Homocoupling Reactions Using Telluronium Salts

Kazunori Hirabayashi, Yuji Takeda, Toshio Shimizu, Nobumasa Kamigata*
Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan
E-mail: kamigata-nobumasa@c.metro-u.ac.jp

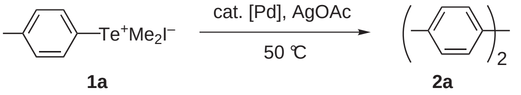
Received 25 May 2005

Abstract: The homocoupling reaction of aryldimethyltelluronium iodides in the presence of a catalytic amount of palladium(II) species and two equivalents of silver(I) acetate proceeded to afford the corresponding biaryls.

Key words: palladium, coupling, organometallic reagents, telluronium salt, silver(I) acetate

Palladium-catalyzed coupling reactions are one of the useful methods for forming carbon–carbon bonds.[1] In those reactions, the homocoupling reaction occurs to synthesize symmetrical compounds, and the utility of various organometallic reagents has been widely investigated.[2] It has been reported that the homocoupling reaction of alkenyl tellurides occurs in the presence of a catalytic amount of palladium species; to the best of our knowledge, however, in the case of aryl tellurides or aryltellurium(IV) compounds, stoichiometric amounts of palladium species are required.[3] Recently, we found that the reaction of aryltelluronium salts with olefins proceeded in the presence of palladium(II) catalyst and silver(I) acetate to afford aryl-substituted olefins (Mizoroki–Heck-type reactions).[4] In that reaction, the aryl groups on tellurium atoms were transferred efficiently to the olefins, and the telluronium salts were relatively stable for a few months in air. Thus, we examined whether the telluronium salts could be used as convenient organometallic reagents for other carbon–carbon bond-forming reactions, and found that the homocoupling reaction proceeded in the presence of a catalytic amount of palladium catalyst. The results are reported herein.

The homocoupling reaction of dimethyl(4-methylphenyl)telluronium iodide (**1a**) was carried out in acetonitrile using palladium as the catalyst and silver(I) acetate as the additive (Scheme 1).[5] The reaction of **1a** proceeded smoothly to give homocoupling product **2a** in 99% yield after six hours (Table 1, entry 1). In this way, the homocoupling reaction of a telluronium salt proceeded in the presence of a catalytic amount of palladium catalyst. Although the reaction proceeded in both polar solvents, such as THF or DMF, and less polar solvents, such as hexane or toluene, a long time was required for its completion (entries 2–5). In the case of DMSO, the yield was low after 72 hours (entry 6). The most effective palladium catalysts were palladium(II) chloride and palladium(II) acetate (entries 1 and 7). When other palladium catalysts were used, the homocoupling products were obtained in low yields after six hours (entries 8–10). These results indicated that phosphine ligands inhibited the reaction. Although other group 10 metal halides such as $NiCl_2$ and $PtCl_2$ were also examined, the yields of **2a** were very low. The reaction was also carried out in the presence of various amounts of silver(I) acetate (entries 11–13). The reaction proceeded in excellent yield after six hours when more than two equivalents of silver(I) acetate was used, whereas the yield of the homocoupling product was drastically decreased in the presence of 1 equivalent of silver(I) acetate. From these results, the present reaction needs at least two equivalents of silver(I) acetate. On the contrary, when $CuCl_2$ or $Cu(OAc)_2$ were used as additives, the reaction did not proceed catalytically.



Scheme 1

Table 1 Optimization of the Palladium-Catalyzed Homocoupling Reaction of **1a**[a]

Entry	Cat. Pd	AgOAc (equiv)	Solvent	Time (h)	Yield (%)[b]
1	$PdCl_2$	4	MeCN	6	99
2	$PdCl_2$	4	THF	12	87
3	$PdCl_2$	4	DMF	12	99
4	$PdCl_2$	4	Hexane	24	99
5	$PdCl_2$	4	Toluene	24	92
6	$PdCl_2$	4	DMSO	72	28
7	$Pd(OAc)_2$	4	MeCN	6	99
8	$Pd_2(dba)_3\cdot CHCl_3$	4	MeCN	6	34
9	$[(\pi\text{-allyl})]PdCl]_2$	4	MeCN	6	8
10	$PdCl_2(PPh_3)_2$	4	MeCN	6	3
11	$PdCl_2$	3	MeCN	6	99
12	$PdCl_2$	2	MeCN	6	99
13	$PdCl_2$	1	MeCN	10	35

[a] The reaction was carried out using **1a** (0.5 mmol) and 10 mol% of palladium catalyst.
[b] The yield was determined by GC analysis.

SYNLETT 2005, No. 14, pp 2230–2232
Advanced online publication: 20.07.2005
DOI: 10.1055/s-2005-872231; Art ID: U16505ST

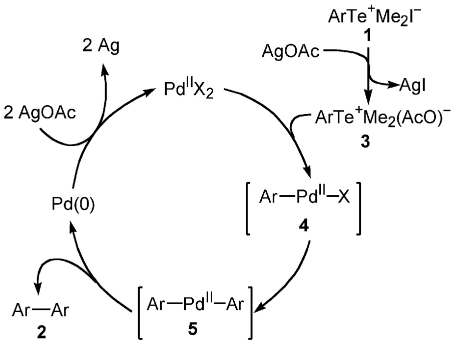
Thus, the homocoupling reaction of various aryldimethyltelluronium iodides was carried out in the presence of a catalytic amount of palladium(II) chloride and two equivalents of silver(I) acetate at 50 °C in acetonitrile, and the results are shown in Table 2.[5] Dimethylphenyltelluronium iodide (**1b**) also reacted to give **2b** in good yield (entry 2). The reactions of telluronium salts that possessed electron-donating or electron-withdrawing groups proceeded smoothly to give the corresponding products in high yields (entries 3–5). By contrast, in the case of telluronium salts possessing a substituent at the 2-position, such as **1f** and **1g**, the yields of the homocoupling products were low (entries 6 and 7). Telluronium salts **1h** and **1i** also gave the coupling products in good yields (entries 8 and 9). From these results, the homocoupling reactions were found to be affected by not the electronic factor but the steric factor. Noteworthy was that the homocoupling products were obtained easily by filtration through silica gel to remove solids (palladium or silver residue) in the reaction mixture.

Table 2 Homocoupling Reaction of Telluronium Salts **1**[a]

Entry	Telluronium salt		Time (h)	Product	Yield (%)[b]
1	4-$MeC_6H_4Te^+Me_2I^-$	(**1a**)	6	**2a**	82
2	$PhTe^+Me_2I^-$	(**1b**)	6	**2b**	88
3	4-$MeOC_6H_4Te^+Me_2I^-$	(**1c**)	6	**2c**	84
4	4-$CF_3C_6H_4Te^+Me_2I^-$	(**1d**)	6	**2d**	99
5	4-$ClC_6H_4Te^+Me_2I^-$	(**1e**)	6	**2e**	91
6	2-$MeC_6H_4Te^+Me_2I^-$	(**1f**)	24	**2f**	46
7	2-$MeOC_6H_4Te^+Me_2I^-$	(**1g**)	12	**2g**	37
8	1-$C_{10}H_7Te^+Me_2I^-$	(**1h**)	6	**2h**	79
9	2-$C_{10}H_7Te^+Me_2I^-$	(**1i**)	6	**2i**	93

[a] The reaction was carried out using **1** (0.5 mmol), 10 mol% of $PdCl_2$, and AgOAc (1 mmol).
[b] Isolated yields.

One plausible mechanism for this reaction is shown in Scheme 2, which refers to the Mizoroki–Heck-type reaction of telluronium salts.[4] Silver(I) acetate plays an important role in the exchange of the counter ion from iodide to acetate in the initial step and in reproducing palladium(II) species in the final step. Thus, silver(I) acetate was converted into AgI and Ag(0). It was also confirmed that AgI and Ag(0) were produced in the present reaction.[6] The aryl group of telluronium salt **3**, which was produced from telluronium salt **1**, was transferred from the tellurium atom to the palladium species to afford arylpalladium species **4**. There might be two possibilities for producing diarylpalladium species **5**; one is the disproportionation[7] of arylpalladium species **4**, and the other is the transmetallation from telluronium salt to arylpalladium species **4**. Then, the reductive elimination of diarylpalladium species **5** occurred to afford homocoupling product **2** and palladium(0) species. In the case of organic tellurides, the reaction did not proceed catalytically, because the organic tellurides might coordinate with palladium species to inhibit the catalytic reaction. The coordination of telluronium salts was weaker than that of organic tellurides. Thus, the present reactions might proceed catalytically.



Scheme 2

In summary, the palladium-catalyzed homocoupling reaction of telluronium salts was achieved. The present reaction proceeded catalytically when silver acetate was used as the additive.

Acknowledgment

This work was supported in part by a Grant-in-Aid for Young Scientists (B), The Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

(1) (a) *Metal-Catalysed Cross-Coupling Reactions*; Diederich, F.; Stang, P., Eds.; Wiley-VCH: Weinheim, **1998**. (b) Tsuji, J. *Palladium Reagents and Catalysts. Innovations in Organic Synthesis*; Wiley-VCH: New York, **1995**. (c) Tsuji, J. *Transition Metal Reagents and Catalysts. Innovations in Organic Synthesis*; Wiley-VCH: New York, **2000**.

(2) For recent reports about palladium-catalyzed homocoupling reaction using organometallic reagents, see: (a) Yoshida, H.; Yamaryo, Y.; Ohshita, J.; Kunai, A. *Tetrahedron Lett.* **2003**, *44*, 1541. (b) Yoshida, H.; Yamaryo, Y.; Ohshita, J.; Kunai, A. *Chem. Commun.* **2003**, 1510. (c) Li, J. H.; Xie, Y. X.; Yin, D. L. *J. Org. Chem.* **2003**, *68*, 9867; and references cited therein.

(3) (a) Uemura, S.; Wakasugi, M.; Okano, M. *J. Organomet. Chem.* **1980**, *194*, 277. (b) Uemura, S.; Ohe, K.; Kim, J.-R.; Kudo, K.; Sugita, N. *J. Chem. Soc., Chem. Commun.* **1985**, 271. (c) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *326*, 35. (d) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859. (e) Nishibayashi, Y.; Cho, C. S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1996**, *526*, 335. (f) Barton, D. H. R.; Ozbalik, N.; Ramesh, M. *Tetrahedron Lett.* **1988**, *29*, 3533. See also: (g) Bergman, J. *Tetrahedron* **1972**, *28*, 3323. (h) Bergman, J.; Carlsson, R.; Sjöberg, B. *Org. Synth. Coll. Vol. VI* **1988**, 468.

(4) Hirabayashi, K.; Nara, Y.; Shimizu, T.; Kamigata, N. *Chem. Lett.* **2004**, *33*, 1280.

(5) **General Procedure.**
Palladium(II) chloride (0.05 mmol), silver(I) acetate (1.0 mmol), telluronium salt (0.5 mmol) and MeCN (3 mL) were placed in a dry screw-capped glass-tube. After stirring at 50 °C for 6–72 h, the resulting mixture was diluted with Et_2O and passed through silica gel pad. The eluate was washed with 1 M HCl aq, $NaHCO_3$ aq, and brine. The organic layer was dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. The product was obtained in adequate purity. Further purification was performed with flash column chromatography on silica gel.

(6) **XRD Pattern of the Residue:** $2c$ (rel. intensity): 22.430 (746), 23.770 (696), 25.400 (342), 31.760 (159), 38.180 (1402), 39.280 (670), 42.730 (326), 44.380 (408), 46.400 (300), 59.380 (108), 64.500 (368), 77.460 (331).
Ag(0): 38.100 (98), 44.369 (60), 64.177 (43), 77.547 (100).
AgI: 22.337 (98), 23.675 (60), 25.321 (68), 32.775 (42), 39.204 (97), 42.624 (100), 45.584 (14), 46.312 (58), 59.303 (28).

(7) (a) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144. (b) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253. (c) See also: Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.