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FULL PAPER

A green alternative for the conversion of arylboronic acids/esters into phenols promoted by a reducing agent, sodium sulphite

Willber D. Castro-Godoy[a], Luciana C. Schmidt[a]* and Juan E. Argüello[a]*

Abstract: Hydroxylation of arylboronic acids and arylboronic esters using sodium sulphite and oxygen as the source of ultimate oxidant proceeds rapidly in water under transition metal-free conditions. This remarkable mild and environmentally benign protocol represents a green alternative to synthesize phenols using inexpensive starting material in a simple methodology. This new application for sodium sulphite shows a wide tolerance of functional groups, and it is compatible with oxidizable functionalities.

Introduction

The synthesis of phenols and related aromatic moieties has attracted attention due to their importance as structural constituents of pharmaceutical compounds, polymers, and natural products.[1]

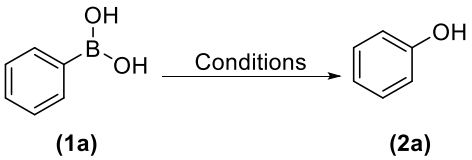
Different approaches can be taken for the preparation of phenolic compounds. Among these, we can mention: i) nucleophilic substitution of aryl halides by hydroxyl group, ii) diazotization of aromatic amines followed by aqueous hydrolysis, iii) C-H aryl ring oxidation and iv) oxidative hydrolysis of arylboronic acids. Recently, due to easy availability, low toxicity and high stability (towards heat, air and humidity) of the precursor arylboronic acids,[2] the synthesis of phenols from arylboronic acids has become increasingly attractive when compared with other methods. As a result, a growing interest in the use of arylboronic acids in a wide range of organic transformations has been reported.[3]

In the last decades the use of arylboronic acids has been described as starting material to give access to phenols that might be difficult to obtain by other methods. Most of the described systems require transition metal catalysts such as palladium complex,[4] copper[5] or iron salts.[6] However, environmentally benign transition metal-free methodologies are preferred. As alternatives, many protocols require an excess of strong oxidants such as hydrogen peroxide,[7] *meta*-chloroperoxybenzoic acid,[8] ammonium persulfate,[9] organic hypervalent iodine,[10] sodium chlorite,[11] N-oxides[12] or oxone®.[13] Although the synthesis of phenols from arylboronic acids has been performed using photo-redox catalysis[14] and electrocatalysis[15] in the presence of molecular oxygen as ultimate oxidant, these approaches require several hours to achieve full conversion. Also, phenols can be obtained using different reducing agents such as thiol[16] and hydrazine derivatives.[17] Recently, the hydroxylation of arylboronic acids mediated by a mild reducing agent -sodium ascorbate- in DMF at room temperature has been reported. But this procedure requires 18 h for a full conversion.[18] In this context, the development of greener reactions for the synthesis of phenols and other aromatic analogues in water using oxygen as the oxidant, shorter reactions times, odorless and non-toxic reagents are highly desirable.

Herein we report, for the first time, an efficient and cost-effective metal-free method for the synthesis of substituted phenols from arylboronic acids in water under mild reaction conditions. Also, we describe a new application for sodium sulphite as reducing agent in the hydroxylation of arylboronic acids reaction, oxygen as ultimate oxidant avoiding conventional oxidant reagents.

Results and Discussion

In order to set the optimums reaction conditions, phenylboronic acid (**1a**, 12,2 mg, 0.1 mmol), sodium sulphite (37.8 mg, 0.3 mmol), air as oxygen source in water and 4 h reaction time were selected as starting settings (scheme 1). Under these conditions, phenol (**2a**) was obtained just in 14% yield (table 1, entry 1). At oxygen saturated atmosphere, **2a** was obtained in 50% and 59% yield using 0.3 and 0.5 mmol of Na_2SO_3 respectively at a 60 min reaction time (table 1, entries 2 and 3). Between these results, 0.5 mmol of Na_2SO_3 was preferred.



Scheme 1. Hydroxylation of phenylboronic acid reaction

The effect of temperature was also screened in order to reduce the reaction time; however, it is necessary to consider a balance between reaction temperature and oxygen solubility because an increase in temperature results in a decrease in its solubility. Based on the reported data, at 50°C oxygen solubility is 5.6 mg/L, which is still enough to run the reaction.[19] Then, conventional heating bath and microwave systems at 50°C afford phenol from

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phenylboronic acid in 46 and 36% yield respectively (table 1, entries 4 and 5). Additionally, this system was tested with oxygen bubbling raising the reaction yield to 94% in 0.5 h (table 1, entry 6). This condition cannot be set using commercial microwave reactor; therefore, conventional heating was preferred to broaden the use of this methodology. A slight increase in reaction temperature speeds up the reaction and very good yields of **2a** were obtained at shorter reaction times. Nevertheless, a 5 h reaction time was enough for a full conversion at room temperature (**2a**, 96% table 1, entry 7). Finally, the reaction in inert atmosphere (N_2) did not result in any product, **2a** was not detected with the quantitative recovery of **1a** (table 1, entry 8). The reaction evolution was followed by ^{1}H-NMR (see Figure S1 in the Supporting Information for a representative experiment).

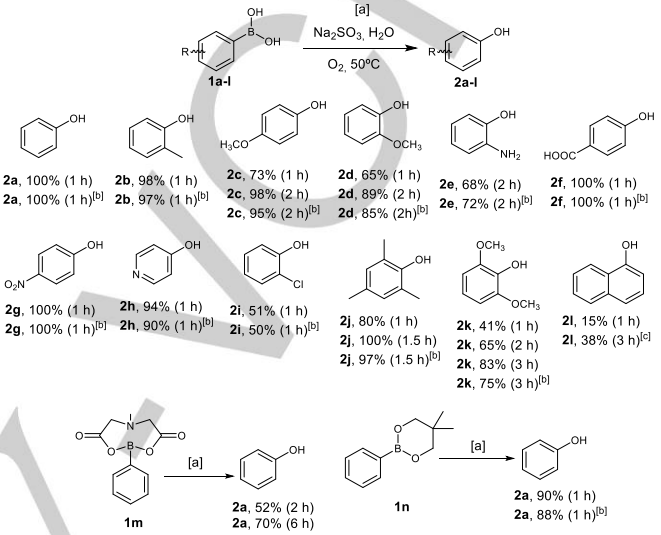
Table 1. Reaction condition optimization for the transformation of phenylboronic (**1a**) acid to phenol (**2a**).

Entry[a]	Sodium sulphite (mmol)	Time (h)	Temperature (ºC)	Atmosphere	Yield **2a** (%)
1	0.3	4	r.t.	Air	14
2	0.3	1	r.t.	Oxygen saturated	50
3	0.5	1	r.t.	Oxygen saturated	59
4[b]	0.5	0.5	50	Oxygen saturated	46
5[c]	0.5	0.17	50	Oxygen saturated	36
6[b]	**0.5**	**0.5**	**50**	**Oxygen bubbling**	**94**
7	**0.5**	**5**	**r.t.**	**Oxygen saturated**	**96**
8[b]	0.5	0.5	50	Nitrogen	0

[a] Reaction Conditions: phenylboronic acid (**1a**, 12.2 mg, 0.1 mmol), water (5 mL), for room temperature experiments acetonitrile (150 μl) was used as a co-solvent. r.t = room temperature. [b] Conventional heating bath. [c] 10 min. microwave irradiation in close system. Yields determined by ^{1}H-NMR from the reaction crude mixture using the internal standard method.

The synthetic scope of the system was studied under the optimized reaction conditions, 0.5 mmol of Na_2SO_3, oxygen bubbling and 50°C reaction temperature in water. The results are summarized in Scheme 2.

As shown in scheme 2, arylboronic acids with electron donating substituents (**1b**, **1c, 1d** and **1e**) were effectively converted into the corresponding phenols (**2b**, **2c, 2d** and **2e**), in very good yields (72-98%). For substrates with electron-withdrawing groups (**1f**, **1g, 1h** and **1i**) the corresponding phenols (**2f**, **2g, 2h** and **2i**) were obtained in very good to excellent yields (94-100%). In addition, a small decrease in the reactivity by *ortho* methyl substitution was observed at one-hour reaction time, where phenylboronic acid was as reactive as *ortho*-methyl phenylboronic acid and slightly more reactive than mesityl boronic acid (**1a** ≈ **1b** > **1j**). Otherwise, when comparing methoxy substituted phenylboronic acid the following reactivity order was observed: **1a** > **1c** > **1d** > **1k**, where the disubstituted *ortho*-methoxy phenylboronic acids is the less reactive, in all cases measured at one-hour reaction time (see Scheme 1). However, the reaction time was optimized for each arylboronic acid in order to maximize the reaction yield for preparative purposes.

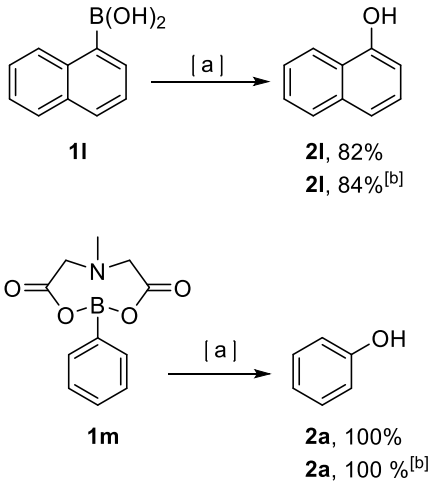


Scheme 2. Reaction Scope for the hydroxylation of arylboronic acid and esters. [a] Reaction Conditions: arylboronic acid (**1**, 0.1 mmol), sodium sulphite (63 mg, 0.5 mmol) oxygen bubbling, water (5 mL), conventional heating (50ºC). Reaction time is indicated between brackets. Yields determined by ^{1}H-NMR of the reaction crude mixture using the internal standard method. [b] isolated yields. [c] 0.5 mmol of sodium sulphite added in 5 aliquots of 0.1 mmol every 30 min.

ortho-chlorophenylboronic acid (**1i**) produced the corresponding phenol **2i** in just a 51% yield, even at longer reaction times this result could not be improved. Unfortunately, when exploring an extended π system such as 1-naphthylboronic acid (**1l**), a low yield of the corresponding phenol (15%, **2l**) was obtained in one hour. This result remained unchanged even at longer reaction times. The yield of 1-naphthol could be slightly improved (38%) by the addition of 0.1 mmol of sulphite salt every half an hour (Scheme 2). Summarizing, this reaction procedure proved to be useful for arylboronic acid bearing electron donor, electron neutral and electron withdrawing groups, and even nitro substituted derivative was effective. The work-up was very simple and involves water dilution, acidification and organic solvent extraction. Moreover, side products which are mainly inorganic salts remain in water while phenols were isolated from the organic phase. Nevertheless, a very clean reaction profile could be observed from the NMR crude reaction.

Finally, the substrate scope of this methodology was extended to arylboronic esters, where this protocol proved to be also effective in the hydroxylation of phenylboronic acid *N*-methyliminodiacetate (MIDA) ester (**1m**), or phenylboronic acid neopentyl glycol ester (**1n**). In both cases phenol (**2a**) was obtained in 70% and 90% yields respectively (Scheme 2).

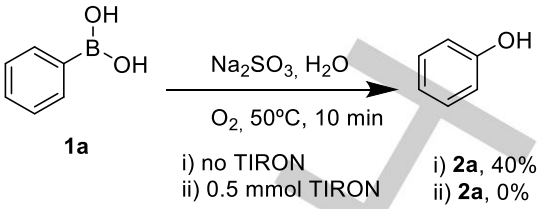
Phosphate anion is able to coordinate to arylboronic acids, the former and the latter act as Lewis's base and acid respectively. This complex improves the leaving character of the boronic group.[20] Within the scope of this study, a new modification was developed by the addition of K_3PO_4 in the reaction. Under this condition, yields of 1-naphthol and phenol were remarkably increased, 82% and 100% were obtained from **1l** and **1m** respectively (Scheme 3). On the other hand, **1l** and **1m** are not reactive in the presence of K_3PO_4 alone.



Scheme 3. Effect of potassium phosphate as additive. [a] Reaction Conditions: arylboronic acid and ester (**1**, 0.1 mmol), sodium sulphite (63 mg, 0.5 mmol), potassium phosphate (21.2 mg, 0.1 mmol), oxygen bubbling, water (5 mL), conventional heating (50ºC), 6 h. Yields determined by ^{1}H-NMR from the reaction crude mixture using the internal standard method. [b] isolated yields.

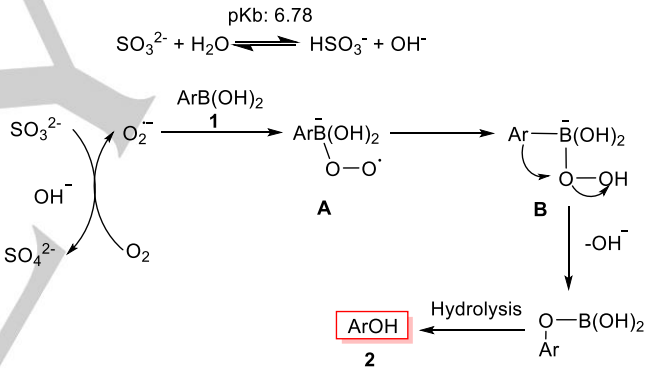
Water soluble sodium sulphite is able to convert arylboronic acids to phenols under very mild conditions. The reducing properties of SO_3^{2-} have been widely exploited as an antioxidant agent;[21] its oxidation to sulfate anion (SO_4^{2-}) at the expense of molecular oxygen is thermodynamically favored.[22] In this reaction, oxygen reactive species are formed, namely superoxide anion, which ultimately oxidizes aryl boronic acids to their corresponding phenols.[23]

The most common arylboronic acids oxidation reactions proceed through reactive oxygen species. Typically, these reactions involve the in-situ generation of $O_2^{\bullet-}$ or H_2O_2 that are able to produce the oxidation reaction.[24] In order to evaluate the presence of reactive oxygen species in the reaction media TIRON (sodium 4,5-dihydroxybenzene-1,3-disulfonate) has been used as a superoxide radical anion scavenger.[25] TIRON effectively inhibits the formation of phenol from phenyl boronic acid (Scheme 4), which indicates the mediation of reactive oxygen species, mainly super oxide anion.



Scheme 4. Inhibition reaction using TIRON.

Considering these last results and based in previous reports,[14h] the plausible reaction mechanism is depicted in Scheme 5. The sulphite anion in aqueous solution is colorless, basic (pK_b SO_3^{2-} = 6.78), reducing and unstable, the atmospheric oxygen is enough to be oxidized to sulfate.[22] In this context, sulphite anion is able to form reactive oxygen species like $O_2^{\bullet-}$, which would be responsible for the final oxidation of arylboronic acids (**1**) to phenols (**2**). This radical anion reacts with arylboronic acid (**1**) forming intermediate **A** which is further reduced to intermediate **B**. Rearrangement of **B** subsequent by hydrolysis leads to the final product phenol (**2**) after the acid-workup.



Scheme 5. Proposed reaction mechanism.

To ensure that our protocol was a green alternative for the conversion of arylboronic acids and esters to phenols, we analyzed the sustainability of this methodology. *EcoScale*[26] and *Green Star*[27] semi-quantitative analysis tools were used in order to evaluate the quality of the overall preparation and to compare different sets of preparations of phenols. Results show that the present methodology could be considered ecofriendly. Likewise, it represents a suitable, efficient and inexpensive metal-free method for the synthesis of substituted phenols from arylboronic acids and esters. (for further details see Supporting Information)

Conclusions

Summing up, we have developed a new environmentally friendly methodology for the synthesis of phenols from the corresponding

arylboronic acids or arylboronic esters with very good to excellent yields in short reaction times. This methodology is free of strong bases, transition metals and strong oxidant such hydrogen peroxide, involves the use of the greenest solvent, i.e., water, generating less toxic waste which is highly valuable in organic synthesis from the green chemistry point of view. In addition, Na_2SO_3 is inexpensive, easy to use and it is also considered non-toxic reagent.

This new reaction protocol takes advantage of the reducing properties of Na_2SO_3 which is able to generate reactive oxygen species in aqueous medium; once formed, superoxide anion efficiently converts arylboronic acids to phenols both at room temperature and at 50°C more quickly.

Experimental Section

Materials and Methods

Arylboronic acids were obtained from Aldrich Chemical Co. Reagents and solvents were of the highest quality available and used as received. All products are known compounds and were characterized by comparison with published NMR data. NMR spectra were recorded at 400 MHz, chemical shift in ppm relative to residual signal of deuterated solvent.

General Procedure for the Hydroxylation of Arylboronic Acids and Esters: A reaction flask equipped with a magnetic stirring bar was charged with 0.1 mmol of arylboronic acid or arylboronic ester and dissolved in 5 mL of water, then 0.5 mmol of sodium sulphite were added to this solution; also, in a few cases, 0.1 mmol of potassium phosphate was added as additive. The whole mixture was stirred at 50°C and bubbled with oxygen for the time indicated in scheme 2. After the indicated reaction time, the resulting solution was diluted and acidified with HCl (0.1 M) up to pH between 6 and 7, then AcOEt (10 mL) was added, and the layers were separated. The aqueous layer was washed with 10 mL of AcOEt, and the combined organic layers were dried over Na_2SO_4 anhydrous and filtered. The solvent of the filtrate was removed under reduced pressure, and the compound was purified by flash chromatography (when necessary). All compounds were characterized by ^{1}H-NMR and ^{13}C-NMR by comparison with the properties of known samples.

Phenylboronic acid MIDA and neopentyl glycol esters were synthesized following reported methodologies.[28]

Acknowledgments

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Keywords: green chemistry • hydroxylation • phenols • synthetic method • water chemistry

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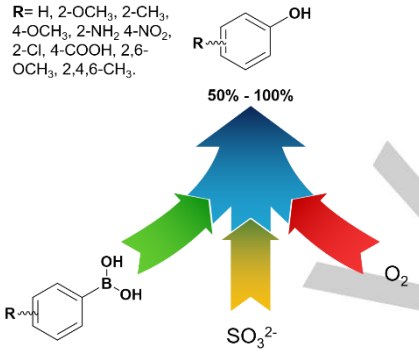
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Hydroxylation of arylboronic acids and esters using sodium sulphite and oxygen as oxidant proceeds efficiently in water under transition metal-free conditions. This mild, rapid, environmentally benign protocol represents a green alternative to synthesize phenols using inexpensive starting material in a simple methodology.



Synthetic method

Willber D. Castro-Godoy, Luciana C. Schmidt and Juan E. Argüello**

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A green alternative for the conversion of arylboronic acids/esters into phenols promoted by a reducing agent, sodium sulphite