



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



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## ABSTRACT

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<sub>2</sub>O<sub>2</sub> 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.

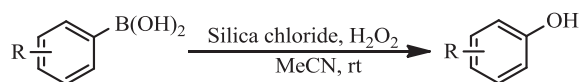
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## Introduction

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<sub>2</sub>O<sub>2</sub> and several reports are available on it.<sup>15–20</sup> Oxidation also worked well with photocatalyst α-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>27,30</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).



Scheme 1. Oxidation of arylboronic acids to phenols.

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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<sub>2</sub>O<sub>2</sub> 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 min. 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.

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 to 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<sub>2</sub>O<sub>2</sub> 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

**Table 1**<sup>a</sup>Comparative study with various oxidants.

Entry	Oxidant (equiv.)	Time (min)	Conv. <sup>b</sup> (%)	Selectivity <sup>b</sup> (%) <b>2a</b>
<b>1</b>	<b>30% H<sub>2</sub>O<sub>2</sub></b>	<b>05</b>	<b>100</b>	<b>100</b>
2	Oxone	30	64	64
3	m-CPBA	30	71	71
4	70% TBHP	30	81	81
5	UHP	30	49	49
6	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	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.**Table 2**<sup>a</sup>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> (%) <b>2a</b>
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
<b>4</b>	<b>MeCN</b>	<b>0.5</b>	<b>1.0</b>	<b>05</b>	<b>100</b>	<b>100</b>
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 <sub>2</sub> O	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<sub>2</sub>O<sub>2</sub> (equiv.), temp. (30–35 °C).<sup>b</sup> Conversion and selectivity determined by GC with the area normalization method.**Table 3**<sup>a</sup>Comparative study with various catalysts and catalyst loading (silica chloride).

Entry	Catalyst	Catalyst (mmol)	Time (min)	Conv. <sup>b</sup> (%)	Selectivity <sup>b</sup> (%) <b>2a</b>
1	Silica gel	0.5	60	21	21
<b>2</b>	<b>Silica chloride</b>	<b>0.5</b>	<b>05</b>	<b>100</b>	<b>100</b>
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<sub>2</sub>O<sub>2</sub> (1.0 equiv.), temp. (30–35 °C).<sup>b</sup> Conversion and selectivity determined by GC with the area normalization method.

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