMe_2SnBr, RPh_2SnBr AND R_2Me_2Sn COMPOUNDS

Compound[b]	Built-in ligand			Sn—Me	Aromatic-H			
R =	NMe[c]	NCH_2[c]	OMe[c]	($J\ ^{119}Sn—H$/ $J\ ^{117}Sn—H$)	H(3)	H(4)	H(5)	H(6)
2-$Me_2NCH_2C_6H_4$								
Ib, $RSnMe_2Br$	1.52	2.90		0.67 (66.25/63.25)	6.82 J(3,4) 6.5 J(3,5) 2.5	7.0-7.4		8.66 J(5,6) ≈ 6.5 J(2,5) ≈ 2.5 J(Sn—H) 70
Ib[d]	2.29	3.58		0.79	7.0	7.1-7.4		8.11
XI, R_2SnMe_2	1.76	3.19		0.49 (53.1/50.9)		6.9-7.3[e]		7.68 J(Sn—H) 52
X, $R_2SnMeBr$	1.70	3.32 (v br)		0.93 (66.1/63.1)	e	e	e	8.09 (v br) J(Sn—H) 72
VIIb, RPh_2SnBr	1.33	2.95			6.83 J(3,4) 7 J(3,5) 2	f		9.04 J(5,6) 7 J(4,6) 2 J(Sn—H) 74
VIIb[g]	1.88	3.56			7.18	f		8.56 J(Sn—H) 74
2,6-$(OMe)_2C_6H_3$								
Vb, RMe_2SnBr			3.25	0.85 (62.5/59.8)	↑	7.08 J(3,4) 8 6.20	↑	
Vb[d]			3.75	0.85	↑	7.21 6.43	↑	

2-MeOC$_6$H$_4$							
IVb, RMe$_2$SnBr		3.10	0.64 (62.2/59.0)	6.38 J(3,4) 8 J(3,5) 1 J(Sn—H) 30	7.14	6.91 J(3,5) 1 J(4,5) 8	7.84 J(5,6) 7 J(4,6) 2 J(Sn—H) 64
VIII, R$_2$Me$_2$Sn		3.24	0.63 (58.5/55.7)	6.54 J(3,4) 8 J(3,5) 1 J(Sn—H) 20	6.92^h	7.20^h	7.50 J(5,6) 7 J(4,6) 2 J(Sn—H) 52
2,4,6-(MeO)$_3$C$_6$H$_2$							
VIb, RMe$_2$SnBr		2,6-MeO 3.21 4-MeO 3.33	0.86^i (62.0/59.5)	5.94 J(Sn—H) 21			
4-MeNC$_6$H$_4$							
IIIb, RMe$_2$SnBr	2.46		0.58 (58.0/55.3)	↑	6.56	↑	7.38^j J(5,6) 8.5 J(Sn—H) 56.0
RMe$_3$Sn^{k,l}	2.54		0.19 (54.0/51.6)				
2-MeNC$_6$H$_4$							
IIb, RMe$_2$SnBr	2.01		0.64 (64.0/61.3)	6.78	6.9-7.3		8.09 J(Sn—H) 62

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[a] δ ppm, J Hz; correct peak area ratios found. [b] In benzene-d_6. [c] Singlets. [d] In CCl$_4$. [e] Masked by resonances due to $C_6D_{6-x}H_x$. [f] δ(H) of the C_6H_5—Sn groups: H(*ortho*) 7.68 ppm, J(Sn—H) 64 Hz (in CDCl$_3$ 7.72 ppm). [g] In CDCl$_3$. [h] Tentatively assigned to H(4) and H(5), respectively. [i] In some cases (samples obtained via the RCu route) a multiplet was observed (width ≈ 3 Hz). [j] Multiplet due to H(2) and H(6). [k] Obtained from the reaction of IIIb with methylmagnesium bromide. [l] J(^{119}Sn—H) 54.2 Hz, see ref. 12. Solvent Et$_2$O/C$_6$H$_6$ 1/7 v/v.

As mentioned above, the NMe and NCH_2 protons, and also to a smaller extent H(3) show upfield shifts in benzene, whereas for H(6) in this solvent there is a downfield shift. This can be explained on the basis of a preferential orientation of the solvent molecules at various sites of the solute [14]; i.e., at the site of the built-in ligand the benzene molecule is oriented in such a way that the protons are in the diamagnetic region. Furthermore, the benzene molecules will tend to keep away from the electron-rich bromine atom, and this is reflected by the downfield solvent shift for H(6).

Discussion

Attempts to synthesize triaryltin halides in one step from SnX_4 and arylmagnesium or -lithium reagents have generally been unsuccessful [5]. Mixtures of $R_{4-n}SnX_n$ compounds are isolated instead. Pure triaryltin halides are usually obtained by synthesis of the tetraorganotin compound followed by a redistribution reaction.

The reactions described above show that arylcopper compounds are useful intermediates for the partial arylation of tin halides. Phenyl groups bound to copper enter readily into exchange reactions with Sn—X bonds or organotin halides $R_{4-n}SnX_n$ where n is 2, 3 or 4, but exchange with the Sn—X bond of triorganotin halides is evidently very slow*. This clear distinction between the ease of reaction of arylcopper compounds with the different types of (organo)-tin halides is not observed for phenyllithium or diphenylcopperlithium**.

When the phenyl group bears a heteroatom-containing substituent this difference appears to be less pronounced, i.e. in both cases the reaction with dimethyltin dibromide can give the triorganotin halide RMe_2SnBr rather than the tetraorganotin derivatives R_2Me_2Sn. However, the course of the reactions of the copper and lithium compounds is determined by different factors. This is demonstrated by the reactions of the 2-Me_2NCH_2 and MeO-substituted phenyl-lithium and -copper compounds with dimethyltin dibromide.

Course of the Me_2SnBr_2/RCu reaction

The 1/1 reaction of 2-[(dimethylamino)methyl]phenylcopper tetramer [11] with dimethyltin dibromide proceeds selectively because of the lower reactivity of the Cu—C bond*** (see PhCu/SnX_4 reactions). As shown in Table 2, even "reverse" addition of the reagents, i.e. addition of Me_2SnBr_2 to excess of the

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* We have observed that *p*-TolC≡CCu also reacts with Me_2SnBr_2 to give the triorganotin halide *p*-TolC≡C—$SnMe_2Br$ (after 17 days 22% yield; NMR (C_6D_6): δ 0.46 (Sn—Me) [6 H, $J(^{119/117}Sn—H)$ 69/66 Hz], δ 1.96 (s, 3H, *p*-CH_3), δ 6.74 and 7.38 ppm (—C_6H_4—) (2 × m, 4H, *J*(*ortho*) 8 Hz). The reported isolation of RC≡C—$SiMe_2Cl$ from the reaction of RC≡CH with Me_2SiCl_2 in the presence of NEt_3 and a catalytic amount of CuCl (at 150°C; autoclave; 100-120 h) [9] can be similarly explained by selective mono-substitution of Me_2SiCl_2 by RC≡CCu.

** This property of metal(IB)-lithium compounds has been used to prepare ligand-free arylgold(I) compounds, e.g. the synthesis of 2-$Me_2NCH_2C_6H_4Au$ via the reaction of (2-$Me_2NCH_2C_6H_4)_4Au_2Li_2$ with Me_3SnBr [10].

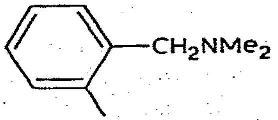
*** The formation of tetraorganotin compounds via the reaction of organocopper compounds with triorganotin halides requires prolonged reaction periods. This is demonstrated by the isolation of 2-$Me_2NCH_2C_6H_4SnMe_3$ from the 1/1 reaction (48 h, see Experimental) of Ia with Me_3SnCl.

arylcopper compound, results in the exclusive formation of the triorganotin halide Ib. The reaction gives the 1/1 complex of the organocopper with cuprous bromide [1].

$$\mathrm{R_4Cu_4 + 2\,Me_2SnBr_2 \xrightarrow{C_6H_6} 2\,\underset{(Ib)}{RMe_2SnBr} + \frac{2}{n}\underset{Red}{[RCu\cdot CuBr]_n}\downarrow} \qquad (6)$$

$$\mathrm{\frac{2}{n}[RCu\cdot CuBr]_n + 2\,Me_2SnBr_2 \rightarrow 2\,\underset{(Ib)}{RMe_2SnBr} + 4\,\underset{White}{CuBr}} \qquad (7)$$

R =



Complex formation between the organocopper and cuprous bromide lowers the reactivity of the Cu—C bond towards the Sn—X bonds, as demonstrated by the following results:

i. The 2/1 reaction of Ia with dimethyltin dibromide affords a quantitative amount of the triorganotin bromide $\mathrm{RMe_2SnBr}$ (Ib) and the 1/1 complex $\mathrm{[RCu\cdot CuBr]}$, (eqn. 6).

ii. A very long reaction period is necessary for the quantitative formation of $\mathrm{2\text{-}Me_2NC_6H_4SnMe_2Br}$ (IIb) from the reaction of $\mathrm{2\text{-}Me_2NC_6H_4Cu}$ with $\mathrm{Me_2SnBr_2}$. In this case the benzene-soluble hexanuclear organocopper—cuprous bromide compound $\mathrm{(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2}$ [3] is formed.

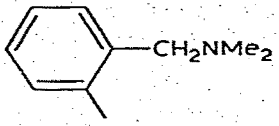
iii. $\mathrm{2\text{-}MeOC_6H_4Cu}$ reacts with $\mathrm{Me_2SnBr_2}$ to give the tetraorganotin compound, whereas its 3/1 complex $\mathrm{(2\text{-}MeOC_6H_4Cu)_3CuBr}$ yields the triorganotin bromide in 80% yield.

Course of Me_2SnBr_2/RLi reaction

The 1/1 addition of 2-[(dimethylamino)methyl]phenyllithium (IX) to a solution of dimethyltin dibromide gives exclusively the triorganotin bromide Ib, see Table 2.

$$\mathrm{Me_2SnBr_2 + \underset{(IX)}{RLi} \rightarrow \underset{(Ib)}{Me_2RSnBr} + LiBr} \qquad (8)$$

R =



In contrast, reverse addition results in the formation of a 1/1 mixture of trimethyltin bromide and {[(2-dimethylamino)methyl]phenyl}dimethyltin bromide (X) (eqn. 11):

$$\mathrm{RLi} + \tfrac{1}{2}\,\mathrm{Me_2SnBr_2} \rightarrow \tfrac{1}{2}\,\underset{\mathrm{(XI)}}{\mathrm{Me_2R_2Sn}} + \mathrm{LiBr} \tag{9}$$

$$\tfrac{1}{2}\,\mathrm{Me_2R_2Sn} + \tfrac{1}{2}\,\mathrm{Me_2SnBr_2} \rightarrow \underset{\mathrm{(X)}}{\mathrm{MeR_2SnBr}} + \mathrm{Me_3SnBr} \tag{10}$$

$$\mathrm{RLi} + \mathrm{Me_2SnBr_2} \rightarrow \underset{\mathrm{(X)}}{\mathrm{MeR_2SnBr}} + \mathrm{Me_3SnBr} \tag{11}$$

In a first step the tetraorganotin compound XI is formed (RLi is present in excess; compare the formation of $\mathrm{Me_2Ph_2Sn}$ in the PhLi/$\mathrm{Me_2SnBr_2}$ reactions), and this in a second step undergoes redistribution with dimethyltin dibromide. The rapid and complete redistribution occurring in a 1/1 mixture of $\mathrm{Me_2SnR_2}$ with $\mathrm{Me_2SnBr_2}$ was demonstrated separately.

The course of the reactions 8 and 11 (9 + 10) can be attributed to the presence of the built-in ligand, which by forming inter- or intra-molecular Sn—N bonds influences the reactivity of the Sn—X and Sn—C bonds. As a result of intramolecular Sn—N coordination, $\mathrm{RMe_2SnBr}$ (Ib) will enter less readily into exchange with RLi (IX) than $\mathrm{Me_2SnBr_2}$, as in reaction 8. The redistribution reaction will take place in an intermediate complex arising from intermolecular Sn—N coordination between $\mathrm{R_2Me_2Sn}$ and $\mathrm{Me_2SnBr_2}$. In the $\mathrm{MeR_2SnBr}$ (X) compound the Sn atom can become hexacoordinate by intramolecular Sn—N bond formation.

Reaction of 2,6-dimethoxy- or 2,4,6-trimethoxy-phenyllithium with dimethyltin dibromide gives the corresponding triorganotin bromides $\mathrm{RMe_2SnBr}$ (Vb and VIb). In these reactions tetraorganotin products $\mathrm{R_2Me_2Sn}$ were not formed, even during the synthesis of Vb in which $\mathrm{Me_2SnBr_2}$ was added to the organolithium suspension (compare this result with eqn. 9). This selective arylation can probably be ascribed to a steric effect exerted by the two methoxy groups *ortho* to the M—C bond.

Experimental

General remarks

The organo-copper and -lithium compounds were prepared by published methods [1,2,7]. The reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled under nitrogen before use.

^{1}H NMR spectra (see Table 4), obtained by Mrs. L. van der Grift-Veldstra, were recorded on a Varian Associates HA-100 NMR spectrometer. The mass spectra were recorded by Mr. C. Versluis on an AEI MS9 mass spectrometer (70 eV, ionization chamber temp. 100-150°C). IR spectra, obtained by Mrs. G.M. Bijlsma-Kreuger, were recorded on a Grubb—Parsons Spectromaster. Elemental analysis (see Table 3) were carried out under the supervision of Mr. W.J. Buis in the Analytical Department of this Institute.

Reactions of tin tetrahalides with phenylcopper

A solution of phenyllithium (10 mmol) in ether was slowly added at 0°C to a suspension of CuBr (10 mmol) in ether (30 ml). The mixture was stirred for $1\frac{1}{2}$ h at 0°C after which the white-brown precipitate was isolated by decanting off the ether solution. Repeated extraction of this solid with ether (removal of LiBr) and benzene resulted in the isolation of white phenylcopper (see also ref. 13). The phenylcopper suspension in ether (or benzene) was then added at 0°C to a solution of tin tetrahalide in ether (or benzene). When the reaction was completed the precipitate was filtered off. The filtrate* was treated (vide infra) with an excess of methylmagnesium bromide in order to convert the organotin compounds formed into tetra-substituted organotin compounds, which were then determined quantitatively by NMR spectroscopy and GLC analysis (see Table 1).

Reactions of dimethyl- and diphenyl-tin dibromide with phenylcopper

As an example of this type of reaction the interaction of phenylcopper and Me_2SnBr_2 is described.

Pure phenylcopper (9 mmol; vide supra) was added at 0°C to a solution of Me_2SnBr_2 in ether (30 ml). This mixture was stirred for 1 h then filtered. The filtrate was treated with a solution of methylmagnesium bromide (12 mmol). After hydrolysis of the resulting mixture with 20 ml 10% NH_4Cl, the ether and water layers were separated. The ethereal layer was dried over $MgSO_4$ and concentrated. The oily residue was dissolved in CCl_4. The amounts of the tetraorganotin products present were established by NMR spectroscopy. (Me_2Ph_2Sn: δ 0.48 ppm, $SnCH_3$; Me_3PhSn: δ 0.27 ppm, $SnCH_3$.) See also Table 1.

Reaction of 2-[(dimethylamino)methyl]phenylcopper tetramer (Ia) with diorganotin halides

Synthesis of Ib from RCu/Me_2SnBr_2 (1/1). A solution of 7.65 mmol of Me_2SnBr_2 in benzene (10 ml) was added at room temperature to a solution of 7.65 mmol of Ia. A red precipitate (RCu·CuBr) was formed initially, but the colour turned to white (CuBr) after addition of the total amount of Me_2SnBr_2. The white precipitate was filtered off. From the filtrate a white solid was obtained by evaporation of the benzene. Recrystallization from petroleum ether (60-80°)/benzene (100/10 v/v) afforded white crystalline Ib.

Reaction of Ia with Me_2SnBr_2 (2/1). This reaction was carried out as described for the 1/1 reaction. During the addition of the Me_2SnBr_2 (3.29 mmol) a red precipitate was formed. This mixture was stirred for $2\frac{1}{2}$ h. The red precipitate was filtered off and extracted with benzene (2 × 10 ml). IR spectroscopy revealed that it was the 1/1 complex RCu·CuBr [1]. (Found: Cu, 33.9. RCu·CuBr calcd.: Cu, 37.26%.) The filtrate was concentrated yielding white solid Ib.

Reaction of Ia with Me_3SnCl. A solution of Me_3SnCl (2.48 mmol) in benzene (20 ml) was added to a solution of Ia in benzene (10 ml). After 3/4 h a red precipitate was slowly formed. After 48 h a red precipitate was still present, and this was isolated by filtration. (Found: Cu, 43.8. RCu·CuCl calcd.: 42.85%.) GLC analysis of the filtrate confirmed the formation of {2-[(dimethylamino)-methyl]phenyl}trimethyltin (by comparison with an analytically pure sample; 1.75 mmol) while unchanged Me_3SnCl was present.

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* Evaporation of the ether afforded almost pure Ph_3SnX.

Synthesis of Ib using Ia prepared in situ. Solid CuBr (46 mmol) was added at —20°C to a solution of IX in ether. The resulting mixture was stirred for 3 h at room temperature. The yellow-green suspension (RCu + Cu^0) was cooled to —78°C and then filtered. The precipitate was extracted with benzene (removal of Cu^0), and the benzene solution titrated with a solution of Me_2SnBr_2. The addition of Me_2SnBr_2 was stopped when the colour of the precipitate turned from red to white, which required 33.5 mmol of Me_2SnBr_2. The white precipitate was filtered off. The filtrate was worked-up as described above.

Synthesis of VIIb. The synthesis of VIIb was carried out as described for Ib. Crude VIIb was recrystallized from hot benzene.

Reaction of 2-[(dimethylamino)methyl]phenyllithium (IX) with dimethyltin dibromide

Addition of Me_2SnBr_2 to IX. Me_2SnBr_2 (7.50 mmol) was added to a suspension of IX (7.50 mmol) in ether. During the addition the solid dissolved. The resulting solution was stirred for 3 h at room temperature. Concentration of the solution followed by extraction of the residue with benzene afforded a white insoluble solid (LiBr). NMR spectroscopy indicated that the benzene extract consisted of a 1/1 mixture of Me_3SnBr (δ 0.50 ppm, $SnCH_3$, $J^{119/117}$ Sn—H 59/56.3 Hz) and bis{2-[(dimethylamino)methyl]phenyl}methyltin bromide (X) (see Table 4). No Ib could be detected.

*NMR spectrum of the 1/1 mixture of Me_2SnBr_2 and bis{2-[(dimethylamino)methyl]phenyl} dimethyltin (XI)**. Me_2SnBr_2 and XI were dissolved in a 1/1 molar ratio in benzene-d_6. An NMR spectrum recorded directly after mixing of the reagents revealed that only Me_3SnBr and X were present.

Reverse addition; addition of IX to Me_2SnBr_2. A suspension of IX (7.50 mmol) in ether (30 ml) was added to a solution of Me_2SnBr_2 (7.50 mmol) in ether (20 ml). The resulting solution was stirred for 3 h and then concentrated. The white residue was extracted with benzene leaving a white insoluble residue (LiBr). NMR spectroscopy of the benzene extract revealed that Ib had been formed almost exclusively. Evaporation of the benzene followed by recrystallization of the residue from petroleum ether (60-80°)/benzene (120/12 v/v) afforded pure Ib.

Synthesis of [2-(dimethylamino)phenyl]dimethyltin bromide (IIb)

Me_2SnBr_2 (6.44 mmol) was added to a suspension of IIa (6.44 mmol) in benzene (25 ml). This mixture was stirred at room temperature until the orange colour of the solution and precipitate ($R_4Cu_6Br_2$) disappeared. The precipitate was separated by centrifugation and then extracted with benzene (2 × 10 ml). The benzene solution was concentrated to give white solid IIb in almost quantitative yield. The solid turns blue upon exposure to the atmosphere. Mass spectrum (70 eV; $T \approx 95°C$): M^+ 349; $(M - CH_3)^+$ 334; $(M - 2\ CH_3)^+$ 319; $(M - 44)^+$ 305; $(M - 44 - 15)^+$ 290; $(M - Br)^+$ 270; $(M - Br - 30)^+$ 240; $(^{120}Sn^{79}Br)^+$ 199.

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* Thanks are due to Mr. K.D. Bos for a gift of a sample of XI.

Synthesis of [4-(dimethylamino)phenyl]dimethyltin bromide (IIIb)

Reaction of IIIa with Me_2SnBr_2. Me_2SnBr_2 (6.54 mmol) was added at room temperature to a suspension of 6.54 mmol of IIIa in benzene (20 ml). The colour of the suspension, which was stirred for $2\frac{1}{2}$ h, turned via purple to grey. The reaction mixture was worked-up as described for IIb. The compound, which can be recrystallized from pentane at —78°C, is highly reactive towards oxidation and hydrolysis. Mass spectrum (70 eV; $T \approx 70°$): M^+ 349; $(M - CH_3)^+$ 334; $(M - 2\,CH_3)^+$ 319; $(M - Br)^+$ 270; $(M - 30 - 44)^+$ 275; $(M - 15 - 44)^+$ 290; $(M - 44)^+$ 305; $(M - Br - 30)^+$ 240; $(^{120}Sn^{79}Br)^+$ 199.

A sample of IIIb was dissolved in benzene and 5 ml of a 6 *N* NH_4OH solution was added. After 1 h both layers were separated. Acid/base work-up of the benzene layer afforded a purple oil which was shown by NMR spectroscopy to be *N,N*-dimethylaniline (89% yield).

Reaction of RLi with Me_2SnBr_2. A suspension of [4-(dimethylamino)-phenyl]lithium (6.75 mmol) in 14 ml of ether was slowly added to a solution of Me_2SnBr_2 (6.75 mmol) in ether (20 ml). The solution, which became purple, was stirred for 3 h. Evaporation of the solvent followed by extraction with benzene (2 × 15 ml) of the remaining solid gave a benzene extract containing only the triorganotin bromide IIIb and *N,N*-dimethylaniline. Work-up as above gave white crystalline IIIb, which had an NMR spectrum identical to that of the compound obtained by the RCu (IIIa)/Me_2SnBr_2 route.

Synthesis of (2,6-dimethoxyphenyl)dimethyltin bromide (Vb)

Reaction of Va with Me_2SnBr_2. Me_2SnBr_2 (6.00 mmol) was added to a suspension of Va (6.00 mmol) in benzene (25 ml). The mixture was stirred until no Me_2SnBr_2 could be detected by NMR spectroscopy. The work-up was as described for IIb.

Reaction of RLi with Me_2SnBr_2. Me_2SnBr_2 (7.5 mmol) was added to a solution of 2,6-dimethoxyphenyllithium (7.5 mmol) in ether (35 ml). This mixture was stirred for 3 h and then worked-up as above. Crude Vb was recrystallized from pentane (15 ml) at —78°C.

Synthesis of (2,4,6-trimethoxyphenyl)dimethyltin bromide (VIb)

This compound was synthesized as described for Vb.

Reaction of Me_2SnBr_2 with 2-methoxyphenylcopper as well as with its 3/1 complex with CuBr

A solution of 7.54 mmol of freshly prepared 2-methoxyphenyllithium in ether (15 ml) was added at 0°C to a suspension of CuBr (7.54 mmol) in ether (10 ml). The mixture was stirred for 1 h at 0°C and for $1\frac{1}{2}$ h at room temperature. Concentration of the reaction mixture was followed by dissolution of the orange-brown residue in benzene. Me_2SnBr_2 was then added until no further colour change was observed (3.28 mmol Me_2SnBr_2). The mixture was stirred for $1\frac{1}{2}$ h and then filtered. The benzene filtrate was concentrated and the residue recrystallized from pentane at —78°C. A white solid was isolated, and elemental analysis indicated that it was slightly contaminated with Me_2SnBr_2. (Found: C, 51.2; H, 5.6; Br, 1.1; Sn, 31.6. $R_2SnMe_2 \cdot 0.025\,Me_2SnBr_2$ calcd.: C, 52.52; H, 5.5; Br, 0.6; Sn, 32.74%.) M.p. 48-50°C.

The reaction of Me_2SnBr_2 with the 3/1 complex of 2-methoxyphenylcopper with CuBr afforded a colourless oil. NMR spectroscopy (see Table 4) showed this (overall yield of "Sn" 92%) to consist of RMe_2SnBr and R_2SnMe_2 (see Table 2).

Acknowledgement

Thanks are due to Drs. E.J. Bulten and H.A. Meinema for helpful discussions. Financial support from the International Copper Research Association, Inc., New York is acknowledged.

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