Available online at www.sciencedirect.com
SCIENCE DIRECT®

Tetrahedron Letters 46 (2005) 8173–8175

Tetrahedron
Letters

An efficient catalyst- and base-free Suzuki-type coupling reaction

Jie Yan,[a,*] Zhongshi Zhou[b] and Min Zhu[b]

[a]College of Chemical Engineering and Materials Sciences, Zhejiang University of Technology, Hangzhou 310032, Zhejiang, PR China
[b]College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou 310015, Zhejiang, PR China

Received 5 August 2005; revised 19 September 2005; accepted 20 September 2005
Available online 10 October 2005

Abstract—Biaryls were prepared in good yields via a fast and efficient catalyst- and base-free Suzuki-type coupling reaction of sodium tetraphenylborate with iodanes in water at room temperature.

The Suzuki reaction is one of the most versatile and utilized reactions for the selective construction of carbon–carbon bonds, in particular for the formation of biaryls.[1] For the development of improved conditions for the Suzuki reaction, a wide range of metal complexes have been used as catalysts in these coupling reactions, attention has particularly been focused on palladium. Recently, Leadbeater and Marco first reported a catalyst-free Suzuki coupling reaction,[2] in which aryl halides reacted with arylboronic acids under microwave irradiation without catalyst and afforded biaryls in good yields (Fig. 1). It was also reported that sodium tetraphenylborate could be used in place of phenylboronic acid as a phenylating agent in the reaction. However, the yields were somewhat low.

The report was very interesting, and we were inspired to wish to find other catalyst-free Suzuki-type coupling reactions to extend the scope of this reaction. In our attempts to find an alternative to halides, we focused our attention on hypervalent iodonium compounds because hypervalent iodonium compounds, in particular, iodonium salts have found synthetic application as powerful electrophilic reagents in the reactions with various nucleophiles,[3] they have also been used to replace aryl halides and triflates in Suzuki reaction under mild conditions and excellent yields have been afforded.[4]

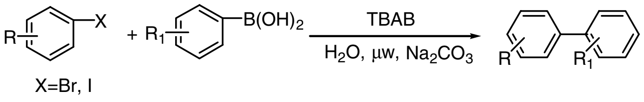
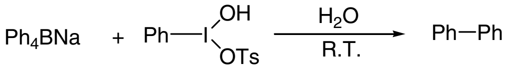


Figure 1.

At the beginning, we found that the catalyst-free Suzuki reactions did not occur when iodonium salts were used to react with phenylboronic acid or sodium tetraphenylborate in water at room temperature or higher temperatures. However, when a readily available iodane, hydroxy(tosyloxy)iodobenzene,[5] referred to as Koser's reagent was used in place of iodonium salts to mix with sodium tetraphenylborate in water at room temperature, a biphenyl was obtained in good yield in a short period of time (Scheme 1).

The result was very exciting, and in order to determine suitable reaction conditions, a series of experiments were performed on the coupling of sodium tetraphenylborate (**1**) with Koser's reagent (**2a**) to form biphenyl (**3a**), we found that when 2 equiv of **1** were used to react with **2a** in water for 0.5 h at room temperature, nearly quantitative biphenyl (**3a**) was formed. Under the optimal reaction conditions, we checked the reactions of a series of typical iodanes stable in water with sodium tetraphenylborate, the results are summarized in Table 1.[6]

It was shown that when Ar was a phenyl with electron-donating group, the yield of **3b** was almost quantitative



$$Ph_4BNa + Ph{-}I(OH)(OTs) \xrightarrow[R.T.]{H_2O} Ph{-}Ph$$

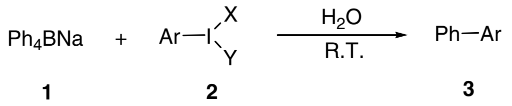
Scheme 1.

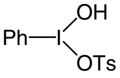
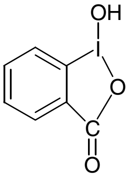
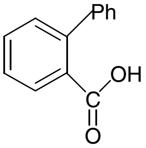
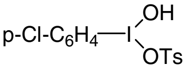
Keywords: Suzuki-type reaction; Sodium tetraphenylborate; Iodanes.

* Corresponding author. Fax: +86 571 88320238; e-mail: jieyan87@hotmail.com

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.09.141

Table 1. The results of the Suzuki reaction of sodium tetraphenylborate with iodanes



Entry	Iodane	Product	Yield (%)[a]
1	**2a**  $PhI(OH)(OTs)$	**3a**[8] Ph–Ph	97
2	**2b** $PhI(OAc)_2$	**3a**	78
3	**2c** $PhI(OCOCF_3)_2$	**3a**	90
4	**2d** Ph–I^+–O–I^+–Ph $2BF_4^-$	**3a**	91
5	**2e** PhI=O	**3a**	55[b]
6	**2f** p-MeO–$C_6H_4I(OAc)_2$	**3b**[9] p-MeO–C_6H_4–Ph	99
7	**2g** p-Cl–$C_6H_4I(OAc)_2$	**3c**[10] p-Cl–C_6H_4–Ph	47
8	**2h** 	**3d**[11] 	90
9	**2i**  $p\text{-Cl-}C_6H_4I(OH)(OTs)$	**3c**	84

[a] Isolated yields.

[b] The reaction was run with sodium tetraphenylborate (2 equiv), iodosylbenzene (1 equiv) and p-TsOH (2 equiv) in water for 0.5 h.

(entry 6), while when Ar was a phenyl with electron-withdrawing group, the yields of **3c** were somewhat lower (entries 7 and 9) compared with **3b** (entry 6) and **3a** (entry 1), respectively. When iodosylbenzene (**2e**) was treated with **1** under the same reaction conditions, the reaction did not occur even when the reaction mixture was stirred for a long time at room temperature or in heating conditions, but after adding 2 equiv of p-TsOH and stirred for 0.5 h, product **3a** was obtained in 55% yield.[7]

Iodonium salts have been used widely in Suzuki reactions. However, few iodanes were used in place of aryl halides and triflates in Suzuki reactions[4a] and to our knowledge, there is no reports about catalyst- and base-free Suzuki coupling reactions of sodium tetraphenylborate with iodanes. The mechanism was probably involved first with nucleophilic substitution of acid radical of iodane by Ph_4B^-, then, an intramolecular coupling reaction was accompanied to yield biaryls. The catalyst-free Suzuki coupling reaction without base has provided a fast and efficient method for preparation of biaryls, it had some advantages such as mild reaction conditions, simple procedure and good yields. Furthermore, the scope of catalyst-free Suzuki coupling reactions could be extended. Further investigation of catalyst-free Suzuki reactions will be reported in due course.

Acknowledgements

Financial support from the Zhejiang Province Natural Science foundation of China (Project Y404016) and Zhejiang Province Education Foundation of China (Project 20040569) is greatly appreciated.

References and notes

1. For recent reviews see: (a) Hassen, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1470; (b) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633–9695; (c) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147–168; (d) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
2. Leadbeater, N. E.; Marco, M. *J. Org. Chem.* **2003**, *68*, 5660–5667.
3. (a) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, 1997; Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179–1255; (b) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123–1178; (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523–2584; (d) Wirth, T.; Hirt, U. H. *Synthesis* **1999**, 1271–1287; (e) Kirschning, A. *Eur. J. Org. Chem.* **1998**, *11*, 2267–2274; (f) Ochiai, M. In *Chemistry of Hypervalent Compounds*; Akibe, K., Ed.; VCH: New York, 1999, Chapter 13, pp 359–387; Ochiai, M. *J. Organomet. Chem.* **2000**, *611*, 494–508; (g) Okuyama, T. *Acc. Chem. Res.* **2002**, *35*, 12–18; (h) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, *54*, 10927–10966; (i) Grushin, V. V. *Chem. Soc. Rev.* **2000**, *29*, 315–324.
4. (a) Kang, S.-K.; Lee, H.-W.; Jang, S.-B.; Ho, P.-S. *J. Org. Chem.* **1996**, *61*, 4720–4724; (b) Kang, S.-K.; Yamagushi, Y.; Kim, T.-H.; Ho, P.-S. *J. Org. Chem.* **1996**, *61*, 9082–9083; (c) Bumagin, N. A.; Luzikova, E. V.; Sukhomlinova, L. I.; Tolstaya, T. P.; Beletskaya, I. P. *Russ. Chem. Bull.* **1995**, *44*, 385–387; (d) Kang, S.-K.; Jung, K.-Y.; Park, C.-H.; Jang, S.-B. *Tetrahedron Lett.* **1995**, *36*, 8047–8050; (e) Moriarty, R. M.; Epa, W. R.; Awashti, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315–6317; (f) Moriarty, R. M.; Epa, W. R. *Tetrahedron Lett.* **1992**, *33*, 4095–4098;

(g) Hinkle, R. J.; Poulter, G. T.; Stang, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 11626–11627.

5. (a) Neiland, O.; Karek, B. *J. Org. Chem USSR (Engl. Trans.)* **1970**, *6*, 889–891; (b) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476–1478.
6. A typical procedure is as follows: sodium tetraphenyl borate (**1**) (342 mg, 1.0 mmol) and hydroxy(tosyloxy)iodobenzene (**2a**) (196 mg, 0.5 mmol) were added in 10 mL H_2O. The mixture was stirred for 0.5 h at room temperature and quenched with brine (5 mL). The mixture was extracted with diethyl ether (20 mL × 3), and the organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by a silica gel plate using hexane as developer and afforded the pure biphenyl (**3a**) (75.0 mg, 97.4%). The spectral and physical data:
   Compound **3a**: mp 68–69 °C (lit.[8] 69–72 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.36 (m, 2H), 7.42–7.46 (m, 4H), 7.58–7.61 (m, 4H); IR (KBr) $\nu = 3035, 1569, 1481, 730\ \text{cm}^{-1}$; MS (70 eV, EI) m/z (%): 154 (M^+, 100); HRMS calcd for $C_{12}H_{10}$ 154.0783, found 154.0779.
   Compound **3b**: mp 86–87 °C (lit.[9] 88 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.96–6.98 (m, 2H), 7.27–7.31 (m, 1H), 7.38–7.42 (m, 4H), 7.51–7.55 (m, 4H); IR (KBr) $\nu = 3068, 3033, 1262, 1035, 835, 761\ \text{cm}^{-1}$; MS (70 eV, EI) m/z (%): 184 (M^+, 100); HRMS calcd for $C_{13}H_{12}O$ 184.0888, found 184.0884.
   Compound **3c**: mp 74–75 °C (lit.[10] 77 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.34 (m, 1H), 7.36–7.39 (m, 2H), 7.40–7.44 (m, 2H), 7.46–7.50 (m, 2H), 7.51–7.55 (m, 2H); IR (KBr) $\nu = 3067, 3035, 1479, 1099, 1005, 833, 760\ \text{cm}^{-1}$; MS (70 eV, EI) m/z (%): 188 (M^+, 100); HRMS calcd for $C_{12}H_9Cl$ 188.0393, found 188.0399.
   Compound **3d**: mp 108–110 °C (lit.[11] 112 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.48 (m, 7H), 7.52–7.55 (m, 1H), 7.89–7.95 (m, 1H), 11.0 (br, 1H); IR (KBr) $\nu = 3400–2400$ (br), 1700, 1685, 1306, 1296 cm^{-1}; MS (70 eV, EI) m/z (%): 198 (M^+, 100); HRMS calcd for $C_{13}H_{10}O_2$ 198.0681, found 198.0677.
7. Ueno, M.; Nabana, T.; Togo, H. *J. Org. Chem.* **2003**, *68*, 6424–6426.
8. Budavari, S.; O'Nell, M. J.; Smith, A.; Hevkelman, P. E. In *The Merck Index*, 11th ed.; Merck and Co.: Rahway, NJ, 1989; p 3314.
9. Beil. **6**, 674.
10. Hey, D. H.; Liang, K. S. Y.; Perkins, M. J.; Williams, G. H. *J. Chem. Soc. (C)* **1967**, 1153.
11. Gassmann, P. G.; Lumb, J. T.; Zalar, F. V. *J. Am. Chem. Soc.* **1967**, *89*, 946–952.