Tetrahedron Letters 58 (2017) 3851–3853

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Borylation of aryldiazonium salts at room temperature in an aqueous solution under catalyst-free conditions

Xinxin Qi [a], Hao-Peng Li [a], Jin-Bao Peng [a], Xiao-Feng Wu [a,b,*]

[a] Department of Chemistry, Zhejiang Sci-Tech University, Xiasha Campus, Hangzhou 310018, People's Republic of China
[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany

ARTICLE INFO

Article history:
Received 19 July 2017
Revised 23 August 2017
Accepted 24 August 2017
Available online 26 August 2017

Keywords:
Green chemistry
Metal-free
Aryldiazonium salt
Arylboronates
Sustainable

ABSTRACT

A general and convenient borylation reaction of aryldiazonium tetrafluoroborate salts with B_2pin_2 has been developed. In this catalytic system, no catalyst, additional ligands or additives were required. The reaction proceeded smoothly in an aqueous solution, and a variety of arylboronates were isolated in moderate to excellent yields under mild reaction conditions.

Introduction

Arylboronic acids and their derivatives play an important role in organic synthesis and have found a wide variety of applications in material science,[1] and medicinal chemisty.[2] Due to their high stability, low toxicity, and easy handling, they are widely used as versatile building blocks in transition-metal-catalyzed C–C bond and C–X bond formation reactions.[3] Thus, synthetic methods for the preparation of arylboronates have been extensively developed in the past few decades. In particular, the reaction of trialkyl borates with lithium or Grignard reagents is one of the most widely used approaches to prepare these boron compounds.[4] However, this method usually suffers from limitations such as requiring rigorously anhydrous conditions and narrow functional group tolerance.[5] Alternatively, the transition-metal-catalyzed borylation reaction has become an effective and popular strategy for the synthesis of arylboronates due to its mild reaction conditions and good substrate compatibility,[6] and a wide range of transition-metal catalysts, including Pd[7], Ni,[8] Cu,[9] Fe,[10] and others,[11] have been explored.

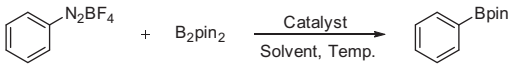
On the other hand, since the end of 20th century, 'Green' processes have become a hot issue in organic synthesis. Thus, the synthesis of arylboronates without transition-metal catalysts has drawn continuous attention and represents a challenge for organic chemists.[12] Ito and co-workers reported the borylation reaction of aryl bromides with a silylborane reagent in the presence of an alkoxy base.[13] The photoinduced borylation of aryl halides with diboron reagents were also independently developed by the groups of Fu, Larionov, and Li.[14] Most recently, Jiao and co-workers disclosed a pyridine-catalyzed borylation of haloarenes with diboron reagents using KOMe as the base.[15] Therefore, the development of an efficient and environmentally friendly catalytic system for arylboronate formation is necessary, important and in high demand. Aryldiazonium tetrafluoroborate salts, which can be easily prepared from readily available aryl amines, are a good alternative to aryl halides and triflates in cross-coupling reactions. Various catalyst systems have been established for their applications in borylation reactions. However, palladium catalysts, light irradiation, organic peroxides, strong base or acid, or high reaction temperature are required.[16] With regard to this background, herein, we describe a general and efficient catalyst-free borylation of aryldiazonium tetrafluoroborate salts with B_2pin_2 in an acetone/H_2O co-solvent under mild reaction conditions.

Recently, gallic acid was reported to activate aryldiazonium salts and applied as a catalyst in cross-coupling reactions with heteroarenes.[17] Thus, we became interested to verify the possibility of using gallic acid as a catalyst in the borylation of aryldiazonium salts. Initially, phenyldiazonium tetrafluoroborate salts and B_2pin_2 were used as model substrates in acetone/H_2O at 20 °C in the presence of catalytic gallic acid. To our delight, the corresponding phenylboronate product was obtained in 82% yield (Table 1, entry 1). Next, various solvents were examined (Entries 2–5);

* Corresponding author at: Department of Chemistry, Zhejiang Sci-Tech University, Xiasha Campus, Hangzhou 310018, People's Republic of China.
E-mail address: xiao-feng.wu@catalysis.de (X.-F. Wu).

http://dx.doi.org/10.1016/j.tetlet.2017.08.060
0040-4039/

Table 1
Screening of reaction conditions.[a]



Entry	Gallic acid (mol%)	Solvent	Temp. (°C)	Yield (%)[b]
1	10	Acetone/H_2O (3/1)	20	82
2	10	Acetone	20	11
3	10	H_2O	20	15
4	10	EtOH	20	13
5	10	EtOH/H_2O (3/1)	20	79
6	10	Acetone/H_2O (2/1)	20	88
7[c]	10	Acetone/H_2O (2/1)	20	99
8[c]	5	Acetone/H_2O (2/1)	20	92
9[c]	20	Acetone/H_2O (2/1)	20	96
10[c]	none	Acetone/H_2O (2/1)	20	89
11[c]	none	Acetone/H_2O (2/1)	20	76
12[c]	none	Acetone/H_2O (2/1)	30	69
13[c]	none	Acetone/H_2O (2/1)	50	63
14[c]	none	Acetone/H_2O (2/1)	10	71

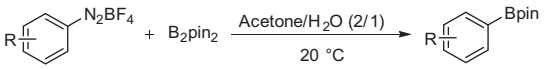
[a] Reagents and conditions: PhN_2BF_4 (0.5 mmol), B_2pin_2 (1 mmol), gallic acid (10 mol%), solvent (4 mL), 1 h.
[b] Yields were determined by GC using dodecane as an internal standard.
[c] B_2pin_2 (1.5 mmol).

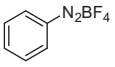
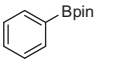
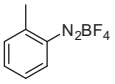
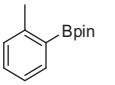
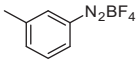
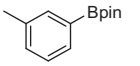
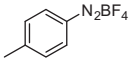
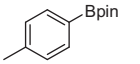
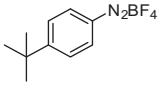
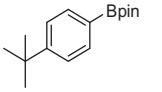
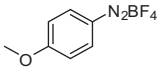
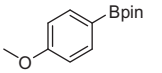
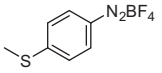
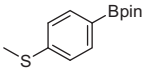
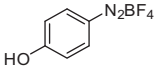
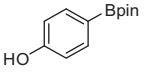
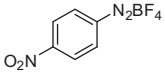
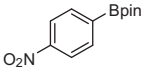
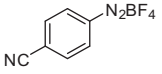
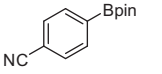
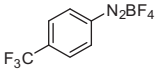
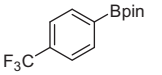
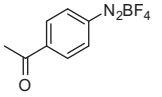
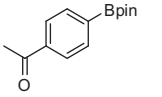
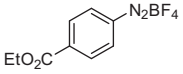
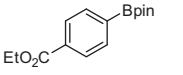
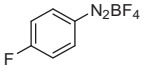
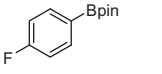
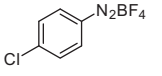
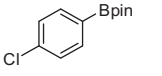
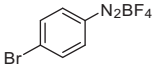
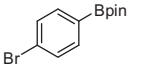
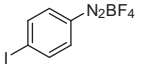
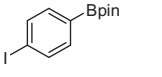
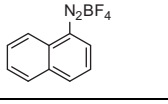
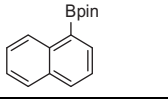
acetone/H_2O was shown to be the best solvent. Furthermore, the ratio of acetone/H_2O was tested and the target product was obtained in 88% yield with a 2/1 ratio (Entry 6). When 3 equivalents of B_2pin_2 were utilized in the reaction, phenylboronate was obtained in 99% yield (Entry 7). Furthermore, different catalyst loadings were tested (Entries 8–10); we found that the reaction outcome is not influenced by this factor. To our surprise, the desired product could also be obtained in 89% yield in the absence of gallic acid (Entry 10). Therefore, we turned our attention to this new catalyst-free borylation system. We found 20 °C to be the best reaction temperature for this transformation and the yields decreased when the temperature was changed to 10, 30 or 50 °C (Entries 12–14).

With the optimal reaction conditions in hand,[18] we continued our investigation with regard to the substrate scope of this transformation using a variety of aryldiazonium tetrafluoroborate salts (Table 2). Substrates with electron-rich groups, such as methyl, *tert*-butyl, methoxy, methylthio, and hydroxyl groups, gave the desired products in moderate to good yields (Entries 2–8). Those with methyl groups substituted at the *para*-position worked better than at the *ortho*- and *meta*- positions (Entries 2–3 *vs.* 4). Electron-deficient groups, including nitro, cyano, trifluoromethyl, ketone, and ester groups, also provided the corresponding arylboronate products in very good yields (Entries 9–13). Remarkably, aryldiazonium tetrafluoroborate salts with halogen substitutions also worked well and afforded the corresponding products in moderate to good yields (Entries 14–17). The halogen groups in the products are important functional group in cross-coupling chemistry. It was noteworthy that the naphthyl group was also well tolerated and gave the desired product in 68% yield (Entry 18). It is important to note that the reaction was totally shut down by the addition of TEMPO or BHT (2 equiv.).

In conclusion, a catalyst-free borylation of aryldiazonium tetrafluoroborate salts with B_2pin_2 in an aqueous solution has been explored. Under mild reaction conditions, moderate to excellent yields of the desired arylboronate products were obtained, and a wide range of functional groups are tolerated.

Table 2
Borylation of aryldiazonium tetrafluoroborate salts with B_2pin_2.[a]



Entry	Substrate	Product	Yield (%)[b]
1			59
2			43
3			46
4			57
5			54
6			48
7			81
8			80
9			66
10			71
11			60
12			74
13			87
14			58
15			68
16			72
17			55
18			68

[a] Reagents and conditions: ArN_2BF_4 (0.5 mmol), B_2pin_2 (1.5 mmol), acetone/H_2O (2/1, 4 mL), 20 °C, 1–2 h.
[b] Isolated yields.

Acknowledgments

The authors thank the financial supports from NSFC (21472174, 21602201, 21602204) and Zhejiang Natural Science Fund for Distinguished Young Scholars (LR16B020002). X.-F. Wu appreciates the general support from Professors Matthias Beller and Armin Börner in LIKAT.

A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2017.08.060.

References

1. a Lorbach A, Huebner A, Wagner M. *Dalton Trans*. 2012;41:6048–6063;
   b Jäkle F. *Top Organomet Chem*. 2015;49:297–325.
2. a Beenen MA, An C, Ellman JA. *J Am Chem Soc*. 2008;130:6910–6911;
   b Milo LJ, Lai Jr JH, Wu W, et al. *J Med Chem*. 2011;54:4365–4377;
   c Einsele H. *Recent Results Cancer Res*. 2010;184:173–187;
   d Trippier PC, McGuigan C. *MedChemComm*. 2010;1:183–198;
   e Ban HS, Nakamura H. *Chem Rec*. 2015;15:616–635.
3. a Jana R, Pathak TP, Sigman MS. *Chem Rev*. 2011;111:1417–1492;
   b Rudolph A, Lautens M. *Angew Chem Int Ed*. 2009;48:2656–2670;
   c Imao D, Glasspoole BW, Laberge VS, Crudden CM. *J Am Chem Soc*. 2009;131:5024–5025;
   d Frisch AC, Beller M. *Angew Chem Int Ed*. 2005;44:674–688;
   e Miyaura N, Suzuki A. *Chem Rev*. 1995;95:2457–2483;
   f Yamaguchi J, Yamaguchi AD, Itami K. *Angew Chem Int Ed*. 2012;51:8960–9009;
   g Xu L, Zhang S, Li P. *Chem Soc Rev*. 2015;44:8848–8858.
4. a Zweifel G, Brown HC. *Org. React.*. 1963;13:1–54;
   b Brown HC, Cole TE. *Organometallics*. 1983;2:1316–1319;
   c Brown HC, Srebnik M, Cole TE. *Organometallics*. 1986;5:2300–2303.
5. a Pintaric C, Olivero S, Gimbert Y, Chavant PY, Duñach E. *J Am Chem Soc*. 2010;132:11825–11827;
   b Baron O, Knochel P. *Angew Chem Int Ed*. 2005;44:3133–3135.
6. Chow WK, Yuen OY, Choy PY, et al. *RSC Adv*. 2013;3:12518–12539.
7. a Chow WK, So CM, Lau CP, Kwong FY. *Chem Eur J*. 2011;17:6913–6917;
   b Molander GA, Trice SLJ, Dreher SD. *J Am Chem Soc*. 2010;132:17701–17703;
   c Tang W, Keshipeddy S, Zhang Y, et al. *Org Lett*. 2011;13:1366–1369;
   d Kawamorita S, Ohmiya H, Iwai T, Sawamura M. *Angew Chem Int Ed*. 2011;50:8363–8366;
   e Molander GA, Trice SLJ, Kennedy SM. *Org Lett*. 2012;14:4814–4817;
   f Molander GA, Trice SLJ, Kennedy SM. *J Org Chem*. 2012;77:8678–8688;
   g Chow WK, Yuen OY, So CM, Wong WT, Kwong FY. *J Org Chem*. 2012;77:3543–3548;
   h Molander GA, Trice SLJ, Kennedy SM, Dreher SD, Tudge MT. *J Am Chem Soc*. 2012;134:11667–11673;
   i Guerrand HDS, Marciasini LD, Jousseaume M, Vaultier M, Pucheault M. *Chem Eur J*. 2014;20:5573–5579;
   j Pandarus V, Marion O, Gingras G, Béland F, Ciriminna R, Pagliaro M. *ChemCatChem*. 2014;6:1340–1348;
   k Xu L, Li P. *Chem Commun*. 2015;51:5656–5659;
   l Smith KB, Logan KM, You W, Brown MK. *Chem Eur J*. 2014;20:12032–12036;
   m Bhanuchandra M, Baralle A, Otsuka S, Nogi K, Yorimitsu H. *Org Lett*. 2016;18:2966–2969;
   n Dzhevakov PB, Topchiy MA, Zharkove DA, Morozov OS, Asachenko AF, Nechaev MS. *Adv Synth Catal*. 2016;358:977–983.
8. a Wilson V, Wilson CJ, Moldoveanu C, et al. *J Am Chem Soc*. 2010;132:1800–1801;
   b Moldoveanu C, Wilson DA, Wilson CJ, et al. *J Org Chem*. 2010;75:5438–5452;
   c Yamamoto T, Morita T, Takagi J, Yamakawa T. *Org Lett*. 2011;13:5766–5769;
   d Huang K, Yu D-G, Zheng S-F, Wu Z-H, Shi Z-J. *Chem Eur J*. 2011;17:786–791;
   e Molander GA, Cavalcanti LN, García-García C. *J Org Chem*. 2013;78:6427–6439;
   f Liu X-W, Echavarren J, Zarate C, Martin R. *J Am Chem Soc*. 2015;137:12470–12473;
   g Hu J, Sun H, Cai W, Pu X, Zhang Y, Shi Z. *J Org Chem*. 2016;81:14–24.
9. a Lin Z, Marder TB. *Angew Chem Int Ed*. 2009;48:5350–5354;
   b Grigg RD, Van Hoveln R, Schomaker JM. *J Am Chem Soc*. 2012;134:16131–16134;
   c Labre F, Gimbert Y, Bannwarth P, Olivero S, Duñach E, Chavant PY. *Org Lett*. 2014;16:2366–2369;
   d Ando S, Matsunaga H, Ishizuka T. *J Org Chem*. 2015;80:9671–9681;
   e Niwa T, Ochiai H, Watanabe Y, Hosoya T. *J Am Chem Soc*. 2015;137:14313–14318;
   f Zhang J, Wang X, Yu H, Ye J. *Synlett*. 2012;23:1394–1396.
10. a Marciasini LD, Richy N, Vaultier M, Pucheault M. *Adv Synth Catal*. 2013;355:1083–1088;
    b Bedford RB, Brenner PB, Carter E, et al. *Organometallics*. 2014;33:5767–5780.
11. a Adams CJ, Baber RA, Batsanov AS, et al. *Dalton Trans*. 2006;11:1370–1373;
    b Frank R, Howell J, Campos J, et al. *Angew Chem Int Ed*. 2015;54:9586–9590;
    c Zhang L, Peng D, Leng X, Huang Z. *Angew Chem Int Ed*. 2013;52:3676–3680;
    d Zhang L, Zuo Z, Wan X, Huang Z. *J Am Chem Soc*. 2014;136:15501–15504;
    e Zhang L, Zuo Z, Leng X, Huang Z. *Angew Chem Int Ed*. 2014;53:2696–2700;
    f Zhang L, Huang Z. *J Am Chem Soc*. 2015;137:15600–15603;
    g Jia X, Huang Z. *Nat Chem*. 2016;8:157–161;
    h Yao W, Fang H, Peng S, Wen H, Zhang L, Hu A. *Organometallics*. 2016;35:1559–1564;
    i Nagashima Y, Takita R, Yoshida K, Hirano K, Uchiyama M. *J Am Chem Soc*. 2013;135:18730–18733;
    j Bose SK, Fucke K, Liu L, Steel PG, Marder TB. *Angew Chem Int Ed*. 2014;53:1799–1803;
    k Bose SK, Marder TB. *Org Lett*. 2014;16:4562–4565.
12. a Cid J, Gulyás H, Carbó JJ, Fernández E. *Chem Soc Rev*. 2012;41:3558–3570;
    b Dewhurst RD, Neeve EC, Braunschweig H, Marder TB. *Chem Commun*. 2015;51:9594–9607.
13. a Yamamoto E, Izumi K, Horita Y, Ito H. *J Am Chem Soc*. 2012;134:19997–20000;
    b Uematsu R, Yamamoto E, Maeda S, Ito H, Taketsugu T. *J Am Chem Soc*. 2015;137:4090–4099;
    c Yamamoto E, Ukigai S, Ito H. *Chem Sci*. 2015;6:2943–2951.
14. a Chen K, Zhang S, He P, Li P. *Chem Sci*. 2016;7:3676–3680;
    b Mfuh AM, Doyle JD, Chhetri B, Arman HD, Larionov OV. *J Am Chem Soc*. 2016;138:2985–2988;
    c Mfuh AM, Nguyen VT, Chhetri B, et al. *J Am Chem Soc*. 2016;138:8408–8411;
    d Jiang M, Yang H, Fu H. *Org Lett*. 2016;18:5248–5251;
    e Chen K, Cheung MS, Lin Z, Li P. *Org Chem Front*. 2016;3:875–879.
15. Zhang L, Jiao L. *J Am Chem Soc*. 2017;139:607–610.
16. a Mo F, Dong G, Zhang Y, Wang J. *Org Biomol Chem*. 2013;11:1582–1593;
    b Zhu C, Yamane M. *Org Lett*. 2012;14:4560–4563;
    c Yu J, Zhang L, Yan G. *Adv Synth Catal*. 2012;354:2625–2628;
    d Mo F, Jiang Y, Qiu D, Zhang Y, Wang J. *Angew Chem Int Ed*. 2010;49:1846–1849;
    e Qiu D, Jin L, Zheng Z, et al. *J Org Chem*. 2013;78:1923–1933;
    f Erb W, Hellal A, Albini M, Rouden J, Blanchet J. *Chem Eur J*. 2014;20:6608–6612.
17. Perretti MD, Monzón DM, Crisóstomo FP, Martín VS, Carrillo R. *Chem Commun*. 2016;52:9036–9039.
18. *General procedure:* Diazonium tetrafluoroborate salts (0.5 mmol) and B_2pin_2 (1.5 mmol) were transferred into an oven-dried tube under air. Then, acetone/H_2O (2/1, 4 mL) were added into the tube *via* syringe. The sealed tube was kept at 20 °C and stirred for 1–2 h. Upon reaction completion, dichloromethane was added to extract the product and the combined organic extracts were dried with Na_2SO_4. The pure product was isolated after column chromatography on silica gel (petroleum ether/ethyl acetate).