



Biosilica as an efficient heterogeneous catalyst for *ipso*-hydroxylation of arylboronic acids



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ABSTRACT

A mild and efficient protocol for the conversion of arylboronic acids to phenol via *ipso*-hydroxylation has been developed using aqueous hydrogen peroxide as oxidant and biosilica as heterogeneous catalyst. The recyclability of the catalyst is also evaluated and could be reused up to six consecutive cycles without a significant loss in catalytic activity.

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Introduction

In today's world 'Green Chemistry' is a major issue taken into consideration seriously when new synthetic methodologies are designed and developed. Hence, now-a-days chemists are found to pay more attention to develop methodologies using environment friendly, clean, safe, and inexpensive chemical reagents/catalysts associated with low *E*-factor¹, high atom economy to reduce the generation of waste product(s). In modern chemistry, innovation of a new synthetic route becomes inefficient without the green approach as green chemistry deals with no pollution or environmental risks. Considering the above facts, development of environment friendly catalyst systems or reagents is a topic of great interest. In this regard, biosilica (diatomaceous earth (DE) or diatomite)² which is a natural, inert, and stable matrix, is considered as a potential green alternative in organic synthesis. Biosilica is a porous inorganic material with an enormous surface area with hydroxyl groups on the surface. Its main constituents are (87–91%) silicon dioxide with small quantities of iron oxide and alumina.³ It is mainly used as catalyst support, adsorbent, filter,⁴ insulating material etc. Biosilica is also considered as the main mineral component of the sponge skeletal element which is commercially available in different forms and varies in particle size,

shape, and porosity. It is non-toxic, and has a great capacity to adsorb water due to its surface property.⁵

In contemporary organic synthesis phenols and their derivatives attract considerable attention owing to their widespread applications in pharmaceuticals,⁶ polymer chemistry, chemical industries, and natural product chemistry⁷ as constituents and synthones. Moreover phenols and polyphenols have been widely used as anti-oxidants⁸ in both simple and polyphenolic forms and as herbicides. Consequently several methodologies have been developed so far for the synthesis of phenols. The general procedures for the preparation of phenols involve pyrolysis of the sodium salt of benzene sulfonic acid, the Dow's process, hydrolysis of diazonium salt etc. In the laboratory scale, phenols are synthesized by nucleophilic substitution of aryl halides activated by electron withdrawing substituents or copper catalyzed transformation of diazoarenes⁹ and Pd catalyzed¹⁰ conversion of aryl halides to phenols using phosphine ligands. Due to the inactive nature of the precursors used in these cases, harsh reaction conditions¹¹ are used and are not compatible with many functional groups. Thus, the exploration of an efficient alternative precursor and catalyst is getting considerable attention not only due to academic interest but to provide additional options. In this regard arylboronic acid is considered as a potential candidate as a precursor for phenols because of the greater stability, structural diversity, and lower toxicity over aryl halides.¹² In recent years, different research groups have reported the transformation of arylboronic acids and their derivatives to phenols via *ipso* hydroxylation by using CuSO₄-phenanthroline,¹³ hydroxylamine,¹⁴ H₂O₂-I₂,¹⁵ H₂O₂-alumina,¹⁶

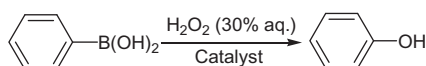
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potassium peroxymonosulfate¹⁷ and Amberlite IR 120 resin,¹⁸ H₃BO₃–H₂O₂,¹⁹ NaClO₂²⁰ supported silver nano particle²¹ etc.. Moreover, biologically, *ipso* hydroxylation plays a very important role in the elimination of sulfonamide antibiotics.²²

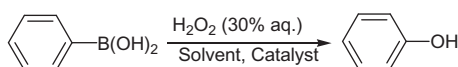
In the literature some reports are available where biosilica is used as a support¹ in many organic reactions. In continuation of our efforts to develop an efficient protocol for the direct transformation of arylboronic acids to phenols, we herein, reported an efficient, facile, and mild protocol for *ipso*-hydroxylation of arylboronic acids to phenols with excellent yields which utilizes biosilica as a catalyst and H₂O₂ (30% aqueous) as an oxidant, at room temperature. Hydrogen peroxide is considered as a stoichiometric, environmentally acceptable oxidant that shows a high efficiency per weight of oxidant.²³

We started our *ipso*-hydroxylation protocol by studying the effectiveness of H₂O₂ (30% aqueous) in the hydroxylation reaction choosing phenylboronic acid as a model substrate and the reactions were carried out at room temperature under aerobic conditions (Scheme 1). At first we carried out the reaction by using only H₂O₂ (2 mL) at room temperature and to our delight phenol was detected as the sole product in 24 h. However, use of biosilica as a catalyst for this reaction provided better yield (76%) of the product (Table 1, entry 2). During the course of the reaction we encountered solubility problem under solvent free conditions and a sticky reaction mass was observed in the reaction vessel. Therefore, to overcome this problem we have carried out the reaction using 2 mL of water as solvent, excellent conversion to phenol was observed under these conditions (Table 1, entry 3). We then tried to fine tune the reaction conditions to obtain the optimized reaction conditions for the conversion of phenylboronic acid to phenol using aqueous H₂O₂ as oxidant and biosilica as the catalyst. To study the effect of solvents in our system, we carried out the reaction in the presence of various solvents by using biosilica as the catalyst and results are summarized in Table 1 (entries 3–10). The reaction was found to proceed in both protic and aprotic solvents although significant variations in yields were noticed. The best result was obtained when water was used as a solvent. We also tried the same reaction in 50% aqueous methanol,



Scheme 1. *ipso*-Hydroxylation of phenylboronic acid with H₂O₂.

Table 1
Optimization of reaction condition^a for biosilica catalyzed *ipso*-hydroxylation of phenylboronic acid²⁴



Entry	Catalyst	Solvent (2 mL)	Time (min)	Yield ^b (%)
1	None	None	1440	57
2	Biosilica	None	45	76
3	Biosilica	Water	0–5	93
4	Biosilica	Methanol	0–5	90
5	Biosilica	Acetonitrile	15	87
6	Biosilica	THF	25	70
7	Biosilica	DCM	15	89
8	Biosilica	Methanol/water (1:1)	10	90
9	Biosilica	Acetonitrile/water (1:1)	15	90
10	Biosilica	THF/water (1:1)	25	80

^a Reaction conditions: phenylboronic acid (1 mmol), H₂O₂ (30% aq, 2 mL), biosilica (50 mg) unless otherwise noted.

^b Isolated yield.

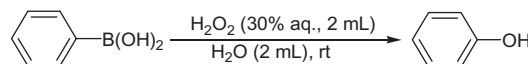
acetonitrile, and THF and found good results in the case of 50% aqueous methanol and aqueous acetonitrile (Table 1, entries 8 and 9) compared to aqueous acetonitrile. From this screening, we observed the best results in the case of water as solvent (Table 1, entry 10). A series of reactions were conducted to find the optimized amount of the catalyst and oxidant. Firstly, when the reaction was attempted with different amounts of the catalyst and taking 2 mL of H₂O₂ it was found that 5 mg of the catalyst was adequate for the efficient conversion of 1 mmol of phenylboronic acid (Table 2, entries 4 vs 5). Next we tried to determine the optimized amount of the oxidant by using 5 mg of catalyst and found that 0.2 mL of the oxidizing agent was sufficient to convert 1 mmol of the phenylboronic acid to phenol²⁴ (Table 2, entries 8 vs 9). However, the reaction did not proceed in the absence of either biosilica or hydrogen peroxide.

To evaluate the scope and limitations of the current procedure, reactions of a wide array of electronically diverse arylboronic acids were examined under optimized reaction conditions using biosilica and hydrogen peroxide (Table 3).²⁴ It has been observed that the electronic nature and the position of the substituents had little effect on the reaction process and both electron donating and withdrawing substituted phenylboronic acids like Me, OMe, Et, F, Cl etc. provided good to excellent yields. Moreover, sterically hindered as well as hetero arylboronic acids also undergo easy transformation with high yield (entries 10–13). Results are summarized in the table 3.

A plausible mechanistic pathway for the *ipso*-hydroxylation of arylboronic acid to phenol has been proposed (Fig. 1). It is assumed that, initially biosilica reacts with H₂O₂ to form a silica-peroxide composite [(i) in the figure] which then reacts with phenylboronic acid to form an adduct (A) which upon rearrangement and subsequent water loss produced the adduct B, which upon hydrolysis gave phenol.

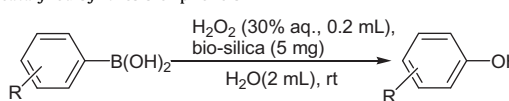
The reusability of the catalyst is a great advantage in the cost reduction of process chemistry. Therefore the reusability of the biosilica catalyst was investigated. For that, we performed the hydroxylation of phenylboronic acid using 1 mmol of the substrate under the optimized reaction conditions. After the completion of the first cycle, the catalyst was filtered and washed with diethyl ether followed by water and then allowed to evaporate the water in an oven overnight (100 °C) and was used for further reaction of *ipso*-hydroxylation of phenylboronic acid. Surprisingly, the catalyst remained efficient and the reaction afforded excellent yields up to the sixth run (Table 4, entries 1–6).

Table 2
Optimization of amount of catalyst and oxidant for hydroxylation of phenylboronic acid^a



Entry	Amount of catalyst (mg)	Amount of H ₂ O ₂ (30% aq) (mL)	Conversion
1	50	2	Full
2	30	2	Full
3	10	2	Full
4	5	2	Full
5	3	2	Incomplete
6	5	1	Full
7	5	0.5	Full
8	5	0.2	Full
9	5	0.1	Incomplete

^a Reaction condition: phenylboronic acid (1 mmol), water (2 mL), the progress of the reaction was monitored by TLC.

Table 3
Biosilica catalyzed synthesis of phenols^a


Entry	R	Time (min)	Yield ^{b,c} (%)
1	H	0–5	93
2	<i>p</i> -OMe	5	92
3	<i>o</i> -Me	5	90
4	<i>m</i> -Me	5	89
5 ^d	<i>p</i> -CHO	10	90
6	<i>p</i> -Cl	5	92
7	<i>p</i> -F	5	93
8 ^e	<i>m</i> -CN	10	88
9	<i>p</i> -Et	5	87
10 ^d	<i>p</i> -tert Butyl	20	88
11	2,4-Difluoro	10	91
12	<i>m</i> -Trifluoromethyl	10	92
13	2-Methoxy-5-pyridinyl	20	89

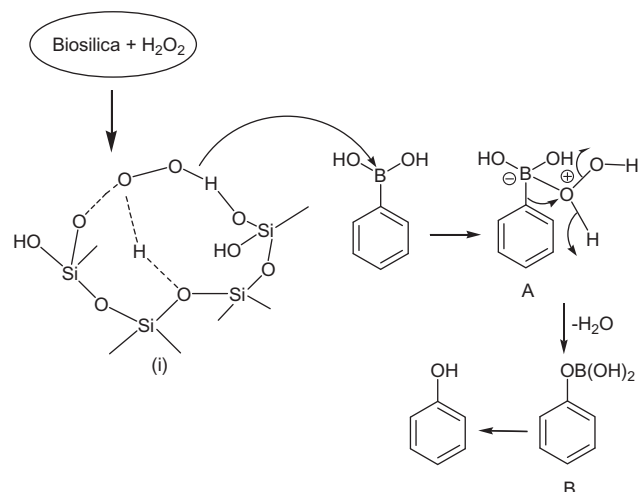
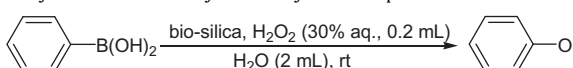
^a Reaction conditions: phenylboronic acid (1 mmol), biosilica (5 mg), H₂O₂ (30% aq., 0.2 mL), water (2 mL).

^b Isolated yield.

^c All compounds are characterized by ¹H NMR, ¹³C NMR, and FT-IR spectroscopy, GC-MS etc.

^d 1 mL of ethanol was added.

^e 1 mL of H₂O₂ was added.

**Figure 1.** Plausible mechanism for the *ipso*-hydroxylation of phenylboronic acid.**Table 4**
Reusability of biosilica as catalyst in the synthesis of phenol^a


Entry	Run	Catalyst (mg)	Time (min)	Yield (%) ^b
1	1st	50	5	93
2	2nd	30	5	92
3	3rd	20	5	90
4	4th	15	5	90
5	5th	10	7	89
6	6th	5	10	88

^a Reaction condition: phenylboronic acid (1 mmol), H₂O₂ (30% aq., 0.2 mL), water (2 mL).

^b Isolated yield.

Table 5

A comparison between 'green-ness' among catalyst/reagents in the hydroxylation of phenylboronic acid to phenol

Entry	Catalyst/reagent	Mass intensity	<i>E</i> -factor	Atom economy	Atom efficiency
1	Al ₂ O ₃ /H ₂ O ₂ ¹⁶	35.3	39	60.25	54.43
2	H ₃ BO ₃ /H ₂ O ₂ ¹⁹	108	109	60.25	54
3	NaClO ₂ ²⁰	54.4	55.4	44.5	43
4	NH ₂ OH/HCl/ NaOH ¹⁴	79.15	78.19	26.86	25
5	Biosilica/H ₂ O ₂	27.72	26.68	60.2	55.98

Finally, the green-ness of our method was investigated by using the parameters of green chemistry.¹ We compared the atom-efficiency and *E*-factors of some reported methods and compared them with our protocol and interestingly we got better results than the others (Table 5).

Conclusion

In conclusion, we have demonstrated a facile, and efficient reusable catalytic protocol for *ipso*-hydroxylation of arylboronic acids to phenols with aqueous hydrogen peroxide as an oxidant and biosilica as a catalyst. Biosilica acts as a novel catalyst in the *ipso*-hydroxylation process and enhances oxidative catalytic action. Our method has several advantages such as mild reaction conditions, safe handling, excellent yield, ligand, base, metal free conditions, short reaction time and so is applicable to a wide variety of functional groups. The green-ness of the reaction condition also makes it superior to the existing methodology.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2015.02.039>.

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24. *General procedure for the ipso-hydroxylation of arylboronic acid:* In a 50 mL round-bottomed flask, a mixture of arylboronic acid (1 mmol), H₂O₂ (30% aq, 0.2 mL), bio-silica (5 mg) and 2 mL of water was added and stirred at room temperature in aerobic condition. The reaction was monitored by TLC. After completion of the reaction the reaction mixture was diluted with 20 mL of water and extracted with (3 × 20) mL of diethylether and the combined organic layer was washed with brine and dried over by Na₂SO₄ and evaporated in a rotary evaporator under reduced pressure. The crude was purified by column chromatography (hexane/ethylacetate, 9:1) on mesh silica (100–200) to get the desired product. The products were confirmed by ¹H NMR, ¹³C NMR, FT-IR spectroscopy and mass spectrometry.