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## Silica chloride: An efficient promoter for oxidation of arylboronic acids to phenols

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### ARTICLE INFO

ABSTRACT

Article history: Received Received in revised form Accepted Available online Keywords: Oxidation Arylboronic acid Phenol Silica chloride This work reports simple, highly efficient protocol for the oxidation of arylboronic acids. Various arylboronic acids were selectively and completely converted into their corresponding oxidized phenols using  $H_2O_2$  as an oxidant in presence of catalytic amount of silica chloride. The results show that silica chloride is a suitable and efficient promoter for the oxidation of arylboronic acids. Heterogeneous catalyst, mild reaction conditions, easy availability of the reagent, easy work-up, excellent yield of corresponding phenols, short reaction time and broad substrate scope makes this protocol attractive and a practical alternative to the existing methods.

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#### 1. Introduction

 $H_2O_2$ 

Phenols are the most important starting materials for synthesis of various industrial products, such as pharmaceuticals, agrochemicals, polymers etc.<sup>1-3</sup> Phenols represent an important class of compounds due to their properties, reactivity and mostly of industrial importance.<sup>4</sup> Therefore, the synthesis of phenols attract the attention of chemist. Phenols are typically synthesized from aryl halides via nucleophilic substitution with metal hydroxides under harsh reaction conditions.<sup>5</sup> Oxidation of arylboronic acid to phenol is the most straightforward reaction. This oxidation process is also termed as "ipso-hydroxylation" of arylboronic acid. Arylboronic acids are inexpensive, stable, safe to use and key reagent found in synthetic chemistry.<sup>6-7</sup> In recent years, chemical research is directed towards developing green processes. High atom economy is also an essential parameter for overall process efficiency. Previous reports suggested that oxidation of arylboronic acid is carried out with metals such as Cu and Ru<sup>8-9</sup>, N-Oxide<sup>10</sup>, NaClO<sub>2</sub><sup>11</sup>, NH<sub>2</sub>-OH<sup>12</sup>, Oxone<sup>13</sup>, MCPBA<sup>14</sup> etc. This type of oxidation is also carried out with  $H_2O_2$  and several reports are available on it.<sup>15-20</sup> Oxidation also worked well with photocatalyst a-Fe<sub>2</sub>O<sub>3</sub>.<sup>21</sup> However, by acknowledging all reported work in this field, hazardous metal contamination or preparation and use of metal catalysts or expensive catalyst, solvents, oxidants, long reaction time, high temperature, toxic waste generation, tedious workup etc. significantly lower their appeal. Therefore, development of new oxidation system to overcome these drawbacks is very much required.

Hydrogen peroxide known as a green oxidant is cheap, attractive, readily available and eco-friendly with water as a byproduct. As per principles of green chemistry, the process is said to be 'green' if techniques/chemicals used are eco-friendly. Heterogeneous reagents have gained significant attraction due to economic and environmental considerations. They can be handled and removed from reaction mixture very easily, making experimental procedures simple. Silica chloride (**SC**) is one of the most versatile and utilized heterogeneous solid acid catalysts. It is also cost effective, insoluble in organic solvents and used in various organic transformations.<sup>22-26</sup> Generally, silica chloride is prepared by reaction of silica gel with thionyl chloride.<sup>27(a)</sup> In this context, with the aim to improve efficiency and eco-friendly conditions of catalytic processes. We have developed a new catalytic oxidation system, Silica chloride-H<sub>2</sub>O<sub>2</sub> as a continuation of our research work on oxidation of organic compounds.<sup>28-29</sup> Herein, we report selective oxidation of arylboronic acid to phenol compounds in presence of catalytic amount of silica chloride and H<sub>2</sub>O<sub>2</sub> as oxidant with acetonitrile (MeCN) as solvent at room temperature (Scheme 1).

$$R \underbrace{\stackrel{fi}{\square}}_{MeCN, rt} B(OH)_2 \underbrace{Silica chloride, H_2O_2}_{MeCN, rt} R \underbrace{\stackrel{fi}{\square}}_{MeCN, rt} OH$$

Scheme 1 Oxidation of arylboronic acids to phenols

The present protocol is found to be effective with MeCN as a solvent. Surprisingly, simple addition of phenylboronic acid in MeCN in the presence of silica chloride as a catalyst using  $H_2O_2$  at room temperature resulted in a dramatic exothermic reaction. This led to complete conversion of phenylboronic acid to phenol within few minutes. This system offers high selectivity, purity, excellent yields, metal free approach and easy workup process.

Initially various oxidants were tried for the oxidation of phenylboronic acid **1a** (PBA) to phenol **2a** in the presence of SC as a catalyst and MeCN as a solvent. Table 1 (entries 1-6) indicates that 30% H<sub>2</sub>O<sub>2</sub> is the best oxidant which gave 100% conversion and selectivity with short reaction time. Other oxidants were found to give poor conversion even after carrying the reaction at room temperature for 30 minutes. In addition to its catalytic oxidation performance, H<sub>2</sub>O<sub>2</sub> is superior to other oxidants in terms of its environmentally benign property.

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### Table 1 Comparative study with various oxidants

Entry	Oxidant (equiv.)	Time (min)	Conv. <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
				2a
1	30% H <sub>2</sub> O <sub>2</sub>	05	100	100
2	Oxone	30	64	64
3	m-CPBA	30	71	71
4	70% TBHP	30	81	81
5	UHP	30	49	49
6	$K_2S_2O_8$	30	55	55

<sup>a</sup>Reaction conditions: **1a** (1 mmol), MeCN (3.0 mL), silica chloride (0.5 mmol), oxidant (1.0 equiv.), temp. (30-35 °C), <sup>b</sup>conversion and selectivity determined by GC with the area normalization method.

Oxidant plays a key role in this reaction. The effect of amount of the oxidant on the reaction was studied by varying the amount of H<sub>2</sub>O<sub>2</sub> from 0.5-1.1 equiv. (Table 2, entries 1-5). H<sub>2</sub>O<sub>2</sub> turned out to be the best oxidant as it gave 100% conversion of starting material (Table 2, entries 4-5). It was observed that 1.0 equiv. of H<sub>2</sub>O<sub>2</sub> gave 100% conversion and selectivity of **1a** to **2a** (Table 2, entry 4). Low conversion was observed when H<sub>2</sub>O<sub>2</sub> was added in less molar ratios (Table 2, entries 1-3). When we increased the amount of  $H_2O_2$  from 1.0 to 1.1 equiv., we obtained similar result as of 1.0 equiv. of H<sub>2</sub>O<sub>2</sub> (Table 2, entry 5). The reaction did not go to completion in the absence of  $H_2O_2$  and/or SC (Table 2, entries 6-8). The product conversion was very less under solvent free reaction condition (Table 2, entry 9). Even though the reaction in MeCN as a solvent goes to the completion, out of scientific curiosity, we carried out model reaction in different solvents such as ethanol (EtOH), water (H<sub>2</sub>O), chloroform (CHCl<sub>3</sub>), toluene, ethyl acetate (EtOAc), tetrahydrofuran (THF), dichloromethane (DCM), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and acetone (Table 2, entries 10-19). This indicates that the said reaction is sensitive to solvents.

 Table 2 Comparative study with various solvents

Entry	Solvent	Silica chloride (mmol)	Oxidant H <sub>2</sub> O <sub>2</sub> (equiv.)	Time (min)	Conv. <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
						2a
1	MeCN	0.5	0.5	30	42	42
2	MeCN	0.5	0.7	30	61	61
3	MeCN	0.5	0.9	30	85	85
4	MeCN	0.5	1.0	05	100	100
5	MeCN	0.5	1.1	05	100	100
6	MeCN	0.5	0	30	0	0
7	MeCN	0	1.0	300	38	38
8	MeCN	0	0	30	0	0
9	-	0.5	1.0	300	02	02
10	EtOH	0.5	1.0	30	93	93
11	$H_2O$	0.5	1.0	30	59	59
12	CHCl <sub>3</sub>	0.5	1.0	30	43	43
13	Toluene	0.5	1.0	30	52	52
14	EtOAc	0.5	1.0	30	60	60
15	THF	0.5	1.0	30	88	88
16	DCM	0.5	1.0	30	73	73
17	DMF	0.5	1.0	30	70	70
18	DMSO	0.5	1.0	30	81	81
19	Acetone	0.5	1.0	30	87	87

<sup>a</sup>Reaction conditions: **1a** (1 mmol), solvent (3.0 mL), silica chloride (mmol), 30%  $H_2O_2$  (equiv.), temp. (30-35 °C), <sup>b</sup> conversion and selectivity determined by GC with the area normalization method.

In this work, various catalysts were used in oxidation of **1a** (PBA) to **2a** with  $H_2O_2$  as an oxidant and MeCN as a solvent. The results are given in Table 3. We found that higher conversion was

obtained only with SC while other catalysts failed to give such high conversion of **1a** to **2a** (Table 3, entries 1-5). Silica bromide also gave 90% conversion but the procedure for preparation of silica bromide is difficult. This proves that SC is the most suitable catalyst for the oxidation of **1a** to **2a**. During catalyst screening study, SC showed excellent catalytic activity and efficiency for the oxidation of **1a** to **2a**. We investigated the influence of various amounts of SC (Table 3, entries 6-8) on the reaction. When molar ratio was 0.2 - 0.4 mmol, the reaction did not go to completion even after 30 min. (Table 3, entries 6-7). We found that higher conversion and selectivity was obtained with SC at 0.5 mmol (Table 3, entry 2). Similar result was obtained by increasing molar ratio of SC from 0.5 - 0.6 mmol (Table 3, entry 8). This shows that 0.5 mmol of SC is sufficient for complete conversion of **1a** to **2a**.

# Table 3 Comparative study with various catalysts and catalyst loading (silica chloride)

Entry	Catalyst	Catalyst	Time	Conv. <sup>b</sup>	Selectivity <sup>b</sup>
		(mmol)	(min)	(%)	(%)
					2a
1	Silica gel	0.5	60	21	21
2	Silica chloride	0.5	05	100	100
3	Silica bromide	0.5	05	90	90
4	Silica sulfuric acid	0.5	60	70	70
5	Dowex-50	0.5	60	19	19
6	Silica chloride	0.2	30	45	45
7	Silica chloride	0.4	30	78	78
8	Silica chloride	0.6	05	100	100

<sup>a</sup>Reaction conditions: **1a** (1 mmol), MeCN (3.0 mL), catalyst (mmol), 30%  $H_2O_2$  (1.0 equiv.), temp. (30-35 °C), <sup>b</sup>conversion and selectivity determined by GC with the area normalization method.

The reaction was also optimized for temperature (Table 4). It — was observed that lower temperature was disadvantageous to oxidation reaction, which greatly prolonged reaction time (Table 4, entries 1-2). Although the best conversion (100%) of oxidation — reaction was given at 30-35 °C (Table 4, entry 3), as temperature was increased to 35-40 °C, similar result was observed (Table 4, entry 4). Hence, finally 30-35 °C was chosen for further study.

 Table 4 Influence of reaction temperature

Entry	Temperature (°C)	Time (min)	Conv. <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
			-	2a
1	20-25	30	55	55
2	25-30	30	88	88
3	30-35	05	100	100
4	35-40	05	100	100

<sup>a</sup>Reaction conditions: **1a** (1 mmol), MeCN (3.0 mL), silica chloride (0.5 mmol), 30%  $H_2O_2$  (1.0 equiv.), temp. (°C), <sup>b</sup>conversion and selectivity determined by GC with the area normalization method.

Eventually, 1 mmol of substrate, 3 mL MeCN as solvent, 0.5 mmol silica chloride catalyst, 1.0 equiv. of 30% H<sub>2</sub>O<sub>2</sub> as a oxidant and 30-35 °C temperature were found to be the optimized reaction conditions for this protocol. We also investigated the substrate scope using various functional groups present on arylboronic acids (Table 5). Oxidation of arylboronic acid produced excellent yields of phenol under the optimized reaction conditions (Table 5, entries 1-17). The phenol formation occurred in specified time as shown in Table 5. Arylboronic acids with various electron-withdrawing or electron-donating groups such as CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, C(CH<sub>3</sub>)<sub>3</sub>, 2,3-dimethyl, OCH<sub>3</sub>, OC<sub>4</sub>H<sub>9</sub>, CHO, Cl, Br, F, CF<sub>3</sub>, 4-Cl-2-CH<sub>3</sub> and NO<sub>2</sub> (Table 5, entries 2–14) underwent oxidation reaction affording excellent yields (95–98%).

Naphthylboronic acids and heteroarene were also converted to their corresponding phenols giving excellent yields (Table 5, entries 15-17).



2k



<sup>a</sup>Reaction conditions: arylboronic acid (1 mmol), MeCN (3.0 mL), silica chloride (0.5 mmol), 30%  $H_2O_2$  (1.0 equiv.), temp. (30-35 °C), <sup>b</sup>Isolated Yield.

The reaction mechanism for oxidation of phenylboronic acid is shown in Fig. 1. It shows that silica gel reacts with  $SOCl_2$  to give SC which subsequently then reacts with  $H_2O_2$  to give silicaperoxide complex. This complex then further reacts with phenylboronic acid and undergoes rearrangement to give phenol.

In summary, we have developed a simple, highly efficient, cheap and environmentally benign methodology for oxidation of arylboronic acids by using new oxidation system i.e (Silica chloride,  $H_2O_2$ ) with short reaction time and excellent yields. The preparation of the catalyst is simple and isolation of products from hetrogenous reaction mixture is easy and not time consuming. It is noteworthy that various functional groups present on arylboronic acids were very well tolerated in this oxidation. Moreover, this protocol is cheap, convenient, easy to handle and safe. We believe that this system will surely surpass the previously reported methods.

3

#### 4

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Figure 1. Possible mechanism for oxidation of phenylboronic acid

### Acknowledgments

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- 30. Typical Procedure for the preparation of silica chloride: To well-stirred silica gel (20 g) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added drop wise SOCl<sub>2</sub> (20 g) at room temperature. Evolution of copious amounts of HCl and SO<sub>2</sub> occurred instantaneously. After stirring for 1 h, the solvent was removed to dryness under reduced pressure. The resulting white-grayish powder of silica chloride could be stored in sealed vessels for 6 months without any critical decline in activity. The amount of chloride in SC (2.6 mmol of Cl per g silica) is calculated by a standard procedure.<sup>27(b)</sup>
- 31. General procedure for the oxidation of arylboronic acids to phenols (Table 5):
  - An oven-dried Schlenk flask was allowed to cool to room temperature and charged sequentially with arylboronic acid (1 mmol), MeCN (3.0 mL) and silica chloride (0.5 mmol). The reaction was then activated by addition of 30%  $H_2O_2$  (1.0 equiv.) and stirred at 30-35 °C for the required time as given in Table 5. The progress of reaction was monitored by TLC. After complete conversion of starting material, the reaction mixture was filtered to remove silica gel. The reaction mixture was neutralized with 5% NaHCO3 solution (5 mL). Then the product was extracted with ethyl acetate (30 mL) and subsequently washed with distilled water (10 mL). The organic extract was dried over Na2SO4 and the solvent was removed under reduced pressure. The resultant product was purified by column chromatography using silica gel with n-hexane and ethyl acetate as solvent to get the pure product. The structure of the product was confirmed by GC-MS, M.P. and <sup>1</sup>H NMR spectroscopic techniques.

#### **Supplementary Material**

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.

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### **Highlights**

- Silica chloride as a heterogeneous catalyst •
- Cheap, transition metal free approach •
- Acception Oxidation using green oxidant  $H_2O_2$ •

5