Pergamon

Tetrahedron Letters, Vol. 37, No. 21, pp. 3723-3726, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00669-7

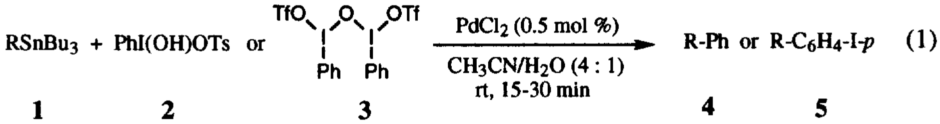
Palladium-Catalyzed Cross-Coupling of Organostannanes with Iodanes

Suk-Ku Kang,* Hong-Woo Lee,[1] Jae-Sun Kim, and Sang-Chul Choi

Department of Chemistry, Sung Kyun Kwan University,
Natural Science Campus, Suwon 440-746, Korea

Abstract: *The palladium-catalyzed coupling of organostannanes with iodanes(Koser's and Zefirov's reagents) in the presence of palladium catalyst was accomplished at room temperature under aqueous conditions to afford phenyl- or 4-iodophenyl-substituted products depending on the iodanes used.*

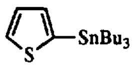
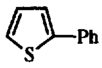
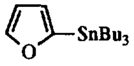
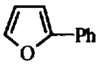
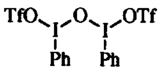
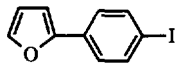
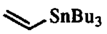
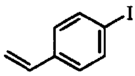
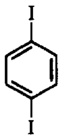
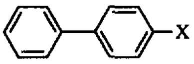
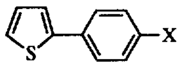
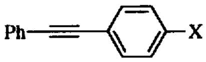
The palladium-mediated cross-coupling of organostannanes with aryl halides, known as the Stille reaction, has developed into an extremely powerful tool for the construction of carbon-carbon bonds.[2] Though recent improvements have been made[3] in the choice of ligands and co-catalysts by copper salts, there is still a feature that limits the usefulness of the Stille cross-coupling. The relatively drastic conditions must be sometimes used to induce coupling and temperature as high as 100 °C is not unusual. Recently, Beletskaya[4] and Collum[5] independently reported the $PdCl_2$-catalyzed cross-coupling of aryl iodides with organotin trihalides and potassium hydroxide *via* hydroxocomplex at 90-100 °C in aqueous medium.[6] We have investigated the Pd-catalyzed coupling of organostannanes with iodanes[7] to carry out the coupling at room temperature in aqueous medium, which is shown below (Eq. 1).[8]



$$\underset{\mathbf{1}}{RSnBu_3} + \underset{\mathbf{2}}{PhI(OH)OTs} \text{ or } \underset{\mathbf{3}}{TfO\text{-}I(Ph)\text{-}O\text{-}I(Ph)\text{-}OTf} \xrightarrow[\substack{CH_3CN/H_2O\ (4:1)\\ \text{rt, 15-30 min}}]{PdCl_2\ (0.5\ \text{mol}\ \%)} \underset{\mathbf{4}}{R\text{-}Ph} \text{ or } \underset{\mathbf{5}}{R\text{-}C_6H_4\text{-}I\text{-}p} \quad (1)$$

The cross-coupling of organostannanes with iodanes is summarized in Table 1.[9] The 2-thienyltributylstannane (**1a**) was coupled with the iodane PhI(OH)OTs (**2**)(Koser's reagent)[10] in the presence of $PdCl_2$(0.5 mol %) in CH_3CN/H_2O (4 : 1) for 15 min to afford 2-phenylthiophene (**4a**)[11] in 91% yield (entry 1 in Table1).[12] Of the catalysts tested, the best choice was $PdCl_2$(0.5 mol %). As solvent, CH_3CN/H_2O (4 : 1) was preferred even if DME/H_2O (4 : 1) was also effective. When the reaction was conducted in dry DMF, the same coupled product was afforded in comparable yield(88%). We coupled 2-furyltributylstannane (**1b**) and phenyltributylstannane (**1c**) with Koser's reagent **2** to afford 2-phenylfuran (**4b**)[13] and biphenyl (**4c**) in 90 and 84% yield,

Table 1. Palladium-Catalyzed Cross-Coupling of Iodanes with Organostannanes

Entry	Organostannanes	Iodanes	Time(min)	Product	Isolated Yield(%)
1	 **1a**	PhI(OH)OTs **2**	15	 **4a**	91
2	 **1b**	**2**	20	 **4b**	90
3	$PhSnBu_3$ **1c**	**2**	25	Ph—Ph **4c**	84
4	$Ph-C\equiv C-SnBu_3$ **1d**	**2**	20	$Ph-C\equiv C-Ph$ **4d**	76
5	**1b**	 **3**	20	 **5a**	58[a]
6	 **1e**	**3**	25	 +  **5b** **6** (1 : 1)	60
7	**1c**	**3**	20	 **4c** X = H **5c** X = I (3 : 5)	72
8	**1a**	**3**	20	 **4a** X = H **5d** X = I (1 : 1)	58
9	**1d**	**3**	30	 **4d** X = H **5e** X = I (1 : 1)	72

---

[a] The coupled product **5a** was afforded in dry DMF in 61% yield.

respectively (entries 2 and 3). This method was also applied to alkynyltributylstannane (**1d**) to provide diphenylacetylene (**4d**) (entry 4). Alternatively, we have investigated the reaction of the other iodane μ–oxobis[(trifluoromethanesulfonato)(phenyl)iodine] (**3**) known as Zefirov's reagent[14] with organostannanes. The coupling of 2-furylbutylstannane (**1b**) with Zefirov's reagent **3** with $PdCl_2$(0.5 mol%) as catalyst afforded 4-iodophenyl-substituted product **5a** in 58% yield(entry 5 in Table 1).[15] Alternatively, the vinylstannane **1e** was treated with Zefirov's reagent **3** to afford 4-iodostylene **5b**[16] and 1,4-diiodobenzene(**6**) (1 : 1) in 60% yield (entry 6). However, for the phenyltributylstannane (**1c**), 4-iodobiphenyl (**5c**)[17] (45%) and biphenyl (**4c**) (27%) were obtained in the ratio of 5 : 3, which were separable by column chromatography (entry 7). It is notable that 2-thienyltributylstannane (**1a**) and alkynyltributylstannane (**1d**) with **3** afforded ~1 : 1 mixtures of phenyl- or 4-iodophenyl-substituted thiophene **4a** and **5d**[18] and phenylacetylene **4d** and **5e**[19] (entries 8 and 9).[20, 21]

The typical procedure is as follows. To a stirred solution of Zefirov's reagent **3**(1.2 g, 1.66 mmol) in CH_3CN/H_2O(4 : 1) (10 mL) was added $PdCl_2$(1.5 mg, 0.5 mol %) followed by 2-(tributylstannyl)furan (**1b**)(650 mg, 1.82 mmol). The reaction mixture was stirred at room temperature for 20 min and quenched with saturated NH_4Cl solution and then extracted with ether(2 x 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated. Thecrude product was separated by SiO_2 column chromatography(hexane, R_f = 0.47) to give **5a** (0.26 g, 58%).

For the formation of the *p*-iodophenyl compounds with Zefirov's reagent **3**, it can be speculated that the intermediate of *p*-iodopalladium complexes generated by the oxidative addition of Pd(0) species to the *para*-position of **3** would couple with organostannanes.[22]

Acknowledgment. Generous financial support by KOSEF-OCRC and Ministry of Education (BSRI-95-3420) is gratefully acknowledged.

References and Notes

1. On leave from Chong Kun Dang Pharm. Co. Ltd..
2. Reviews: (a) Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508-524. (b) Mitchell, T. N. *Synthesis* **1992**, 803-815.
3. Modification of ligands: (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585-9595. (b) Farina, V.; Roth, G. P. *Tetrahedron Lett.* **1991**, *32*, 4243-4246. (c) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434-5444. Addition of copper salts as co-catalysts: (d) Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905-5911. (e) Ye, J.; Bhatt, R. K.; Falck, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 1-5.
4. Roshchin, A. I.; Bumagin, N. A.; Beletskaya, I. P. *Tetrahedron Lett.* **1995**, *36*, 125-128.
5. Rai, R.; Aubrecht, K. B.; Collum, D. B. *Tetrahedron Lett.* **1995**, *36*, 3111-3114.
6. Pd-catalyzed Stille coupling using R_4Sn derivatives in aqueous THF at 50 °C have been repoted. See, Busacca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Rodger, C. A. *J. Org. Chem.* **1994**, *59*, 7553-7556.
7. Review: Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365-383.

8. Heck-type C-C coupling with iodonium salts: Kang, S-K.; Jung, K-Y.; Park, C-H.; Jang, S-B. *Tetrahedron Lett.* **1995**, *36*, 8047-8050 and references therein.
9. Satisfactory spectral and physical data were obtained for the new compounds in accord with the structure. Selected physical and spectral data are as follows. **5a**: TLC, SiO_2, hexane, $R_f = 0.47$. IR(KBr) 3052, 1760, 1568, 1475, 800, 701 cm^{-1}. MS(m/e) 270(M^+), 241, 143, 115(base peak), 113, 63. ^1H NMR($CDCl_3$, 400 MHz) δ 6.47(dd, $J = 3.5$, 1.6 Hz, 1H), 6.66(d, $J = 3.5$ Hz, 1H), 7.40(m, 2H), 7.47(d, $J = 1.6$ Hz, 1H), 7.71(m, 2H). Anal. Calcd for C_9H_7IO: C, 44.47; H, 2.61. Found: C, 44.42; H, 2.86. **5b**: TLC, SiO_2, hexane, $R_f = 0.64$. IR(KBr) 3021, 1625, 1560, 1482, 918 cm^{-1}. MS(m/e) 230(M^+, base peak), 127, 103, 77. ^1H NMR($CDCl_3$, 400 MHz) δ 5.27(d, $J = 10.8$ Hz, 1H), 5.75(d, $J = 17.5$ Hz, 1H), 6.63(dd, $J = 17.5$, 10.8 Hz, 1H), 7.14(m, 2H), 7.65(m, 2H). **5c**: TLC, SiO_2, hexane, $R_f = 0.55$. IR(KBr) 3024, 1559, 1478, 899, 690 cm^{-1}. MS(m/e) 280(M^+), 153(base peak), 141, 127, 77. ^1H NMR($CDCl_3$, 400 MHz) δ 7.35(m, 3H), 7.44 (m, 2H), 7.55(m, 2H), 7.77(m, 2H). **5d**: TLC, SiO_2, hexane, $R_f = 0.53$. IR(KBr) 3054, 1601, 1472, 824, 701 cm^{-1}. MS(m/e) 286(M^+, base peak), 160, 115, 90. ^1H NMR($CDCl_3$, 400 MHz) δ 7.08(m, 1H), 7.31(m, 2H), 7.35(m, 2H), 7.69(m, 2H). **5e**: TLC, SiO_2, hexane, $R_f = 0.50$. IR(KBr) 3052, 1610, 1482, 1067, 750, 688 cm^{-1}. MS(m/e) 304(M^+, base peak), 177, 176, 151, 89. ^1H NMR($CDCl_3$, 400 MHz) δ 7.26(m, 2H), 7.35(m, 3H), 7.53(m, 2H), 7.69(m, 2H).
10. Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenze, B. A. *J. Org. Chem.* **1976**, 41, 3609-3611.
11. Negishi, E.; Luo, F. T.; Frisbee, R.; Matsushita, H. *Heterocycles* **1982**, *18*, 117-122.
12. The Pd-catalyzed coupling of 2-thienyltributylstannane (**1a**) with PhI(OH)OTs was carried out under the same conditions with $Pd(OAc)_2$(0.5 mol %) for 15 min, $Pd_2(dba)_3 \cdot CHCl_3$(5 mol %) for 5 h, and $Pd(PPh_3)_4$ (5 mol %) for 2 h to give **4a** in 91, 82, and 68% yield, respectively.
13. Pelter, A.; Rowlands, M.; Clements, G. *Synthesis* **1987**, 51-53.
14. Gallos, J.; Varvoglis, A.; Alcock, N. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 757-763 and references therein.
15. For the optimization of the catalyst in the coupling 2-furyltributylstannane (**1b**) with Zefirov's reagent **3**, $PdCl_2$ was chosen. Under the same conditions, $Pd(OAc)_2$(0.5 mol %) for 30 min, Pd/C(2 mol %) for 2 h gave the coupled product **5a** in 55 and 61% yield, respectively.
16. Kikukawa, K.; Ikenaga, K.; Kono, K.; Toritani, K.; Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1984**, *270*, 277-282.
17. Muathen, H., A. *J. Chem. Res. Synop.* **1994**, *11*, 405.
18. Polyakov, V. K.; Zaplyuisvechka, Z. P.; Pivovarevich, L. P.; Surov, Y. N.; Tsukerman, S.V. *Khim. Geterosikl. Soedin* **1976**, 1196 (*Chem. Abstr.* **1980**, *92*, 180916j).
19. Meng, Q.; Sun, S.; Bu, X.; You, X. *Gaodeng Xuexiao Huaxue Xuebo* **1988**, *9*, 856 (*Chem. Abstr.* **1989**, *111*, 195045j).
20. 1,4-Diiodobenzene was recovered (~10% yield) along with iodobenzene(50%).
21. The ratios of 4-iodophenyl-substituted thiophene **5d** and 4-iodophenyl-phenylacetylene **5e** can be increased to 4 : 1 and 2 : 1 respectively by utilizing Kitamura's reagent. For Kitamura's reagent, see, Kitamura, T.; Furuki, R.; Nagata, K.; Zheng, L.; Taniguchi, H. *Synlett* **1993**, 193-194.
22. As indirect evidence of the intermediary of intermediate A, only unreacted starting materials **4a-4c** were recovered when **4a-4c** were reacted with Zefirov's reagent **3** under the same conditions, which can be ruled out the direct iodination by the reagent **3**. Under the same conditions without addition of $RSnBu_3$ we could not detect any 1,4-diiodobenzene formed.

(*Received in Japan* 26 *February* 1996; *revised* 5 *April* 1996; *accepted* 8 *April* 1996)