International Journal for Multidisciplinary Research (IJFMR)
E-ISSN: 2582-2160 ● Website: www.ijfmr.com ● Email: editor@ijfmr.com

Benzoic Acid as an Efficient Catalyst for Synthesis of Phenols

Balaji P. Kotkar

Adarsh Education Society's Arts, Commerce and Science College, Akola Road, Hingoli – 431513.

Abstract

A straightforward synthesis of phenols from aryl boronic acids has been demonstrated using benzoic acid as a catalyst. Variety of arylboronic acids bearing electron rich and electron withdrawing substituents gave the respective phenols in good yields.

Keywords: Arylboronic acid; Phenol; Benzoic Acid; *ipso*-Hydroxylation

Introduction

Phenol and its derivatives are versatile intermediates in agrochemicals, pharmaceuticals, polymers and different natural products.The classical methods for the syntheses of phenols involves Dow's process, Hock's process[1] and hydrolysis of diazonium salts[2]. Unfortunately, these processes suffered from harsh reaction conditions and inferior yield. Therefore, in last few decades, due to versatile nature, easy availability and greater stability arylboronic acids are explored as a new synthetic precursor for the synthesis of phenol.

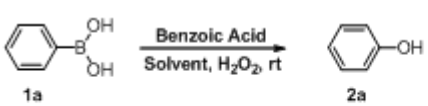
In past decade, various protocols were reported for the synthesis of phenol from arylboronic acid and the catalysts used were $CuSO_4$-phenanthroline,[3] KOH-TBHP,[4]benzoquinones,[5] organic hypervalent iodine (III),[6] $NaClO_2$,[7] N-oxides,[8]I_2-$H2O_2$,[9] H_3BO_4-H_2O_2,[10] Al_2O_3-H_2O_2,[11] lactic acid-H_2O_2,[12], Amberlite IR 120 resin,[13] supported silver nano particle,[14]etc. However, these methods are associated with certain unavoidable drawbacks such as use of transition metal catalysts, base additive, ligands, high reaction temperatures, excess oxidizing agent and toxic organic solvents.Therefore, to avoid such drawbacks, there is a serious need for more simple and convenient protocols toward the *ipso*-hydroxylation of arylboronic acids under mild reaction conditions.

Herein, we report simple and efficient route for benzoic acidcatalyzed oxidative hydroxylation of arylboronic acids using H_2O_2 as oxidant.

Results and discussion

Table 1

Benzoic Acid Catalyzed*ipso*-Hydroxylation of Boronic Acid

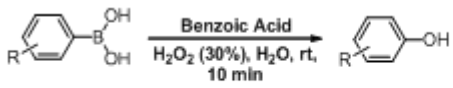


Entry	Benzoic acid (mg)	H_2O_2 (ml)	Solvent (2ml)	Time (min)	Yield (%)[b]
1	50	-	H_2O	60	-
2	-	0.50	H_2O	60	25
3	50	0.50	H_2O	15	96
4	20	0.50	H_2O	15	96
5	10	0.50	H_2O	15	87
6	20	0.50	$CHCl_3$	60	15
7	20	0.50	THF	60	25
8	20	0.50	Diethyl ether	60	65
9	20	0.50	CH_3CN	15	66
10	20	0.25	H_2O	15	81

[a] Reaction condition: Phenylboronic acid (1 mmol), H_2O_2 (30% aq), Benzoic acid catalyst.

[b] Isolated yields.

Table 2 Substrate scope[a]



Entry	R	Yield[b](%)
1	H	95
2	*p*-Me	94
3	*p*-OMe	90
4	*o*-Me	91
5	*p*-NO_2	94
6	*p*-NH_2	93
7	*p*-Cl	89
8	α-Naphthol	93
9	β-Naphthol	91
10	*p*-OH	92
11	*p*-CHO	90
12	*p*-$COCH_3$	95
13	*m*-CN	93
14	*p*-I	92

[a] Reaction conditions: Arylboronic acid (1 mmol), 30% H_2O_2 (0.5 mL), Benzoic acid (20 mg) in water (2 ml) at room temperature.

[b] Isolated yield.

Herein, the potentiality of benzoic acid is investigated using commercially available phenylboronic acid (1a) as a model substrate and subjected for oxidative hydroxylation with H_2O_2 in various solvents (Table 1). The precise quantity of the benzoic acid required to achieve maximum yield was screened and found that 20 mg is enough to attain the complete conversion (Table 1, entry 4). When we have used 20 mg of benzoic acid as catalyst and we obtained 96% of isolated yield (Table 1, entry 4). By lowering the catalyst loading to 10 mg resulted a lower yield (87%) (Table 1, entry 5). However, increase in the catalyst loading to 50 mg did not significantly improve the yield (Table 1, entry 3). Among the various solvents, only water provided the desired phenol in aquantitative yield (96%) within 15 min (Table 1, entry 4) while in chloroform, tetrahydrofuran (THF), diethyl ether and acetonitrile the reaction did not go to completion after prolonged reaction time (Table 1, entries 6–9).

With the optimized reaction conditions in hand, we next examined the substrate scope of this benzoic acid-initiated ipso hydroxylation of structurally and electronically diverse arylboronic acids with H_2O_2 (Table 2). Arylboronic acids bearing electron withdrawing groups such as -NO_2, -Cl, -CHO, -$COCH_3$, -CN and electron donating groups like -Me, -OMe, -NH_2, -OH, -I were used and provided the desired phenols in good yields irrespective of their positions. Results are summarized in the table 2.

Conclusion

In the present work, we have disclosed benzoic acid as versatile, inexpensiveand commercially available reagent for the hydroxylation of organoboronic acid to phenols in the presence of H_2O_2.A variety of electronically diverse arylboronic acids were transformed to the corresponding phenols in good yields.We believe that this environment friendly protocol can be useful to industrial scale phenol synthesis.

General procedure for ipso hydroxylation: To a stirred solution of phenylboronic acid (entry 1) (1 mmol) in water (2 mL) was added benzoic acid (20 mg). To the above mixture was added hydrogen peroxide (0.5 mL) and stirred at room temperature for 15 min. After completion, the reaction mixture was diluted with water and extracted with ethylacetate (3 x 10 mL). The ethylacetate layer was washed with brine and concentrated under reduced pressure to give the product (96%).

Spectral data of some selected phenols

Phenol: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (d, *J* = 8Hz, 2H), 6.85 (d, *J* = 8Hz, 3H), 4.22 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.5, 129.4, 120.9, 115.2

4-Nitrophenol:^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.15 (d, *J* = 8Hz, 2H), 6.91 (d, *J* = 8Hz, 2H), 5.95 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.9, 141.7, 126.4, 115.7

4-chlorophenol: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.19 (d, *J* = 8Hz, 2H), 6.74 (d, *J* = 8Hz, 2H), 5.21 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.7, 129.1, 125.9, 116.9

4-hydroxybenzaldehyde ^{1}H NMR (DMSO, 400 MHz) δ 10.54 (s, 1H), 9.79 (s, 1H), 7.84 – 7.69 (m, 2H), 7.01 – 6.80 (m, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ 190.97, 163.32, 132.15, 128.45, 115.91.

References

1. H. Hock, S. Lang, *Ber. Dtsch. Chem. Ges. B***1944**, 77, 257–264.
2. J. P. Lambooy, *J. Am. Chem. Soc*., **1950**, 72, 5327–5328

3. J. Xu, X. Wang, C. Shao, D. Su, G. Cheng, Y. Hu, *Org Lett*. **2010**, 12, 1964–1967.
4. S. Guo, L. Lu, H. Cai, *Synlett*. **2014**, 24, 1712–1714.
5. K.Ohkubo, K. Hirose and S. Fukuzumi, *Chem. – Eur. J*., **2015**, 21, 2855–2861;.
6. N. Chatterjee, A. Goswami, *Tetrahedron Lett*. **2015**, 56, 1524-1527.
7. P. Gogoi, P. Bezboruah, J. Gogoi and R. C. Boruah, *Eur. J. Org.Chem*., **2013**, 7291-7294.
8. Zhu C, Wang R, Falck JR. *Org Lett*. **2012**, 14, 3494–3497.
9. A. Gogoi, U. Bora, *Synlett***2012**, 1079-1081.
10. K. Gogoi, A. Dewan, A. Gogoi, G. Borah, U. Bora, *HeteroatomChem*. **2014**, 25, 127-130.
11. A. Gogoi, U. Bora, *Tetrahedron Lett*. **2013**, 54, 1821-1823.
12. 12. S. Gupta, P. Chaudhary, L. Seva, S. Sabiah, J. Kandasamy, *RSC Adv*. **2015**, 5, 89133-89138.
13. Mulakayala, N.; Ismail; Kumar, K. M.; Rapolu, R. K.; Kandagatla,B.; Rao, P.; Oruganti,S.; Pal, M. *Tetrahedron Lett*. **2012**, *53*,6004-6007.
14. Begum,T.;Gogoi, A.; Gogoi, P. K.; Bora, U. *Tetrahedron Lett*.http://dx.doi.org/10.1016/j.tetlet.2014.11.018