J. Org. Chem. **1997,** *62,* 5242−5243

Communications

New Monoorganostannanes as Efficient Reagents for Palladium-Catalyzed Coupling Reactions

Eric Fouquet,* Michel Pereyre, and
Alain L. Rodriguez

Laboratoire de Chimie Organique et Organométallique,
URA CNRS No. 35, Université Bordeaux I,
351 Cours de la Libération, 33405 Talence Cedex, France

Received March 14, 1997

The creation of carbon−carbon bonds using organotin reagents and a transition-metal catalyst has been widely developed in the last 10 years. While several metals have shown their ability to promote this type of reaction, the most popular method remains by far the palladium-catalyzed reaction, also named Stille coupling.[1] It has always been asserted for this reaction that the reactivity of the organotin reagent was critically dependent on the substitution of the tin atom.[2] Until recently, the deactivating nature of halogen ligands discouraged the use of monoorganotins for metal-catalyzed coupling reactions. Although trihalogenoorganotins have been used for Stille couplings in aqueous solution,[3] the strongly basic conditions required are a serious limitation for synthetic purposes. With the aim of promoting the chemistry of nontoxic and easily removable tin reagents, we were interested in the direct synthesis of new monoallyltins **2a**−**c** prepared from Lappert's stannylene **1**,[4] which was shown to be efficient for radical allylic transfer.[5] The possibility of conceiving one-pot procedures in which organotin reagents are formed *in-situ* encouraged us to assess the ability of these monoallyltins for coupling reactions with organic halides under palladium^0 catalysis (Figure 1).

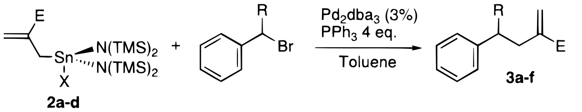


Figure 1.

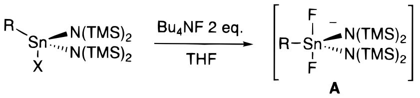


Figure 2.

Table 1. Reaction of Allyltins with Benzylic Bromides

	allyltin E	X	substrate R	condns (°C,	h)	product yield (%)	
2a	CO_2Et	Br	CO_2Me	90	0.2	**3a**	71
2b	CN	Br	CO_2Me	110	2	**3b**	54
2c	Cl	I	CO_2Me	110	3	**3c**	44
2a	CO_2Et	Br	H	110	0.2	**3d**	65
2a	CO_2Et	Br	Me	90	2	**3e**	66
4	CO_2Et	Bu_3	CO_2Me	110	0.2	**3a**	56

The results shown in Table 1 reveal the ability of monoallyltins **2** to achieve the coupling reaction with benzylic substrates. An impressive result in term of reactivity is obtained when using the intramolecularly coordinated organotin **2a**, which appears to be even more efficient than the parent tetraalkyl organotin **4**.[6] The influence of pentacoordination on the limiting step of the reaction is outlined with **2b** and **2c**, which do not undergo such an intramolecular complexation. Then, compared to **2a**, their lower reactivity made the reaction ineffective at 90 °C and forced it to be carried out at 110 °C with a 10-fold longer reaction time. The activating effect caused by an additional coordination of the tin atom has been established recently for tetraorganotins[7] and the transfer of the extra coordination from tin to palladium is also accounted for, explaining the rate acceleration.[8] Nevertheless, this is the first time that this has been shown for the transfer of allyl groups from monoorganotins, which are believed to be far less reactive in Stille coupling than organotins with tin−sp^2 carbon bonds.

The ready avaibility of these monoorganotins, in quantitative yields, simply starting from the corresponding organic halides led us to turn our attention to various types of monoorganotin reagents. In order to take advantage of the nucleophilic assistance brought by the coordination, we modified our initial system by adding 3 equiv of TBAF (tetrabutylammonium fluoride), so that the active organotin can be considered as the pentavalent difluorinated tin **A** (Figure 2).[9] The ease of halogen replacement by a fluorine atom has been widely used for the removal of organotins side products.[10] Moreover, hypervalent fluorinated organotin species have been known for over a decade,[11] but, in contrast with their organosilicon counterparts[12], their use for synthetic

---

* To whom correspondence should be addressed: Tel: +33 05 56 84 28 29. Fax: +33 05 56 84 69 94. E-mail: e.fouquet@lcoo.u-bordeaux.fr.

[1] Mitchell, T. N. *Synthesis* **1992**, 803. Farina, V. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. A., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: London, 1995; Vol. 12, pp 200−221. Farina, V. *Pure Appl. Chem.* **1996**, *68*, 73. Hegedus, L. S. *Coord. Chem. Rev.* **1996**, *147*, 443.

[2] (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Yamamoto, Y.; Hatsuya, S.; Yamada, J. *J. Org. Chem.* **1990**, *55*, 3118.

[3] Roshchin, A. I.; Bumagin, N. A.; Beletskaya, I. P. *Tetrahedron Lett.* **1995**, *36*, 125. Rai, R.; Aubrecht, K. B.; Collum, D. B. *Tetrahedron Lett.* **1995**, *36*, 3111.

[4] Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895. Schaeffer, C. D.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 7160. Lappert, M. F.; Misra, M. C.; Onyszchuk, M.; Rowe, R. S.; Power, P. P.; Slade, M. J. *J. Organomet. Chem.* **1987**, *330*, 31.

[5] Fouquet, E.; Pereyre, M.; Roulet, T. *J. Chem. Soc., Chem. Commun.* **1995**, 2387.

[6] The intramolecular coordination of the tin atom by the carbonyl group is clearly shown by IR spectroscopy with the bathochromic shift of the carbonyl band (1663 cm^{-1} for **2a** compared to 1710 cm^{-1} for **4**). This also influences the ^{119}Sn NMR spectrum by shielding the signal ($\delta = -129.1$ ppm for **2a** compared to −81.8 ppm for **2b** and −84.6 ppm for **7**). For similar phenomena observed on monoallyltrihalogenotins see also: Fouquet, E.; Gabriel, A.; Maillard, B.; Pereyre, M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 590.

[7] Brown, J. M.; Pearson, M.; Jastrzebski, J. T. B. H.; Van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1440. Vedejs, E.; Haight, A. R.; Moss, W. O. *J. Am. Chem. Soc.* **1992**, *114*, 6556.

[8] Crisp, G. T.; Gebauer, M. G. *Tetrahedron Lett.* **1995**, *36*, 3111.

[9] Three equivalents are the optimal amount of TBAF to form the active organotin **A** all along the reaction. The first equivalent readily gives the insoluble monofluoroorganotin^{IV}, the second one changes it to the soluble difluoroorganotin^{V} anion **A**, and the third equivalent is consumed for the halogen exchange of the tin−halogen bond created during the coupling.

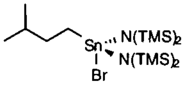
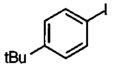
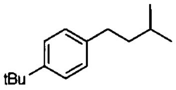
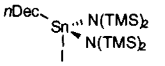
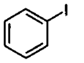
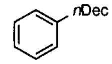
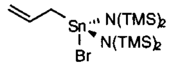
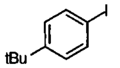
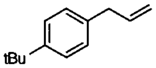
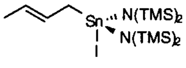
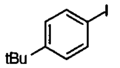
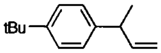
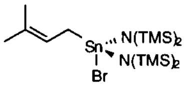
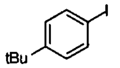
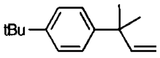
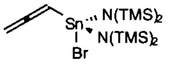
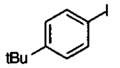
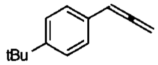
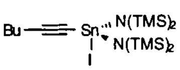
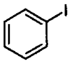
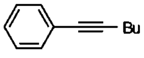
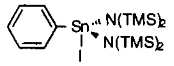
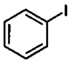
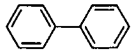
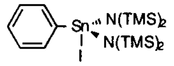
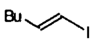
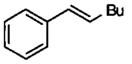
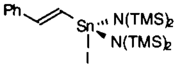
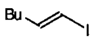
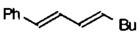
[10] Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449. Barton, D. H. R.; Motherwell, W. B.; Stange, A. *Synthesis* **1981**, 743.

[11] Crawe, A. J. *J. Organomet. Chem.* **1982**, *224*, 223. Blunden, S. J.; Hill, H. *J. Organomet. Chem.* **1989**, *371*, 145. Gingras, M. *Tetrahedron Lett.* **1991**, *32*, 7381.

[12] Hiyama, T. ; Hatanaka, *Pure Appl. Chem.* **1994**, *66*, 1471.

S0022-3263(97)00465-9 CCC: $14.00

Table 2. Palladium^0-Catalyzed Reaction of Monoorganotins with Aryl and Vinyl Iodides

Entry	Monoorganotin		Substrate	Conditions (°C, h)		Product		Yield (%)
1		**5**		101	12		**14**	76
2		**6**		101	12		**15**	71
3		**7**		80	0.5		**16**	88
4		**8**		75	0.5		**17**	89
5		**9**		65	12		**18**	81
6		**10**		35	3		**19**	63
7		**11**		101	2		**20**	83
8		**12**		101	12		**21**	100
9		**12**		101	12		**22**	75
10		**13**		101	12		**23**	77

purposes has been rather limited until now.[13] An exception can be noted from a recent communication,[14] in which TBAF was also used for activating tetraorganotins.

The results are summarized in Table 2 and show the wide range of utility of these monoorganotins, which are active with less than 1% of $Pd(PPh_3)_4$.[15] It can be pointed out that, contrary to the common organotin compounds used in Stille coupling, these reagents are able to transfer alkyl groups in good yields (Table 2, entries 1 and 2).[6,16] There are also major changes in the reactivity order,[17] which can be considered as the following: allyl ≈ crotyl ≈ allenyl > alkynyl > alkenyl ≈ aromatic ≈ alkyl. Furthermore, this reaction appears to be totally regioselective for crotyl (Table 2, entry 4)[18] or prenyl transfer (Table 2, entry 5),[19] affording exclusively the transposed products **17** and **18**. The allenyl transfer is also achieved under particularly mild conditions (Table 2, entry 6),[20] and double bond stereochemistry is totally preserved (Table 2, entries 9 and 10). Then, the use of a vinyl iodide as substrate allows a straightforward preparation of diene unit **23**.

Finally, it is noteworthy that all the products are obtained free of organotin contamination, since the trifluorotin side product is easily removed. Thus is solved a major drawback of the use of organotins reagents in Pd-catalyzed coupling reactions. In conclusion, the direct and quantitative preparation of monoorganotin reagents from Lappert's stannylene avoids syntheses and purifications of intermediate tetraorganotins. Moreover, their high reactivity to undergo cross-coupling reactions as well as the ease in the removal of tin side products clearly highlight their synthetic value, which is currently under investigation.

Supporting Information Available: Preparation procedure and NMR data (^1H, ^{13}C, ^{119}Sn) of monoorganotins **2a**–**c** and **5**–**13**, experimental procedures for both types of coupling reactions, and characterization of coupling products **3a**–**e** and **14**–**23** (5 pages).

JO970465G

---

(13) Martinez, A. G.; Barcina, J. O.; de Fresno Cerezo, A.; Subramanian, L. R. *Synlett* **1994**, 1047.

(14) Buffnoir, S.; Mestdagh, E.; Rolando, C. *Electron. Conf. Trends Org. Chem.* [CD-ROM], Rzepa, H. S.; Leach, C.; Goodman, J. M., Eds.; Royal Chemical Society: Cambridge, 1996, Paper 42.

(15) Typical procedure: 1-Iodohexyne (1.85 mmol) was added to a solution of stannylene **1** (1.85 mmol) in THF (4 mL) and stirred for 30 min at rt. TBAF (5.9 mL, 1 M) was added, after concentration, dioxane (8 mL), iodobenzene (1.23 mmol), and tetrakis(triphenylphosphine)palladium (0.015 mmol) were added, and the reaction mixture was refluxed for 2 h. After cooling and removal of the solvent, purification on silica gel afforded **20** in 83% yield.

(16) Brigas, A. F.; Johnstone, A. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1440. Mamos, P.; Van Aershot, A. A.; Weyns, N. J.; Herdewijn, P. A. *Tetrahedron Lett.* **1992**, *33*, 2413.

(17) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

(18) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. Obora, Y.; Tsuji, Y.; Kobayashi, M.; Kawamura, T. *J. Org. Chem.* **1995**, *60*, 4647.

(19) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595.

(20) Badone, D.; Cardamone, R.; Guzzi, U. *Tetrahedron Lett.* **1994**, *30*, 5477.