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PALLADIUM-CATALYZED CROSS-COUPLING OF ORGANOTELLURIUM COMPOUNDS WITH HYPERVALENT IODONIUM SALTS

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PALLADIUM-CATALYZED CROSS-COUPLING OF ORGANOTELLURIUM COMPOUNDS WITH HYPERVALENT IODONIUM SALTS

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ABSTRACT

The palladium-catalyzed cross-coupling of hypervalent iodonium salts with organotellurium dichloride was achieved with $PdCl_2$ (10 mol %) in the presence of NaOMe (3 equiv) in $CH_3CN/MeOH$ at room temperature.

Organotellurium compounds are becoming increasingly important in organic synthesis.¹ However utilization of organotellurium compounds in carbon-carbon bond formation is rather limited. In the literature, cross-coupling of alkyl or aryltellurides with Grignard reagents in the presence of palladium, cobalt, or nickel catalyst is known.^{2,3} The substitution of the tellurium moiety of vinyl tellurides has been performed with lower and higher order cuprates.⁴ It is also known that vinyltellurides can be exchanged with aluminium or zinc species *via* transmetallation.⁵ Recently Uemura *et al.*⁶

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reported the palladium-catalyzed carbonylation and homocoupling of vinyl tellurides as well as Heck-type coupling of vinyltellurides. In connection with our programs to utilize hypervalent iodonium salts in palladium-catalyzed cross-coupling.⁷ We found that diaryl or divinyltellurium dichlorides can be readily coupled with iodonium salts in the presence of palladium catalyst. Here we wish to report palladium-catalyzed cross-coupling of iodonium salts with diaryl or divinyltellurium dichlorides (Eqn 1).

$$\begin{array}{rcl} \mathrm{RI}^{\mathrm{+}}\mathrm{Ph}\;\mathrm{X}^{\mathrm{-}} &+& \mathrm{Ar_{2}TeCl_{2}} & \xrightarrow{\mathrm{PdCl_{2}}\left(10\;\mathrm{mol}\;\%\right)} & \mathrm{R}\text{-}\mathrm{Ar} & (1)\\ & & \mathbf{1} & \mathbf{2} & \xrightarrow{\mathrm{NaOMe}\left(3\;\mathrm{equiv}\right),\;\mathrm{rt},\;7\;\mathrm{h}} & \mathbf{3} & \\ \mathrm{R} &= p-\mathrm{MeOC_{6}H_{4}}, & \mathrm{Ar} = \mathrm{Ph}, p-\mathrm{MeOC_{6}H_{4}} & \\ & & 2\text{-thienyl} & \\ & & (E)\mbox{-}\beta\mbox{-}\mathrm{styryl} & \\ \mathrm{X} &= \mathrm{OTs},\;\mathrm{OTf},\;\mathrm{BF_{4}} & \end{array}$$

The results of the palladium-catalyzed cross-coupling of hypervalent iodonium salts with organotellurium dichlorides are summarized in Table 1. The *p*-methoxyphenyl(phenyl)iodonium triflate (1a) reacted with diphenyltellurium dichloride (2a) in the presence of PdCl₂ (10 mol %) and NaOMe (3 equiv) in CH₃CN/MeOH (1:1) at room temperature for 7h to afford p-methoxybiphenyl (3a) in 88% yield (entry 1). Of the catalyst tested PdCl₂, Pd₂(dba)₃, and PdCl₂(PPh₃)₂, Pd(PPh₃)₄, PdCl₂ was the best choice. As a solvent, $CH_3CN/MeOH$ (1:1) was the most suitable among the solvent toluene, CH₃CN, MeOH, CH₃CN/MeOH (1:1), DMF tested. The addition of NaOMe is critical in this coupling. With the iodonium salt **1b** under the same conditions the coupling gave the same coupled product 3a in 85% yield. For the di(p-methoxyphenyl)tellurium dichloride (2b) the reaction with Ph_2IBF_4 (1c) gave the cross-coupled product 3a in 81% yield (entry 2). When the iodonium salt **1a** was reacted with *p*-methoxyphenyl-substituted tellurium dichloride 2b, 4,4-dimethoxybiphenyl (3b) was obtained in 81% yield (entry 3). Treatment of 2-thienyl(phenyl)iodonium tetrafluoroborate (1d) and tosylate (1e) with 2b, 2-(p-methoxyphenyl)thiophene (3c) which the 2-thienyl group was coupled was obtained as the sole product in 86% and 83% yields, respectively (entry 4). This method was extended to the coupling of alkenyl substituted iodonium salt 1f. Reaction of the alkenyl iodonium tetrafluoroborate **1f** with organotellurium dichlorides and 2a and 2b afforded the product 3d and 3e is 72 and 70% yields, respectively (entries 5 and 6).

Although the mechanism for this palladium-catalyzed coupling of organotellurium compounds with hypervalent iodonium salts remains to

ORGANOTELLURIUM COMPOUNDS

Table	1.	The Palladium-Catalyzed	Cross-Coupling of Organotellurium with Hyper
valent	Iod	onium Salts	

Entry	Iodonium Salt	Organotellurium Compounds	Product	Isolated Yield(%)
1	$MeO - I^+ Ph X^-$	Ph ₂ TeCl ₂	MeO-Ph	
	1a X = OTf	2a	3a	88
	1b $X = OTs$			85
2	$Ph_2I^+BF_4^-$ M		3a	81
	IC	20		
3	$MeO - I^+ Ph X^-$ $1a X = OTf$	Ме 2b		Me 81
	1b $X = OTs$		50	80
4	$\int_{1}^{S} I^{+}Ph X^{-}$ 1d X = BF ₄ 1e X = OTs	2b	S 3c	86 83
5	Ph $I^+ Ph BF_4$ 1f	2a	Ph 3d	72
6	1f	2b	Ph 3e	e 70

be elucidated, it is presumed that the oxidative addition of Pd(0) and hypervalent iodonium salts to form $RPdBF_4$ which is subjected to transmetallation with $Ar_2Te(OMe)_2$ from Ar_2TeCl_2 and NaOMe followed by reductive elimination to afford the coupled product (Scheme 1).



In conclusion the palladium-catalyzed cross-coupling of hypervalent iodonium salts with organotellurium dichlorides was achieved in the presence of $PdCl_2$ (10 mol %) at room temperature under mild conditions.

EXPERIMENTAL

Typical Procedures

Preparation of *p*-Methoxybiphenyl (3a)

To a stirred solution of Ph₂TeCl₂ (716 mg, 1.40 mmol), PdCl₂ (25 mg, 0.14 mmol), and NaOMe (220 mg, 4.20 mmol) in CH₃CN/MeOH (20 mL) under nitrogen atmosphere was added 4-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**1a**) (556 mg, 1.40 mmol) at room temperature. The reaction mixture was stirred at room temperature for 7 h. The reaction mixture was extracted with diethyl ether (20 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (hexanes, R_f =0.17) to afford the coupled product **3a** (219 mg, 85%). TLC, SiO₂, hexanes, R_f =0.17. ¹H NMR (500 MHz, CDCl₃) δ 3.87 (s, 3H), 7.01 (m, 2H), 7.34 (m, 1H), 7.45 (m, 2H), 7.58 (m, 4H). IR (KBr) 3055, 1265, 1115 cm⁻¹. MS (EI): m/e (relative intensity) = 185 (12), 184 (100), 169 (80), 141 (29), 115.

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REFERENCES

- 1. Petragnani, N. In *Tellurium in Organic Synthesis*, Academic Press, London, 1994.
- Comasseto, J.V.; Ling, L.W.; Petragnani, N.; Stefani, H.A. Synthesis 1997, 373–403.
- (a) Uemura, S.; Fukuzawa, S.-I.; Patil, S.R. J. Organomet. Chem. 1983, 243, 9–18.
 (b) Huang, X.; Zhao, C.-Q. Synth. Commun. 1997, 27, 237–241.
 (c) Huang, X.; Wang, Y.-P. Tetrahedron Lett. 1996, 37, 7417–7420.
- (a) Tucci, F.C.; Chieffi, A.; Camasseto, J.V. Tetrahedron Lett. 1992, 33, 5721–5724. (b) Marino, J.P.; Tucci, F.; Comasseto, J. V. Synlett 1993,

ORGANOTELLURIUM COMPOUNDS

761–763. (c) Ogawa, A.; Tsuboi, Y.; Obayashi, R.; Yokoyama, K.; Ryu, I.; Donoda, N. J. Org. Chem. **1994**, *59*, 1600–1601. (d) de Araujo, M.A.; Comasseto, J.V. *Synlett.* **1995**, 1145–1148. (e) Chieffi, A.; Comasseto, J. V.; Marino, J.P. J. Org. Chem. **1996**, *61*, 4975– 4989. (g) Huang, Y.-Z.; Mo, X.-S.; Wanf, L. Tetrahedron Lett. **1998**, *39*, 419–422.

- Terao, J.; Kambe, N.; Sonoda, N. Synlett. 1996, 779–780. (b) Terao, J.; Kambe, N.; Sonoda, N. Tetrahedron Lett. 1996, 37, 4741–4744. (c) Studemann, T.; Gupta, V.; Engman, L.; Knochel, P. Tetrahedron Lett. 1997, 38, 1005–1008.
- (a) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. J. Org. Chem. 1987, 82, 4859–4863. (b) Nishibashi, Y.; Cho, C.-S.; Ohe, K.; Uemura, S. J. Organomet. Chem. 1996, 526, 335–339. (c) Nishibashi, Y.; Cho, C.-S.; Ohe, K.; Uemura, S. J. Organomet. Chem. 1996, 527, 197–200.
- (a) Kang, S.-K.; Lee, H.-W.; Jang, S.-B.; Ho, P.-S. J. Org. Chem. 1996, 7. 61, 4720–4724. (b) Kang, S.-K.; Lee, H.-W.; Jang, S.-B.; Kim, T.-H.; Pyun, S.-J, J. Org. Chem. 1996, 61, 2604-2605. (c) Kang, S.-K.; Yamaguchi, T.; Hong, R.-K.; Kim, T.-H.; Pyun, S.-J. Tetrahedron 1997, 53, 3027–3037. (d) Kang, S.-K.; Lee, H.-W.; Kim, J.-S.; Choi, S.-C. Tetrahedron Lett. 1996, 37, 3723-3726. (e) Kang, S.-K.; Yamaguchi, T.; Ho, P.-S.; Kim, W.-Y.; Yoon, S.-K. Tetrahedron Lett. 1997, 38, 1947–1950. (f) Kang, S.-K.; Yamaguchi, T.; Pyun, S.-J.; Lee, Y.-T.; Baik, T.-G. Tetrahedron Lett. 1998, 39, 2127–2130. (g) Kang, S.-K.; Yamaguchi, T.; Ho, P-S.; Kim, W.-Y.; Ryu, H.-C. J. Chem. Soc., Perkin Trans. 1 1998, 841-842. (h) Kang, S-K.; Baik, T.-G.; Kulak, A.N. Synlett. 1999, 324–326. (i) Kang, S-K.; Lee, Y.-T.; Lee, S-H. Tetrahedron Lett. **1999**, 40, 3573–3576. (j) Kang, S.-K.; Baik, T.-G.; Hur, Y. Tetrahedron 1999, 55, 6863–6870. (k) Kang, S.-K.; Ryu, H.-C.; Lee, S.-W. J. Chem. Soc., Perkin Trans. 1 1999, 2661-2663.

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