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PALLADIUM-CATALYZED COUPLING OF ORGANO-STANNANES WITH HYPERVALENT IODONIUM SALTS

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Abstract: The palladium-catalyzed cross-coupling of organostannanes with iodonium salts in the presence of $PdCl_2(0.5 \text{ mol }\%)$ or Pd/C(2 mol %) as Pd(0) source was accomplished at room temperature under aqueous conditions.

The palladium-mediated cross-coupling of organostannanes with aryl or vinyl halides and triflates(collectively known as the Stille reaction) has developed into an extremely powerful tool for the construction of carbon-carbon bonds in the past few years.¹ This is due to the ready availability of the organostannanes,² their stability to air and moisture, and no need for protection which is necessity with most organometallic reactions. However, though recent

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improvements have been made³ in the choice of ligand and significant cocatalysis 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, which may reduce the yields due to the thermal instability of substrates, products, or the catalyst itself. Recently, Beletskaya⁴ and Collum⁵ independently reported the PdCl₂-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 hypervalent iodonium salts⁷ as alternatives to aryl halides to carry out the coupling at room temperature in aqueous medium, which is shown below(Equation 1).⁸

$$nBu_{3}SnR_{1} + R_{2}I^{+}Ph X^{-} \frac{PdCl_{2}(0.5 \text{ mol }\%)}{CH_{3}CN/H_{2}O(5:1)} R_{1}^{-}R_{2} \quad (1)$$

$$rt \qquad R_{1} = R_{2} = phenyl- X = BF_{4} \qquad 3$$

$$lb R_{1} = 2-furyl- 2b R_{2} = p-CH_{3}C_{6}H_{4} - X = BF_{4} \qquad 3$$

$$lc R_{1} = phenyl- 2c R_{2} = 2-thienyl- X = OTs$$

$$ld R_{1} = HC \equiv C- 2d R_{2} = (E)-PhHC = CH- X = BF_{4} \qquad 1$$

$$le R_{1} = Ph-HC \equiv C- 1$$

$$lf R_{1} = H_{2}C = CH- \qquad 1$$

The cross-coupling of organostannanes with hypervalent iodonium salts is summarized in Table 1. The 2-thienyltributyltin (1a) was subjected to couple with diphenyliodonium tetrafluoroborate (2a) in the presence of $PdCl_2(0.5 \text{ mol }\%)$ in $CH_3CN/H_2O(5:1)$ at room temperature for 30 min to afford 2-phenylthiophene (3a)⁹ in 87% yield(entry 1 in Table 1). Of the catalysts,

Entry	Organo-	Iodonium	Reaction	Time	Product	Isolated
	stannanes	Saits	Conditions [*]			rield(%)
1	SnBu ₃	Ph ₂ I ⁺ BF ₄ ⁻	Α	30 min		87
	14	La			38	
2	1a	p-MeC6H4IPh ⁺ B	F4 ⁻ A	25min	$\langle \mathcal{V} \rangle$	— Сн₃ 88
		20			3b	
3	1 a	I+Ph-O	_{Ts} A	20 min	\sqrt{s}) 94
		2c			3c	
4	SnBu ₃	Ph I ⁺ Ph	BF ₄ B	2 h	$\sqrt[n]{}$	54 Ph
	1b	2d			3d	
5	PhSnBu ₃	2a	В	2 h	Ph— Ph 3 c	95
	lc				30	
6	1c	2b	Α	30 min	Ph-	·сн ₃ 90
					3f	
7	1c	2c	Α	30 min	3a	90
8	1c	2d	B	2 h	Ph 3g Pl	^h 82
9	H — SnBr	^u 3 2a	В	4 h		ı 93
	10				30	
10	Ph	u3 2b	A	1h Ph		— СН₃ 68
	IC				<u> </u>	÷
11	1e	2c	Α	45 min	< <u>_</u>	-Ph 74
12	1e	2d	Α	30 min		Ph 68
					 3k	
13	SnBu ₃	2a	В	1.5 h		96
_	1 f				31	

 Table 1. Palladium-Catalyzed Cross-Coupling of Organostannanes with Hypervalent Iodonium Salts

^aA: PdCl₂(0.5 mol %), CH₃CN/H₂O(4 : 1), rt. B: Pd/C(10%)(2 mol %), CH₃CN/H₂O(5 : 1), rt.

PdCl₂(0.5 mol %), Pd/C(2 mol %), Pd/CaCO₃, Pd/Al₂O₃(5 mol %), Pd(OAc)₂(0.5 mol %), Pd(PPh₂)₄(5 mol %) tested, PdCl₂(0.5 mol %), Pd/C(2 mol %), and Pd(OAc)₂(0.5 mol %) were effective for the coupling. The best choice was PdCl₂(0.5 mol %). As solvent system, CH₂CN/H₂O(4 : 1) was the best of choice. Alternatively, DME/H₂O(4 : 1) was also effective. It is notable that p-tolyl(phenyl)iodonium tetrafluoroborate (2b) with 1a afforded p-tolyl-2thiophene $(3b)^{10}$ as the sole product(entry 2). In the reaction of 1a with 2thienyl(phenyl)iodonium tosylate (2c), only thienyl group was coupled to provide dithiophene (3c) in 94% yield(entry 3). This cross-coupling was applied to alkenyl(phenyl)iodonium salt 2d and the reaction of 2d with 1b to afford the coupled product 3d¹¹ in a rather low yield(54%) (entry 4).¹² For the phenyltributyltin (1c), the reaction with iodonium salt 2a gave the biphenyl (3e) in 95% yield(entry 5). The cross-coupling of 1c with p-tolyl- and 2thienyl(phenyl)iodonium salts 2b and 2c afforded p-tolyl- and 2-thienylsubstituted benzenes 3f and 3a, respectively(entries 6 and 7). Treatment of 1c with alkenyl(phenyl)iodonium salt 2d provided 3g(entry 8). This coupling was successfully applied to the alkynyl-substituted organostannes. The organostannes 1d was reacted with diphenyliodonium salt 2a to yield phenylacetylene (3h)(entry 9). The phenyl-substituted alkynyltributyltin 1e was reacted with the iodonium salts 2b-2d to provided the coupled products 3i,¹³ 3j,¹⁴ and 3k,¹⁵ respectively(entries 10-12). Finally, the vinylstannanes 1f with diphenyliodonium salt 2a afforded 3l(entries 13).

In summary, facile palladium-mediated cross coupling of organostannanes with hypervalent iodonium salts has been carried out at room temperature under aqeous conditions.

Experimental Section

Typical Procedure: Method A. 2-Phenylthiophene(3a).

To a stirred solution of diphenyliodonium tetrafluoroborate(1.50 g, 4.0 mmol) and PdCl₂(3.6 mg, 0.5 mol %) in CH₃CN/H₂O(4 : 1)(10 mL) was added 2-(tributylstannyl)thiophene(1.60 g, 4.3 mmol). The reaction mixture was stirred at room temperature for 30 min and quenched with saturated NH₄Cl solution(10 mL), and then extracted with ether(2 X 20 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography(hexanes, R_f = 0.52) to give **3a**(0.57 g, 87%). TLC, SiO₂, hexanes, R_f = 0.52. IR(KBr) 3070, 1608, 1477, 832, 708 cm⁻¹. ¹H NMR(CDCl₃, 400 MHz) δ 7.09(dd, 1H, *J* = 5.1, 3.5 Hz), 7.27 (m, 2H), 7.32(dd, 1H, *J* = 3.5, 1.1 Hz), 7.38(m, 2H), 7.62(m, 2H). MS(m/e) 160(M⁺, base peak), 128, 115, 102, 89.

Method B. Styrene(31).

To a stirred solution of diphenyliodonium tetrafluoroborate(150 mg, 0.42 mmol) and Pd/C(10%)(0.9 mg, 2 mol %) was added vinyltributyltin(200 mg, 0.63 mmol) in CH₃CN/H₂O(5 : 1)(5mL) at room temperature. The reaction mixture was stirred at room temperature for 1.5 h and quenched with saturated NH₄Cl solution(5 mL), and then extracted with ether(2 X 20 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography(hexanes, R_t = 0.58) to give **3l**(41 mg, 96%).

p-Tolyl-2-thiophene(3b): TLC, SiO₂, hexanes, $R_f = 0.52$. IR(KBr) 3044, 1602, 1369, 900, 684 cm⁻¹. ¹H NMR(CDCl₃, 400 MHz) δ 2.37(s, 3H), 7.06(m, 1H), 7.18(m, 2H), 7.25(m, 2H), 7.50(m, 2H). MS(m/e) 174(M⁺, base peak), 173, 141, 128, 115.

2-(2-Phenylethenyl)furan(3d): TLC, SiO₂, hexanes, $R_f = 0.40$. IR(KBr) 3040, 1603, 1482, 1372, 1068, 960 cm⁻¹. ¹H NMR(CDCl₃, 400 MHz) δ 6.36(δ , 1H, J = 3.2 Hz), 6.43(m, 1H), 6.90(d, 1H, J = 16.3 Hz), 7.05(d, 1H, J = 16.3 Hz), 7.27 ~ 7.48 (m, 6H). MS(m/e) 170(M⁺, base peak), 142, 140,116, 90.

1-Methyl-4-(phenylethynyl)benzene(3i): TLC, SiO₂, hexanes, $R_f = 0.40$. IR(KBr) 3084, 2964, 1612, 1480, 1372, 695 cm⁻¹. ¹H NMR(CDCl₃, 400 MHz) δ 2.37(s, 3H), 7.17(d, 2H, J = 7.8 Hz), 7.33 ~ 7.36(m, 3H), 7.42(m, 2H), 7.51 ~ 7.55(m, 2H). MS(m/e) 192(M⁺, base peak), 191, 189, 165, 115.

1-Phenyl-2-thienylacetylene(3j): TLC, SiO₂, hexanes, $R_f = 0.42$. IR(neat) 3058, 3020, 2951, 1600, 1384, 732 cm⁻¹. ¹H NMR(CDCl₃, 400 MHz) δ 7.01(m, 1H), 7.28(m, 2H), 7.35(m, 3H), 7.53(m, 2H). MS(m/e) 184(M⁺, base peak), 152, 139, 126.

1,4-Diphenylbut-3-en-1-yne(3k): TLC, SiO₂, hexanes, $R_f = 0.45$. IR(KBr) 3041, 3010, 1605, 1471, 843 cm⁻¹. ¹H NMR(CDCl₃, 400 MHz) δ 6.40(d, 1H, J = 16.0 Hz), 7.06(d, 1H, J = 16.0 Hz), 7.31 ~ 7.34(m, 6H), 7.42 ~ 7. 47(m, 4H). MS(m/e) 204(M⁺), 202(base peak), 103, 90.

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