The Ullmann Coupling Reaction: A New Approach to Tetraarylstannanes

Nadim S. Shaikh,[†] Sean Parkin,[‡] and Hans-Joachim Lehmler*,[†]

Department of Occupational and Environmental Health, The University of Iowa, College of Public Health, 100 Oakdale Campus, 124 IREH, Iowa City, Iowa 52242, and Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Received May 24, 2006

Several iodobenzenes form tetraarylstannanes, in addition to other products, under reaction conditions typically employed for the Ullmann reaction, i.e., activated copper bronze (a copper−tin alloy) and 7 days at 230 °C. The isolated yields of the tetraarylstannanes were low to good (8−58%). Significantly higher yields (54−64%) of tetraphenylstannane were obtained by the direct reaction of iodobenzene with an excess of tin powder (iodobenzene:tin = 1:1 w/w) under the same conditions. Crystal structure analysis reveals that tetrakis(4-carbomethoxyphenyl)stannane crystallizes in a tetragonal space group and has $\bar{4}$ symmetry, which is the case for many symmetrical tetraarylstannanes. However, tetrakis(2,4-dichlorophenyl)stannane, tetrakis(3,4-dichlorophenyl)stannane, and tetrakis(2,4-dimethylphenyl)stannane do not crystallize in a tetragonal space group and do not have real $\bar{4}$ symmetry.

Introduction

The Ullmann reaction, initially reported in 1901,[1] was a breakthrough in the area of aryl−aryl and carbon−heteroatom bond formation. Several reviews have discussed this methodology in great detail.[2−4] Typically, 2 mol of aryl halides react with 1 equiv of copper at high temperature (above 200 °C) to form biaryls and copper halides.[5] Several modifications and improvements of the Ullmann reaction employ copper and its derivatives,[6−9] but the most frequently used form of copper is activated copper bronze (or bronze powder), a 9:1 mixture of copper with tin.[10] Typically, the copper bronze is activated prior to the coupling reaction using iodine in acetone followed by washing the bronze with concentrated HCl in acetone.[11] This classical Ullmann reaction is still the only reaction that allows the synthesis of certain highly ortho-substituted biaryls,[2,12] for example environmentally relevant polychlorinated biphenyls (PCBs) with ≥3 ortho chlorine substituents.

As a part of our efforts to investigate the disposition and toxicity of ortho-substituted PCB congeners,[13−16] we employed the copper-bronze-mediated classical Ullmann coupling reaction to synthesize several PCB congeners of interest. To our surprise, with some starting materials, a chlorinated tetraarylstannane was isolated as a product along with the desired PCB congener. To the best of our knowledge, the formation of chlorinated tetraarylstannanes as a product of the Ullmann reaction has not been reported previously. Therefore, the present study investigates the formation of tetraarylstannanes by the reaction of functionalized iodobenzenes (Cl-, MeO-, F-, MeOCO-, Me-, and O_2N-) with copper bronze or elemental tin under typical Ullmann reaction. The crystal structures of several of the synthesized tetraarylstannanes are discussed.

Results and Discussion

Ullmann Coupling Reactions of Chlorinated Iodobenzenes. The Ullmann coupling reaction is the only reaction that allows the synthesis of PCB congeners with ≥3 ortho chlorine substituents in good yields. During a synthesis of 2,2′,4,4′-tetrachlorobiphenyl (**2a**) via the Ullmann reaction we isolated two fractions with similar R_f-values that both resembled our target molecule according to preliminary characterization by ^{1}H NMR spectroscopy. Further characterization revealed that the isolated products were tetrakis(2,4-dichlorophenyl)stannane (**3a**) and the desired PCB congener **2a**, respectively. In contrast, no stannane **3d** was isolated during the synthesis of 2,2′,3,3′,6,6′-hexachlorobiphenyl, **2d**. Because it is important for toxicological studies to have access to highly pure test compounds free of possible tetraarylstannane impurities, this study investigates experimental conditions (e.g., activation of the copper bronze, ratio of aryl halide to metal, workup procedure) that result in the formation of significant amounts of chlorinated tetraarylstannanes.

---

* Corresponding author. Phone: (319) 335-4211. Fax: (319) 335-4290. E-mail: hans-joachim-lehmler@uiowa.edu.

[†] Department of Occupational and Environmental Health.

[‡] Department of Chemistry.

(1) Ullmann, F.; Bielecki, J. *Chem. Ber.* **1901**, *34*, 2174−2185.

(2) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359−1469.

(3) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327−3359.

(4) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem.* **1990**, *102*, 1006−1019.

(5) Lewin, A. H.; Cohen, T. *Tetrahedron Lett.* **1965**, 4531−4536.

(6) Meyers, A. I.; Himmelsbach, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 682−685.

(7) Meyers, A. I.; Flisak, J. R.; Aitken, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5446−5452.

(8) Meyers, A. I.; Willemsen, J. J. *Chem. Commun.* **1997**, 1573−1574.

(9) Nelson, T. D.; Meyers, A. I. *Tetrahedron Lett.* **1993**, *34*, 3061−3062.

(10) Fanta, P. E. *Synthesis* **1974**, 9−21.

(11) Kleiderer, E. C.; Adams, R. *J. Am. Chem. Soc.* **1933**, *55*, 4219−4225.

(12) Hassan, J.; Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron* **1998**, *54*, 13793−13804.

(13) Lehmler, H.-J.; Price, D. J.; Garrison, A. W.; Birge, W. J.; Robertson, L. W. *Fresenius Environ. Bull.* **2003**, *12*, 254−260.

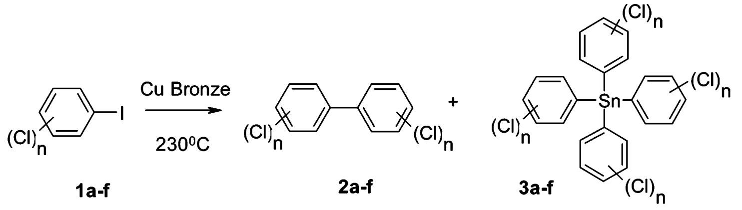
(14) Kania-Korwel, I.; Hornbuckle, K. C.; Peck, A.; Ludewig, G.; Robertson, L. W.; Sulkowski, W. W.; Espandiari, P.; Gairola, C. G.; Lehmler, H.-J. *Environ. Sci. Technol.* **2005**, 3513−3520.

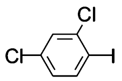
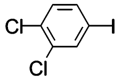
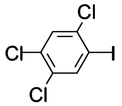
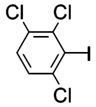
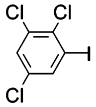
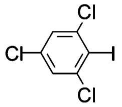
(15) Lehmler, H.-J.; Robertson, L. W.; Garrison, A. W.; Kodavanti, P. R. S. *Toxicol. Lett.* **2005**, *156*, 391−400.

(16) Kania-Korwel, I.; Garrison, A. W.; Avants, J. K.; Hornbuckle, K. C.; Robertson, L. W.; Sulkowski, W. W.; Lehmler, H.-J. *Environ. Sci. Technol.* **2006**, *40*, 3704−3710.

10.1021/om060456a CCC: $33.50

Table 1. Ullmann Coupling Reaction of Chlorinated Iodobenzenes[a]



entry	chlorinated iodobenzenes (1)		products			
			biphenyl (2)	yield[b] g (%)	tetraphenyl stannane (3)	yield[b] g (%)
1-1	**1a**		**2a**	0.426 (28)	**3a**	0.315 (16)
1-2			**2a**	*nd*	**3a**	0.120 (8)[c]
1-3	**1b**		**2b**	0.238 (15)	**3b**	0.518 (25)
1-4	**1c**		**2c**	0.470 (27)	**3c**	0.170 (8)
1-5	**1d**		**2d**	0.561 (32)	**3d**	*ni*
1-6	**1e**		**2e**	0.525 (30)	**3e**	*ni*
1-7	**1f**		**2f**	0.450 (26)	**3f**	0.400[d] (20)

[a] Unless otherwise stated, all the reactions were carried out at 230 °C using 3 g of **1a**−**f** and 7 g of purified copper bronze. [b] Yields of isolated (crude) products. [c] Reaction was performed using tin powder (5 molar equiv). [d] Yield of impure product. *nd*: not detected. *ni*: a tetraphenyl stannane was formed according to ^{119}Sn NMR spectroscopy but could not be isolated by column chromatography.

Initial experiments investigated the Ullmann reaction with a 3:7 (w/w) ratio of 2,4-dichloroiodobenzene (**1a**) to copper bronze at 230 °C (entry 1-1 in Table 1). This model reaction was reproduced several times (see Supporting Information) and, according to GC-MS and ^{119}Sn NMR analysis of the crude reaction mixtures, always resulted in the formation of biphenyl **2a**, 1,3-dichlorobenzene (the dehalogenated product of **1a**), tetraarylstannane **3a**, and several other organotin compounds. Unfortunately, these organotin species could not be isolated by column chromatography. Complete conversion of **1a** was observed after 7 days. Tetraarylstannane **3a** was also formed, in addition to the desired biphenyl **2a**, when nonactivated copper bronze or different batches of copper bronze were used. Significantly more ^{119}Sn signals were observed in the ^{119}Sn NMR spectra of reactions using nonactivated copper bronze.

When the same reaction was carried out with a smaller amount of copper bronze (3:3 w/w instead of 3:7 w/w), only the ^{119}Sn NMR signal of **3a** at −143.6 ppm was observed. Similarly, **3a** was formed when a 3:1 weight ratio of **1a** to copper bronze was employed. We also investigated the reaction of **1a** with activated tin powder (entry 1-2 in Table 1). After 7 days more than 50% of starting iodide was converted to 1,3-dichlorobenzene and neither biphenyl **2a** or tetraarylstannane **3a** was formed. However, a ^{119}Sn NMR signal at −175.6 ppm indicates the formation of a small quantity of an unknown organotin compound. This organotin compound could not be isolated by column chromatography. However, when untreated tin powder was employed, the reaction resulted in the formation of 8% of tetraarylstannane **3a**. No biphenyl **2a** was detected under these conditions.

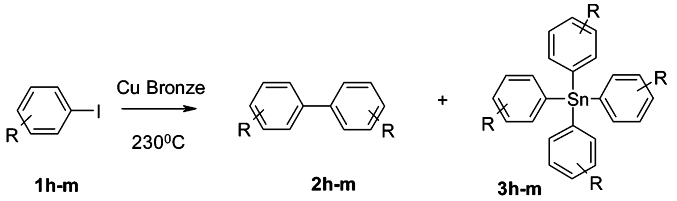
In addition to **1a**, the Ullmann coupling of chloroiodobenzenes **1b**−**f** was investigated. The respective target compounds **2b**−**f** are environmentally relevant PCB congeners. The results of these experiments are summarized in Table 1. Similar to **1a**, the Ullmann reaction of these chloroiodobenzenes resulted in the formation of the biphenyls **2b**−**f**, respectively. We were also able to detect significant amounts of the respective deiodinated chlorobenzene by GC-MS. In addition, one or more signals indicative of the formation of organotin compounds were observed in the ^{119}Sn NMR spectrum of all crude reaction mixtures. Isolation of the tetraarylstannanes **3** was successful for **1b** and **1c** (entries 1-2 and 1-3), but not for the two trichloroiodobenzenes **1d** and **1e** (entries 1-5 and 1-6). Stannane **3f** was isolated in impure form and was found to decompose during our purification attempts (entry 1-7).

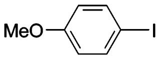
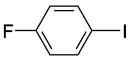
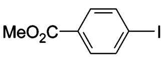
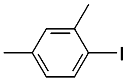
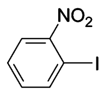
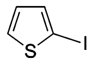
These finding suggest that some tetrakis(trichlorophenyl)-stannanes may be unstable, which is surprising because the highly chlorinated tetrakis(pentachlorophenyl)stannane, $Sn(C_6Cl_5)_4$, is apparently stable under ambient conditions.[17] However,

---

[17] Ara, I.; Fornies, J.; Garcia-Monforte, M. A.; Martin, A.; Menjon, B. *Chem. Eur. J.* **2004**, *10*, 4186−4197.

Table 2. Ullmann Reaction of Functionalized Iodobenzenes



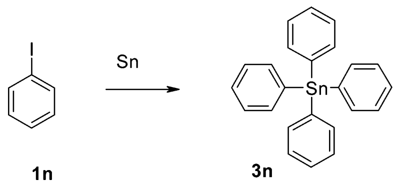
entry	chlorinated iodobenzenes (1)		products			
			biphenyl (2)	yield[a] g (%)	tetraaryl stannane (3)	yield[a] g (%)
2-1	**1h**		**2h**	0.134 (14)	**3h**	0.174 (14)
2-2[b]	**1i**		**2i**	0.365 (16)	**3i**	0.282 (20)
2-3	**1j**		**2j**	0.346 (23)	**3j**	0.150 (8)
2-4	**1k**		**2k**	0.151 (12)	**3k**	0.300 (18)
2-5	**1l**		**2l**	*ni*	**3l**	*nd*
2-6	**1m**		**2m**	*nf*	**3m**	*nd*

[a] Yields of isolated (crude) products. *ni*: **2l** was the only product formed according to GC-MS analysis; its yield was not determined. *nd*: not detected by ^{119}Sn NMR spectroscopy. *nf*: not formed according to GC-MS analysis.

this compound was synthesized by reaction of [$SnCl_4(thf)_2$] with LiC_6Cl_5 at −78 °C and recrystallized from $CCl_2{=}CCl_2$. By contrast, in the present study the Ullmann reactions were performed at 230 °C with a reaction time of 7 days, and column chromatography was employed in our attempts to separate the tetraarylstannanes **3d** and **3e** from other reaction products. The drastic reaction conditions and/or the column chromatographic purification may explain why **3d** and **3e** could not be isolated from the Ullmann reaction mixtures. Alternatively, the tetraarylstannanes **3d**−**f** may be unstable as a result of the substitution pattern.

Ullmann Coupling Reactions of Miscellaneous Iodobenzenes. Tetraarylstannanes **3** were also formed with iodobenzenes with functional groups such as methoxy, fluoro, ester, and methyl. As shown in Tables 2 and 3, 4-methoxy-1-iodobenzene (**1h**), 4-fluoroiodobenzene (**1i**), methyl-4-iodobenzoate (**1j**), 2,4-dimethyliodobenzene (**1k**), and iodobenzene (**1n**) gave the corresponding biphenyls **2h**−**k** and **2n** as well as the tetraarylstannanes **3i**−**k** and **3n** (entries 2-1 to 2-4; entry 3-1). 2-Nitroiodobenzene gave the corresponding biphenyl **2l**, but no tetraarylstannane was formed according to the ^{119}Sn NMR spectrum of the crude reaction mixture (entry 2-5). No biphenyl derivative **2m** and no tetraarylstannanes **3m** was formed during the Ullmann reaction of iodothiophene **1m**. Within this series of starting materials, the formation of stannane **3j** directly from methyl-4-iodobenzoate (**1j**) is of particular interest because tetraarylstannanes with C=O functional groups cannot be synthesized directly using conventional approaches, for example the reaction of Grignard or organolithium reagents with $SnCl_4$.[18]

Table 3. Direct Synthesis of Tetraphenylstannane Using Iodobenzene and Tin



entry	reaction conditions			conversion (%)[a]	yield (%)[a]
	weight ratio (Ar−I:Sn)	temperature (°C)	duration (days)		
3-1	3:7[b,c]	230	7	100	67 (58)[d]
3-2	3:0.7[c]	230	7	20	8
3-3	1:0.7	230	4	25	6
3-4	1:0.7	230	7	52	20
3-5	1:1	230	7	91	69 (64)[d]
3-6	1:2	230	7	97	66 (54)[d]
3-7	1:1	300	2	30	15[e]
3-8	1:1	300	4	98	1[e]
3-9	1:2[c]	150 (DMF)	2	20	5
3-10	1:2[c]	150 (DMF)	4	48	16
3-11	1:2[c]	150 (DMF)	6	100	20

[a] Determined by GC. All reactions were carried out in a sealed glass tube using 1 g of **1n** unless otherwise stated. [b] Reaction was performed using copper bronze (3 g of **1n** and 7 g of copper bronze). [c] Reactions were carried out using 3 g of **1n** and Sn powder. [d] Yields in parentheses refer to isolated yields with purity >98% (GC). [e] Biphenyl (**2n**) was also detected (GC-MS).

Synthesis of Tetraarylstannanes with Tin Powder. To further optimize the synthesis of tetraarylstannanes, we investigated the reaction of iodobenzene (**1n**) with elemental tin. The reaction of alkyl halides with tin and tin alloys is a classical approach for the synthesis of symmetrical organotin compounds of the type R_4Sn.[18,19] However, there is only one report that describes the direct synthesis of a tetraarylstannane (i.e., $Sn(C_6F_5)_4$) by the reaction of elemental tin with an iodobenzene at 260 °C.[20] Considering the great interest in functionalized tetraarylstannanes, we further investigated the observation that the reaction of untreated tin power with iodobenzene **1a** results in the formation of tetraarylstannane **3a**. As part of this investigation, iodobenzene **1n** was treated with tin powder under different reaction conditions, and the conversion and yields of tetraphenylstannane **3n** were determined by GC (Table 3).

As mentioned above, the reaction of **1n** with copper bronze gave complete conversion with 67% yield (58% isolated yields) of **3n** (entry 3-1). In this reaction approximately 0.7 g of pure tin was present (equals 10% of 7 g of copper bronze). In a parallel experiment we used 0.7 g of pure tin instead of copper bronze (entry 3-2). Analogous to a similar reaction with **2a** (entry 1-2), the conversion and yields of this reaction were surprisingly poor. Even increasing the amount of tin to a weight ratio of **1n**:tin of 1:0.7 resulted in only 25% and 52% conversion after 4 and 7 days, respectively (entries 3-3 and 3-4). However, when an equal amount of tin was used, a conversion of 91% was observed with a good yield of the desired product **3n** (entry 3-5). Only a slight improvement in conversion but not in yield was observed when 2 equiv of tin was used (entry 3-6, 97% conversion and 66% yield). The fact that copper bronze results in a good yield of tetraphenylstannane whereas larger quantities of tin powder are needed suggests different reaction mechanisms, possibly involving copper intermediates in the reactions with copper bronze.

When the reaction was carried out at 300 °C, a conversion of 30% and a yield of 15% were observed after 2 days (entry 3-7). But **1n** completely disappeared after 4 days and only a negligible amount of **3n** was detected, indicating the decomposition of the tetraphenylstannane (**3n**) at a temperature of 300 °C (entry 3-8). According to GC-MS analysis, biphenyl **2n** was formed as a byproduct under these conditions, possibly from the decomposition of **3n** or its putative intermediate, e.g., diphenyltin diiodide (Ph_2SnI_2). A preliminary experiment showed that the reaction of **1d** with tin using the optimized reaction conditions from entry 3-5 resulted in the formation of biphenyl **2d** and tetraarylstannane **3d**.

In a search for milder reaction conditions we also studied the reaction of iodobenzene **1n** with tin in DMF, a solvent frequently used for Ullmann reactions. Iodobenzene (**1n**) was treated with tin suspended in DMF at 150 °C, and the reaction was monitored by GC after 2, 4, and 6 days (entries 3-9 to 3-11). Although quantitative conversion was observed after 6 days, the yield of tetraphenylstannane **3n** was poor (20%).

Crystal Structures of Tetraarylstannanes. The crystal structures of several tetraarylstannanes, typically with meta or para substituents, have been reported (please see the Supporting Information for a list of published crystal structures with the general formula Ar_4Sn). To add to the number of available crystal structures, the crystal structures of the two ortho substituent tetraarylstannanes **3a** and **3k**, and of the non-ortho-substituted tetraarylstannanes **3b** and **3j**, were determined. The molecular structures of these compounds and the respective numbering scheme are shown in Figure 1. Crystallographic data and structure determination details are given in Table 4, and relevant geometrical parameters (selected bond lengths and bond angles) are given in Table 5. As shown in Table 5, the Sn−C bond distances of all four tetraarylstannanes are within the range previously reported for other tetraarylstannanes [2.120(8)−2.152(8) Å]. All four compounds show the deviation of the phenyl rings from ideal D_{6h} geometry that is typical for this class of compounds. Although the sum of all six interior C−C−C angles is 720.0° for every phenyl ring, the individual C−C−C angles vary from 116.3(2)° to 123.4(2)° (**3a**), 118.3(2)° to 121.5(2)° (**3b**), 118.24(18)° to 121.36(18)° (**3j**), and 117.98(18)° to 122.51(18)° (**3k**), respectively.

Tetraarylstannanes typically crystallize in a variety of tetragonal space groups, for example space group $P\bar{4}2_1c$, $I\bar{4}$, $P4_1/a$, or $P4_2/n$.[21,22] At the same time they have $\bar{4}$ symmetry,[21,22] which represents the lowest-energy molecular conformation for compounds of the type Ar_4Sn.[23] In compounds with ring substituents that are small and preferably in the 4-position, this conformation also allows close packing of the quasi-spherical molecules required to minimize free volume in the crystals.[24] As shown in Table 4, only **3j** crystallized in a tetragonal space group ($I4_1/a$) and had $\bar{4}$ symmetry. The two C−Sn−C bond angles β and θ are 108.26(5)° and 111.93(10)°, respectively (the $\bar{4}$ symmetry axis falls through two C−Sn−C bond angles which are referred to as β and θ; see refs 23, 24 for a detailed explanation); that is, compound **3j** deviates only slightly from ideal tetrahedral symmetry. The dihedral angle φ, which is used to describe the aryl ring orientation, is 19.3° (φ is defined as the angle between the plane of the aryl ring and the C−Sn−C plane containing the principal axis[23,24]), which is relatively small compared to other tetraarylstannanes with $\bar{4}$ symmetry.[24]

To maintain both the molecular and crystal symmetry, all four ester groups of **3j** are rotated by ∼8° out of the plane of the benzene ring, with O1 0.142(4) Å and O2 0.176(4) Å above and below this plane, respectively. This slightly twisted conformation of the ester group allows for efficient filling of space and hence maintains a relatively dense packing of the **3j** molecules in the crystal, despite the relative complexity of the ester groups in **3j** compared to the chloro and methyl substituents in **3a**, **3b**, and **3k**. Similarly, other tetraarylstannanes with large 4-substituents, for example tetra[4-(*tert*-butyl)phenyl]stannane and tetrakis[4-(trifluoromethyl)phenyl]stannane, also crystallize with tetragonal space groups and have $\bar{4}$ symmetry. In contrast, tetrakis(4-ethoxyphenyl)stannane, a compound with a functional group of a size similar to $-CO_2Me$, has point symmetry 1 and crystallizes in space group $P2_1/c$.[25] In the crystal structure of tetrakis(4-ethoxyphenyl)stannane the $C_{Ar}-C_{Ar}-O-CH_2$ torsion angles of three of the ethoxy groups are approximately 180° (178.4(5)−179.3(6)°); that is, the $-OCH_2-$ fragment lies in the plane defined by the benzene ring. As a result of intermolecular interactions, one ethoxy group is rotated relative to the plane of the benzene ring with a torsion angle $C_{Ar}-C_{Ar}-O-CH_2$ of 169.4(6)°, thus resulting in a total loss of symmetry. These observations suggest that an increased size of the functional group is not necessarily causing loss of symmetry of 4-substituted tetraarylstannanes.

---

[18] Davies, A. G. *Organotin Chemistry*, 2nd ed.; John Wiley & Sons: Chichester, UK, 2004.

[19] Neumann, W. P. *The Organic Chemistry of Tin*; John Wiley & Sons: London, 1970.

[20] Cohen, S. C.; Reddy, M. L. N.; Massey, A. G. *Chem. Commun.* **1967**, 451−453.

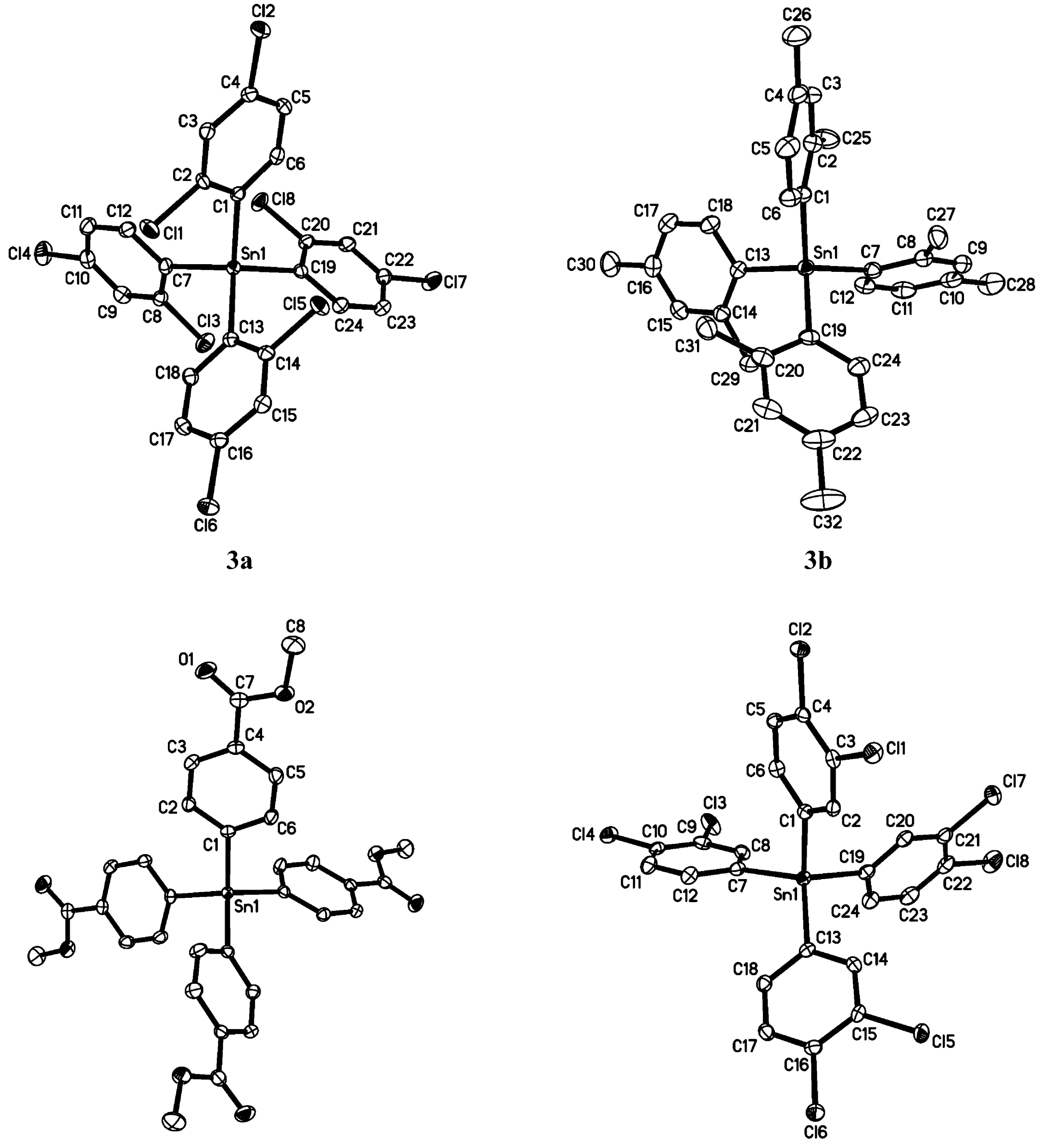
[21] Wharf, I.; Belanger-Gariepy, F. *Acta Crystallogr.* **2003**, *E59*, m661−m663.

[22] Wharf, I.; Simard, M. G.; Lamparski, H. *Can. J. Chem.* **1990**, *68*, 1277−1282.

[23] Hutchings, M. G.; Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 4553−4561.

[24] Wharf, I.; Simard, M. G. *Acta Crystallogr.* **1995**, *B51*, 973−980.

[25] Wharf, I.; Simard, M. G. *Acta Crystallogr.* **1991**, *C47*, 1314−1315.



3a **3b**

3j **3k**

Figure 1. View of stannanes **3a**, **3b**, **3j**, and **3k** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The stannanes **3a**, **3b**, and **3k** do not crystallize in tetragonal space groups. Rather, **3b** and **3k** crystallize in the triclinic space group $P\bar{1}$, and **3a** crystallizes in the orthorhombic space group *Pbca*. Especially for **3a** and **3b**, the deviation from tetragonal symmetry is not surprising because of the large, obtrusive chlorine substituents, which are known to cause loss of close packing as a result of the extramolecular steric requirements of the Cl substituents.[17,26,27] Two of the crystal structures show evidence of $\pi-\pi$ interactions between phenyl rings. In **3b** rings are related via an inversion center to rings on adjacent molecules such that (for example) the plane of the C1−C6 ring is 3.483(3) Å from an inversion-related ring. In **3k** the situation is similar, but the interplanar distance is 3.473(3) Å. To our knowledge, this is the first time that such $\pi-\pi$ interactions have been reported for tetraarylstannanes. It is not surprising that **3a**, **3b**, and **3k** also deviate more significantly compared to **3j** from tetrahedral geometry (Table 5). **3b** does not have a $\bar{4}$ symmetry axis, whereas both **3a** and **3k** have an approximate $\bar{4}$ symmetry axis. Overall, the $\pi-\pi$ interactions, the deviations from tetrahedral geometry around the central Sn atom, and the orientation of the phenyl rings relative to the approximate $\bar{4}$ symmetry axis (φ(**3a**) = 49.3°, 49.9°, 48.0°, and 45.2° and φ(**3k**) = −133.0°, −135.7°, 45.4°, and 46.2°, respectively) allow a more dense packing of **3b** and **3k** in the solid state, thus compensating for the extramolecular steric requirements of the Cl and methyl substituents, respectively.

Conclusion

The present study describes the formation of biaryls **2** and tetraarylstannanes **3** during the reaction of iodobenzenes **1** with copper bronze under reaction conditions typically employed for the Ullmann reaction (Tables 1, 2, and 3). Depending on the iodobenzene starting material **1**, the yields of the biaryl **2** and the tetraarylstannane **3** are low to good (12−32% and 8−58%, respectively). Although ^{119}Sn NMR spectroscopy indicated the formation of organotin compounds, no tetraarylstannane could

---

(26) Ng, S. W. *Acta Crystallogr.* **1997**, *C53*, 273−274.

(27) Wharf, I.; Lebuis, A. M. *Acta Crystallogr.* **2003**, *E59*, m794−m796.

Table 4. Crystallographic Data and Structure Determination Details for Compounds 3a, 3b, 3j, and 3k

	3a	3b	3j	3k
molecular formula (*M*)	$C_{24}H_{12}Cl_8Sn$	$C_{24}H_{12}Cl_8Sn$	$C_{32}H_{28}O_8Sn$	$C_{32}H_{36}Sn$
fw	702.63	702.63	659.23	539.30
cryst type	colorless block	colorless block	colorless plate	yellow block
cryst size (mm)	0.30 × 0.25 × 0.20	0.17 × 0.13 × 0.10	0.30 × 0.27 × 0.03	0.22 × 0.18 × 0.12
a (Å)	16.7318(2)	9.8948(1)	8.5731(1)	10.9038(1)
b (Å)	16.5324(2)	11.2574(2)	8.5731(1)	12.0001(1)
c (Å)	18.7277(3)	11.7771(2)	39.7548(7)	12.4461(1)
α (deg)	90.00	97.9527(6)	90.00	66.4013(4)
β (deg)	90.00	98.0515(6)	90.00	69.3562(4)
γ (deg)	90.00	94.0355(7)	90.00	70.6943(4)
symmetry (space group)	orthorhombic (*Pbca*)	triclinic ($P\bar{1}$)	tetragonal ($I4_1/a$)	triclinic ($P\bar{1}$)
D_{expt} (g cm^{-3})	1.802	1.822	1.499	1.315
abs coeff (μ)	1.825	1.845	0.925	0.955
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
cell volume (Å^3); *Z*	5180.40(12); 8	1281.02(3); 2	2921.90(7); 4	1362.00(2); 2
T (K)	90.0(2)	90.0(2)	90.0(2)	90.0(2)
θ-range (deg)	1.00−27.48	1.00−27.48	1.00−27.48	1.00−27.48
no. of indep reflns	45 671	29 569	13 588	31 543
no. of params	299	298	94	306
R_1, wR_2 (>2σ(I))	0.0371; 0.0256	0.0339; 0.0258	0.0319; 0.0245	0.0263, 0.0225
R_1, wR_2 (all data)	0.0585; 0.0546	0.0573; 0.0537	0.0551; 0.0517	0.0545, 0.0526

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds 3a, 3b, 3j, and 3k[a]

parameter	3a	3b	3j	3k
Sn1−C1	2.142(2)	2.138(2)	2.1351(19)	2.1482(17)
Sn1−C9	2.138(2)	2.137(2)	or	2.1433(17)
Sn1−C13	2.143(2)	2.139(2)	2.1352(19)	2.1473(17)
Sn1−C19	2.139(2)	2.143(2)		2.1494(17)
C1−Sn1−C9	108.43(8) [β]	104.40(9)	108.26(5) [β]	112.64(7) [θ]
C1−Sn1−C13	113.97(8) [θ]	111.00(8)	111.93(10) [θ]	108.34(6) [β]
C1−Sn1−C19	106.69(8) [β]	106.84(9)		107.59(7) [β]
C9−Sn1−C13	107.38(8) [β]	114.30(9)		109.31(7) [β]
C9−Sn1−C19	112.48(8) [θ]	110.22(9)		107.64(7) [β]
C13−Sn1−C19	108.00(8) [β]	109.73(9)		111.34(7) [θ]

[a] [β] and [θ]: see text for explanation.

be isolated with 2,3,6-trichloro- or 2,3,5-trichloroiodobenzene as starting material. The reaction of iodobenzene **1n** with tin powder was investigated to further improve the yield of the tetraarylstannanes (Table 3). In this model reaction, tetraarylstannane **3n** was obtained in good yield (54−64%) at weight ratios of **1n**:tin = 1:1 or higher. Despite the high reaction temperature and the long reaction time, this reaction may be an alternative route to symmetrical tetraarylstannanes with functional groups that are sensitive to the reaction conditions of other, conventional approaches to tetraarylstannanes.

The present study also investigates structural features of tetraarylstannanes. Symmetric tetraarylstannanes are generally expected to display $\bar{4}$ symmetry in the crystalline state. Out of the four compounds investigated by crystal structure analysis, only **3j** crystallizes in a tetragonal space group ($I4_1/a$) and has $\bar{4}$ symmetry, whereas **3a**, **3b**, and **3k** do not crystallize in tetragonal space groups and do not have true $\bar{4}$ symmetry. These findings suggest that, for example, ortho chlorine or methyl substituents (**3a** and **3k)** and/or several large chlorine substituents (**3a** and **3b**) strongly influence molecular point symmetry in tetraaryl stannanes.

Experimental Section

General Information. Three different batches of copper bronze (also referred to as bronze powder) were purchased from commercial sources. Batch A: Alfa Aesar (Ward Hill, MA), lot no. F26M27 (copper 90.25%, tin 9.75%, lube 0.75%, ~100 mesh, 99.0% metals basis). Batch B: Alfa Aesar, lot no. K05P10 (copper 89.99%, tin 10.01%, lube 0.75%, ~100 mesh, 99.0% metals basis). batch C: Atlantic Equipment Engineers (Bergenfield, NJ), lot no. 509504 (copper 89.59%, tin 10.41%, lube 0.75%, ~100 mesh, 99.0% metals basis). The copper bronze was activated prior to use as described below. Tin powder was purchased from Alfa Aesar and used without any further treatment. Aryl iodides were purchased from Lancaster (Pelham, NH) or Alfa Aesar and used as received. A sample of tetraphenyl stannane **3n** was also purchased from Alfa Aesar. 2,3,6-Trichloroiodobenzene was prepared from 2,6-dichloroiodobenzene using a literature procedure.[28]

^{1}H, ^{13}C, and ^{119}Sn{^{1}H} NMR analyses were carried out on a Bruker DRX 400 MHz instrument. ^{1}H and ^{13}C NMR chemical shifts were determined relative to $CDCl_3$. In the ^{13}C NMR spectra of each tetraarylstannane Sn−C satellites are observed due to the spin−spin coupling between ^{117}Sn and ^{119}Sn with ^{13}C nuclei. ^{119}Sn{^{1}H} NMR chemical shifts were determined using tetramethylstannane as an internal standard. ^{19}F NMR was carried out on a Bruker AC 300 MHz instrument using $CFCl_3$ as a reference. Elemental analyses were obtained from Atlantic Microlab Inc. (Norcross, GA). Crude reaction mixtures and, if possible, purified products were analyzed using a GC 6890 series gas chromatograph (Agilent Technologies, Palo Alto, CA) equipped with a J&W Scientific HP-1 capillary column (Agilent Technologies, Wilmington, DE) and a flame ionization detector. The following program was employed: initial temperature 50 °C, initial time 1 min, rate 10 °C/min, final temperature 250 °C, final time 2 min. Quantitative GC analysis was carried out by using the following, modified temperature program: initial temperature 45 °C, initial time 2 min, rate 14°/min, final temperature 260 °C. Mass spectral analysis (EI-MS) was carried out at 70 eV on a Voyager GC-MS (ThermoFinigan, San Jose, CA) instrument in solid probe mode. GC-MS analysis was carried out on the same instrument in GC-MS mode using a ZB-1 column (15 m, 0.35 mm i.d.) at 50 °C, rate 10 °C/min, final temperature 250 °C, final time 8 min. Melting points were determined in capillary tubes using a MelTemp apparatus and are uncorrected. High-resolution mass was carried out on a Micromass Autospec by electron impact.

Activation of Copper Bronze.[11] The copper bronze (100 gm) was treated with 1000 mL of a solution of iodine (2%) in acetone for 5−10 min. The product was then collected in a Buchner funnel, removed, washed by stirring with 500 mL of concentrated HCl in acetone (1:1, v/v), and filtered again. The residue was washed with acetone (3 × 150 mL) and dried under vacuum to yield 82 g of activated copper bronze.

General Procedure for Ullmann Coupling. A mixture of aryl iodide (3 gm) and activated copper bronze (7 gm) in a sealed glass

---

[28] Waller, S. C.; Mash, E. A. *Org. Prep. Proc. Int.* **1997**, *29*, 679−685.

ampule flushed with nitrogen was heated in a sand bath at 230 °C. The reaction mixture was heated for 7 days and allowed to cool to room temperature. The ampule was opened, and the contents were extracted with boiling CH_2Cl_2 (3 × 100 mL). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated to give a dark brown, viscous liquid. Column chromatography on silica gel eluted with hexanes gave the corresponding biphenyl derivative **2** and the tetraphenyl stannane **3**, respectively.

Tetrakis(2,4-dichlorophenyl)stannane (3a). This compound was purified by column chromatography over silica gel using hexanes. Recrystallization from hot methanol gave colorless crystals suitable for X-ray crystal structure analysis: white solid, mp 217−219 °C, R_f 0.59 (hexanes). ^{1}H NMR ($CDCl_3$): δ 7.29 (dd, J = 8 Hz, J = 2 Hz, 4 × H-5), 7.44 (d, J = 2.0 Hz, 4 × H-3), 7.49 (d, J = 8.0 Hz, 4 × H-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 127.51 (4 × C-5, $^3J(^{13}C-^{117}Sn) = 55.3$ Hz, $^3J(^{13}C-^{119}Sn) = 54.3$ Hz), 128.83 (4 × C-3, $^3J(C-Sn) = 34.1$ Hz), 137.01 (4 × C-4, $^4J(C-Sn) = 12.9$ Hz), 137.31 (4 × C-1, $^1J(^{13}C-^{117}Sn) = 614.5$ Hz, $^1J(^{13}C-^{119}Sn) = 587.2$ Hz), 139.41 (4 × C-6, $^2J(C-Sn) = 38.8$ Hz), 141.99 (4 × C-2, $^2J(C-Sn) = 13.8$ Hz). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −143.81 (s). IR (cm^{-1}, KBr): 437, 547, 791, 810, 1020, 1088, 1101, 1355, 1450, 1543, 1561. Anal. Calcd for $C_{24}H_{12}Cl_8Sn$: C 41.02, H 1.72. Found: C 41.24, H 1.64.

Tetrakis(3,4-dichlorophenyl)stannane (3b). This compound was purified by column chromatography over silica gel using hexanes. Recrystallization from dichloromethane and methanol gave colorless crystals suitable for X-ray crystal structure analysis: white solid, mp 172−174 °C (methanol), R_f 0.34 (hexanes). ^{1}H NMR ($CDCl_3$): δ 7.32 (dd, J = 7.8 Hz, J = 1.3 Hz, 4 × H-6), 7.51−7.57 (m, 4 × H-2/H-5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 131.30 (4 × C-5, $^3J(^{13}C-^{117}Sn) = 58.7$ Hz, $^3J(^{13}C-^{119}Sn) = 56.3$ Hz), 134.08 (4 × C-3, $^3J(^{13}C-^{117}Sn) = 74.3$ Hz, $^3J(^{13}C-^{119}Sn) = 71.0$ Hz), 135.03 (4×C-4, $^4J(C-Sn) = 13.1$ Hz), 135.17 (4 × C-1, $^1J(^{13}C-^{117}Sn) = 541.0$ Hz, $^1J(^{13}C-^{119}Sn) = 517.0$ Hz), 135.64 (4 × C-2*, $^2J(C-Sn) = 38.7$ Hz), 138.01 (4 × C-6*, $^2J(C-Sn) = 46.3$ Hz). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −122.11 (s). IR (cm^{-1}, $CHCl_3$): 670, 812, 1026, 1130, 1357, 1461, 1510. Anal. Calcd for $C_{24}H_{12}Cl_8Sn$: C 41.02, H 1.72. Found: C 40.86, H 1.52.

Tetrakis(2,4,5-trichlorophenyl)stannane (3c). This compound was purified by column chromatography over silica gel using hexanes. Recrystallization from chloroform gave colorless crystals: white solid, mp 254−256 °C, R_f 0.62 (hexanes). ^{1}H NMR ($CDCl_3$): δ 7.54 (s, 4 × H-6), 7.57 (s, 4 × H-3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 130.59 (4 × C-3, $^3J(C-Sn) = 36.6$ Hz), 132.63 (4 × C-5), 135.86 (4 × C-4, $^4J(C-Sn) = 12.8$ Hz), 138.12 (4 × C-1), 139.02 (4 × C-6, $^2J(C-Sn) = 42.7$ Hz), 139.50 (4 × C-2). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −149.6 (s). IR (cm^{-1}, $CHCl_3$): 770, 1020, 1088, 1140, 1256, 1357, 1450, 1586, 1639, 2349. Anal. Calcd for $C_{24}H_8Cl_{12}Sn$: C 34.3, H 0.96. Found: C 34.16, H 0.75.

Tetrakis(2,3,6-trichlorophenyl)stannane (3d). This compound could not be isolated by column chromatography. However, a strong ^{119}Sn{^{1}H} signal was observed in the crude reaction mixture at δ −187.4 (s).

Tetrakis(2,3,5-trichlorophenyl)stannane (3e). This compound could not be isolated by column chromatography. However, a strong ^{119}Sn{^{1}H} signal was observed in the crude reaction mixture at δ −116.9 (s).

Tetrakis(2,4,6-trichlorophenyl)stannane (3f). An impure sample of this compound was obtained after column chromatography over silica gel using hexanes. Further purification by recrystallization was not successful due to the poor solubility and, possibly, decomposition of this compound: white solid, R_f 0.56 (hexanes). $_1$H NMR ($CDCl_3$): δ 7.29 (s, 4 × H-3/H-5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 127.92 (4 × C-3/C-5, $^3J(C-Sn) = 33.3$ Hz), 136.32 (4 × C-4, $^4J(C-Sn) = 10.6$ Hz), 142.94 (4 × C-2/C-6, $^2J(C-Sn) = 9.5$ Hz), 144.19 (4 × C-1). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −167.6 (s).

Tetrakis(4-methoxyphenyl)stannane (3h).[29−31] Biphenyl **2h** and stannane **3h** were separated by fractional crystallization from dichloromethane and methanol: yellow solid, mp 127−129 °C (lit. 134.8 °C[30] and 135.5−136.5 °C[31]), R_f 0.48 (hexanes). ^{1}H NMR ($CDCl_3$): δ 3.83 (s, 12H, −OMe), 6.93−7.00 (m, 4 × H-3/H-5), 7.44−7.60 (m, 4 × H-2/H-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 55.02 (4 × OCH_3), 114.43 (4 × C-3/C-5, $^3J(^{13}C-^{117}Sn) = 56.2$ Hz, $^3J(^{13}C-^{119}Sn) = 53.9$ Hz), 128.73 (4 × C-1, $^1J(^{13}C-^{117}Sn) = 540.9$ Hz, $^1J(^{13}C-^{119}Sn) = 535.2$ Hz), 138.26 (4 × C-2/C-6, $^2J(^{13}C-^{117}Sn) = 43.6$ Hz, $^2J(^{13}C-^{119}Sn) = 42.1$ Hz), 160.41 (4 × C-4, $^4J(C-Sn) = 11.8$ Hz). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −116.84 (s). IR (cm^{-1}, $CHCl_3$): 817, 1025, 1073, 1179, 1244, 1276, 1494, 1584, 2924. Anal. Calcd for $C_{28}H_{28}O_4Sn$: C 61.46, H 5.15. Found: C 61.31, H 5.15.

Tetrakis(4-fluorophenyl)stannane (3i).[29,32,33] This compound was purified by column chromatography over silica gel using 10−15% ethyl acetate in hexanes. The compound was further purified by recrystallization from a mixture of hexane and ethyl acetate (1:1, v/v) to give colorless crystals with 99% purity (by GC): mp 130−132 °C (lit. 144−145 °C[33]), R_f 0.48 (12% ethyl acetate in hexanes). ^{1}H NMR ($CDCl_3$): δ 7.00−7.11 (m, 4 × H-3/H-5), 7.37−7.54 (m, 4 × H-2/H-6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 116.2 (4 × C-3/C-5, $^3J(^{13}C-^{117}Sn) = 57.7$ Hz, $^3J(^{13}C-^{119}Sn) = 55.3$ Hz, $^2J(C-F) = 19.5$ Hz,), 132.1 (4 × C-1, $^4J(C-F) = 4.1$ Hz), 138.6 (4 × C-2/C-6, $^2J(^{13}C-^{117}Sn) = 43.9$ Hz, $^3J(C-F) = 7.1$ Hz), 164.04 (4 × C-4, $^1J(C-F) = 247.5$ Hz). ^{119}Sn{^{1}H} ($CDCl_3$): δ −119.64 (m). ^{19}F (300 MHz, $CDCl_3$): δ −111.14 to −111.02 (m). IR (cm^{-1}, $CHCl_3$): 758, 820, 1019, 1066, 1161, 1227, 1385, 1489, 1581, 3023. MS (EI): m/z 499 (M^+), 405 ($M^+ -$ Ar), 309 ($M^+ -$ 2Ar), 215 ($M^+ -$ 3Ar), 120.59 $(Sn)^+$, 95, 75.

Tetrakis(4-carbomethoxyphenyl)stannane (3j). This compound was purified by column chromatography using 5−10% ethyl acetate in hexanes. Further purification was carried out by recrystallization from dichloromethane and methanol to yield crystals suitable for X-ray crystal structure analysis: colorless crystals, mp 178−180 °C, R_f 0.09 (45% ethyl acetate in hexanes). ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 12H, $-CO_2CH_3$), 7.54−7.70 (m, 4 × H-2/H-6), 7.98−8.07 (m, 4 × H-3/H-5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 52.11 (4 × $-CO_2CH_3$), 129.39 (4 × C-2/C-6, $^2J(^{13}C-^{117}Sn) = 53.2$ Hz, $^2J(^{13}C-^{119}Sn) = 51.2$ Hz), 131.25 (4 × C-4, $^4J(C-Sn) = 11.7$ Hz), 137.03 (4 × C-3/C-5, $^3J(C-Sn) = 38.7$ Hz), 142.74 (4 × C-1, $^1J(^{13}C-^{117}Sn) = 528.2$ Hz, $^1J(^{13}C-^{117}Sn) = 504.8$ Hz), 166.77 (4 × $-COOCH_3$). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −133.47 (s). IR (cm^{-1}, $CHCl_3$): 693, 745, 1015, 1131, 1278, 1435, 1592, 1720, 2952. MS (EI): m/z 660 ($M^{+\bullet} + 1$, Ar_4Sn + H), 523 ($M^+ -$ Ar, 100%), 390 ($M^+ -$ 2Ar), 253 ($M^+ -$ 3Ar), 181, 103, 76. HRMS (EI): m/z 660.0803 ($M^{+\bullet}$, exact mass calculated for $C_{32}H_{35}Sn$ 660.0806).

Tetrakis(2,4-dimethylphenyl)stannane (3k).[34] This compound was purified by column chromatography using 5% ethyl acetate in hexanes. Further purification was carried out by recrystallization from mixture of dichloromethane and methanol to give a pale yellow solid, mp 228−230 °C, R_f 0.14 (hexanes). ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 12H, $-Me_{para}$), 2.44 (s, 12H, $-Me_{ortho}$), 7.05−7.25 (m, 4 × H-5/H-6), 7.42−7.62 (m, 4 × H-3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.31 (4 × Me_{para}), 24.9 (4 × Me_{ortho}), 126.49 (4 × C-5, $^3J(C-Sn) = 53.0$ Hz), 130.51 (4 × C-3, $^3J(C-Sn) = 43.8$ Hz), 136.12 (4 × C-6, $^2J(C-Sn) = 42.5$ Hz), 137.44 (4 × C-4, $^4J(C-Sn) = 10$ Hz), 138.7 (4 × C-2, $^2J(C-Sn) = 33.3$ Hz), 144.93

---

[29] Wharf, I. *Inorg. Chim. Acta* **1989**, *159*, 41−48.

[30] Talalaeva, T. V.; Kocheshkov, K. A. *Zh. Obshch. Khim.* **1942**, *12*, 403−408.

[31] Ohe, T.; Wakita, T.; Motofusa, S.-i.; Cho, C. S.; Ohe, K.; Uemura, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2149−2155.

[32] Miller, J. M.; Luo, Y.; Wharf, I. *J. Organomet. Chem.* **1997**, *542*, 89−98.

[33] Fuchs, O.; Post, H. W. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 566−569.

[34] Schneider-Koglin, C.; Mathiasch, B.; Draeger, M. *J. Organomet. Chem.* **1994**, *469*, 25−32.

(4 × C-1, $^1J(^{13}C-^{117}Sn) = 529.0$ Hz, $^1J(^{13}C-^{119}Sn) = 503.7$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −120.32 (s). IR (cm^{-1}, $CHCl_3$): 756, 1227, 1443, 1597, 2919. MS (EI): *m*/*z* 539 ($M^{+\bullet}$, Ar_4Sn), 435 ($M^+ - Ar$), 329 ($M^+ - 2Ar$), 225 ($M^+ - 3Ar$), 120 (Sn), 104 (Ar), 77. HRMS (EI): *m*/*z* 539.1771 ($M^{+\bullet}$, exact mass calculated for $C_{32}H_{36}Sn$ 539.1761).

Optimization of the Synthesis of Tetraphenyl Stannane 3n Using Tin Powder. A mixture of iodobenzene and tin powder in a sealed glass ampule flushed with nitrogen was heated in a sand bath using the reaction conditions shown in Table 3. The reaction mixture was allowed to cool to room temperature. The ampule was opened, and the contents were extracted with boiling $CHCl_3$ (3 × 100 mL) followed by addition of the GC standard (diethylene glycol dibutyl ether, 100 mg). Then 1 μL of the sample was analyzed by GC and the peaks of iodobenzene, standard, and product were integrated. The identities of the compounds present in the solution were confirmed by comparison with the retention times of the respective standard. Yields were determined using diethyleneglycol dibutyl ether as an internal standard (see Supporting Information). After GC quantification, the combined extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated to give a dark brown, viscous liquid. Tetraphenyl stannane **3n** was isolated from the crude product by recrystallization from $CHCl_3$ and methanol (1:1, v/v) as colorless crystals, thus allowing the determination of the isolated yields for selected experiments (see Table 3).

Structure Determination and Refinement. X-ray diffraction data for **3a**, **3b**, **3j**, and **3k** were collected at 90 K on a Nonius kappaCCD diffractometer from either block-shaped (**3b**, **3j**, and **3k**) or plate-shaped (**3a**) crystals, mounted in oil on a glass fiber. Cell parameters were obtained (DENZO-SMN[35]) from 10 1° frames and refined using the full data set (SCALEPACK, DENZO-SMN[35]). Lorentz/polarization and absorption corrections (SADABS[36]) were applied during data reduction. The structures were solved by direct methods (SHELXS97[36]) and difference Fourier (SHELXL97[36]). Refinement was carried out against F^2 by weighted full-matrix least-squares (SHELXL97[36]). Hydrogen atoms were found in difference maps, subsequently placed at calculated positions, and refined using riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography.[37]

Acknowledgment. Thanks to John Snyder for his help with recording the ^{119}Sn NMR spectra and to Vic Parcel for the HRMS analysis (both Department of Chemistry, University of Iowa). This research was supported by grant ES012475 from the National Institute of Environmental Health Sciences, NIH.

Supporting Information Available: Tables and text giving results of the $^{119}Sn\{^1H\}$ NMR analysis of all crude reaction mixtures, the procedure for the quantitative GC analysis, NMR data for biphenyls **2a**−**f** and **2h**−**j**, packing diagrams of **3a**, **3b**, **3j**, and **3k**, and a summary of published crystal structures of tetraarylstannanes; crystallographic and structural data of **3a**, **3b**, **3j**, and **3k** are also provided in CIF form. This material is available free of charge via Internet at http://pubs.acs.org.

OM060456A

---

(35) Otwinowski, Z.; Minor, W. In *Methods in Enzymology Volume 276: Macromolecular Crystallography Part A*; Carter, C. W., Jr., Swet, R. M., Eds.; Academic Press: New York, 1997.

(36) Sheldrick, G. M. *SHELXL97*; University of Gottingen: Germany, 1997.

(37) Hahn, T. *International Tables for Crystallography. Vol C: Physical and Chemical Tables*; Kluwer Academic Publishers: Holland, 1992.