

Palladium-catalysed cross-coupling of organotellurium compounds with organoboronic acids[†]

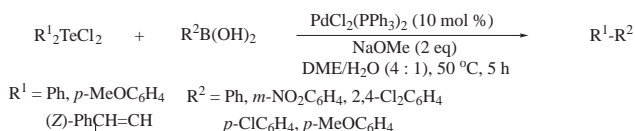
Suk-Ku Kang*, Young-Taek Hong, Doo-Hwan Kim and Sun-Hwan Lee

Department of Chemistry and Institute for Basic Sciences, Sungkyunkwan University,
Suwon 440-746, Korea

The palladium-catalysed cross-coupling of diaryl- and divinyl-tellurium dichlorides with organoboronic acids has been accomplished in the presence of PdCl₂(PPh₃)₂ and NaOMe (2 equiv) in DME/H₂O (4 : 1) at 50 °C in moderate yields.

Keywords: palladium catalysed cross-coupling, organotellurium compounds

The palladium-catalysed cross-coupling of organoboranes with an organic electrophiles (*i.e.* halides and triflates), known as the Suzuki reaction¹ has become an extremely versatile method for carbon–carbon bond formation. As alternatives to organic electrophiles hypervalent iodonium salts were utilized in the cross-coupling with organoboranes.² Although organotellurium compounds become increasingly important in organic synthesis,³ the use of these compounds in carbon–carbon bond formation is rather limited. The cross-coupling of alkyl- or aryltellurides with Grignard reagents in the presence of palladium, cobalt, and nickel catalyst is known.^{4,5} The substitution of the tellurium moiety of vinyl tellurides has been performed with organocuprates.⁶ Recently, Uemura *et al.*⁷ reported the palladium-catalyzed carbonylation^{7a} and homo-coupling^{7b} of vinyl tellurides as well as the Heck-type coupling^{7c} of vinyl tellurides. However, the cross-coupling of aryl- or vinyltellurium dichlorides with organoboronic acids is not known.⁸ We assumed that the use of tellurium as one of the 6A group metals would expand the scope of the cross-coupling reaction. Here we report the palladium-catalysed cross-coupling of diaryl- and divinyltellurium dichlorides with organoboronic acids (Scheme 1).



Scheme 1

The results of palladium-catalysed cross-coupling of diaryl- and divinyltellurium dichlorides are summarized in Table 1. The palladium-catalysed coupling of diphenyltellurium dichloride **1a** with *m*-nitrophenylboronic acid **2a** was carried out to find optimum conditions. Of catalysts tested Pd(PPh₃)₄, Pd(OAc)₂, PdCl₂, PdCl₂(dppf), and PdCl₂(PPh₃)₂, PdCl₂(PPh₃)₂ was the best of choice. As bases used NaOMe, K₂CO₃, Cs₂CO₃, Na₂CO₃, NaOAc, KOAc, Et₃N, the base NaOMe was the most preferable. The use of other bases gave the products in a rather low yields. As solvent DME/H₂O (4 : 1) was the most suitable. Diphenyltellurium dichloride (**1a**) reacted with *m*-nitrophenylboronic acid (**2a**) in the presence of PdCl₂(PPh₃)₂ (10 mol %) and NaOMe (2 equiv) in DME/H₂O

(4 : 1) at 50 °C for 5 h to afford 3-nitrobiphenyl (**3a**) in 76% yield (entry 1 in Table 1). Under the same conditions the treatment of **1a** with *p*-chlorophenylboronic acid (**2b**) to give the coupled product **3b** in 68% yield (entry 2). The coupling of **1a** with **2c** and **2d** proceeded to provide the products **3c** and **3d** in 75 and 72% yields, respectively (entries 3 and 4). The compound di-*p*-methoxyphenyltellurium dichloride (**1b**) was smoothly coupled with **2a** to give the substituted biphenyl **3e** in 83% yield (entry 5). When the tellurium dichloride **1b** reacted with the substituted phenylboronic acids **2b** and **2c**, the coupled products **3f** and **3g** were readily obtained in 72 and 80% yields (entries 6 and 7). This coupling method was also applied to alkenyl-substituted tellurium dichloride **1c**. The (*Z*)-substituted alkenyl-substituted tellurium dichloride **1c** reacted with **2a** to afford (*Z*)-substituted alkene **3h** in 38% yield (entry 9). Finally, di[β-(*Z*)-styryl]tellurium dichloride (**1c**) was coupled with boronic acid **2d** to give the (*Z*)-alkenes **3i** in 54% yield (entry 10).

In summary the palladium-catalysed cross-coupling of diorgano-tellurium dichlorides with organoboronic acids was achieved under mild conditions in moderate yields.

Experimental

To a mixture of diphenyltellurium dichloride (**1a**) (211 mg, 0.60 mmol), PdCl₂(PPh₃)₂ (42 mg, 10 mol %) and NaOMe (65 mg, 1.2 mmol) in DME/H₂O (4 : 1) (3 ml) at 50 °C was added *m*-nitrophenylboronic acid (**2a**) (100 mg, 0.60 mmol). The reaction mixture was stirred for 5 h at 50 °C. 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 (EtOAc/hexanes 1:30, R_f = 0.42) to afford 3-nitrobiphenyl (**3a**) (91 mg, 76%): TLC, SiO₂, EtOAc/hexanes 1 : 30, R_f = 0.42. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (m, 1H), 7.50 (m, 2H), 7.62 (m, 3H), 7.92 (m, 1H), 8.21 (m, 1H), 8.46 (m, 1H). IR(KBr) 3056, 1532, 1352, 1266 cm⁻¹. MS (EI): *m/e* (relative intensity) = 200 (M⁺), 199 (99), 153 (57), 152 (100), 151 (26).

4-Chlorobiphenyl (**3b**): TLC, SiO₂, hexane, R_f = 0.52. ¹H NMR (500 MHz, CDCl₃) δ 7.55 (m, 3H), 7.52 (m, 2H), 7.47 (m, 2H), 7.42 (m, 3H). IR (KBr) 3055, 1266, 747 cm⁻¹. MS (EI): *m/e* (relative intensity) = 189 (M⁺), 188 (100), 152 (75), 94 (11), 76 (42).

2,4-Dichlorobiphenyl (**3c**): TLC, SiO₂, hexane, R_f = 0.30. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (m, 3H), 7.43 (m, 1H), 7.51 (m, 1H). IR (KBr) 3060, 1588, 1465, 741 cm⁻¹. MS (EI): *m/e* (relative intensity) = 223 (M⁺), 222 (100), 186, 152, 150, 93, 75.

4-Methoxybiphenyl (**3d**): TLC, SiO₂, hexane, R_f = 0.17. ¹H NMR (500 MHz, CDCl₃) δ 8.87 (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 (M⁺), 184 (100), 169 (43), 141 (44).

4'-Methoxy-3-nitrobiphenyl (**3e**): TLC, SiO₂, EA/hexane = 1 : 30, R_f = 0.18. ¹H NMR (500 MHz, CDCl₃) δ 3.88 (s, 3H), 7.03 (m, 2H), 7.58 (m, 3H), 7.88 (m, 1H), 8.15 (m, 1H), 8.42 (m, 1H). IR (KBr) 3055, 1518, 1352, 1265, 1182 cm⁻¹. MS (EI): *m/e* (relative intensity)

* To receive any correspondence. E-mail: skkang@chem.skku.ac.kr

[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Palladium-catalysed cross-coupling of organoboronic acids with organotellurium dichlorides

Entry	Organotellurium dichlorides	Organoboronic acids	Products	Isolated yield/%
1	Ph ₂ TeCl ₂ 1a	 2a	 3a	76
2	1a	 2b	 3b	68
3	1a	 2c	 3c	75
4	1a	 2d	 3d	72
5	 1b	2a	 3e	83
6	1b	2b	 3f	72
7	1b	2c	 3g	80
8	1b	 2e	 3d	81
9	 1c	2a	 3h	38
10	1c	2d	 3i	54

^aAll the reactions were run in the presence of PdCl₂(PPh₃)₂ (10 mol %) and NaOMe (2 equiv) in DME/H₂O (4 : 1) at 50 °C for 5 h.

= 230 (M⁺), 229 (79), 183 (26), 168 (40), 152 (30), 140 (56), 139 (100).

4-Chloro-4'-methoxybiphenyl (3f): TLC, SiO₂, EA/hexane = 1 : 30, R_f = 0.42. ¹H NMR (500 MHz, CDCl₃) δ 3.85 (s, 3H), 6.98 (m, 2H), 7.38 (m, 2H), 7.48 (m, 4H). IR (KBr) 3055, 1265, 742 cm⁻¹. MS (EI): *m/e* (relative intensity) = 219 (M⁺), 218 (100), 203 (55), 175 (47), 139 (60).

2,4-Dichloro-4'-methoxybiphenyl (3g): TLC, SiO₂, EA/hexane = 1 : 30, R_f = 0.33. ¹H NMR (500 MHz, CDCl₃) δ 3.86 (s, 3H), 6.97 (m, 2H), 7.26 (m, 2H), 7.27 (m, 1H), 7.35 (m, 2H). IR (KBr) 3055, 1432, 1265, 744 cm⁻¹. MS (EI): *m/e* (relative intensity) = 255 (M⁺), 254 (72), 252 (100), 239 (25), 237 (32), 211 (25), 209 (33), 139 (55).

(Z)-β-Styryl-3-nitrobenzene (3h): TLC, SiO₂, EA/hexane = 1 : 30, R_f = 0.35. ¹H NMR (500 MHz, CDCl₃) δ 6.61 (d, 1H, *J* = 12 Hz), 6.78 (d, 1H, *J* = 12 Hz), 7.23 (m, 5H), 7.37 (m, 1H), 7.54 (m, 1H), 8.06 (m, 2H). IR (KBr) 3055, 1608, 1432, 1353, 1265 cm⁻¹. MS (EI): *m/e*

(relative intensity) = 226 (M⁺), 225 (47), 179 (25), 178 (100), 176 (20), 152 (31), 89 (19).

(Z)-β-Styryl-4-methoxybenzene (3i): TLC, SiO₂, EA/hexane = 1 : 30, R_f = 0.37. ¹H NMR (500 MHz, CDCl₃) δ 3.78 (s, 3H), 6.52 (d, 1H, *J* = 12 Hz), 6.75 (d, 1H, *J* = 12 Hz), 7.18 (m, 3H), 7.25 (m, 4H). IR (KBr) 3055, 1606, 1511, 1264, 1178 cm⁻¹. MS (EI): *m/e* (relative intensity) = 211 (M⁺), 210 (100, base peak), 167 (53), 165 (87), 152 (53), 89 (16).

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