



Facile and effective approach for oxidation of boronic acids



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ABSTRACT

This present work illustrates facile and effective approach for oxidation of boronic acids using environmentally benign dimethyl carbonate (DMC) as a solvent with H_2O_2 as an oxidant at room temperature. In contrast to previous reaction reports, which make use of metal catalyst, hazardous reagent and oxidants that creates environmental concern. This method provides good to excellent yield of products and showed better tolerance towards various functional groups present on boronic acids. Moreover, this developed process is an alternative in terms of inexpensive, non toxic and easy reaction conditions.

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Introduction

Oxidations of organic compounds are useful transformation in organic chemistry as these compounds are widely used in industries. Phenols are one of the well-known class of organic compounds mainly used in synthesis of pharmaceuticals, agrochemicals, polymers etc.^{1–3} Traditionally synthesis of phenol includes substitution of aryl halides. However, due to the harsh reaction conditions with toxic reagents, chemicals and transition metals make this approach unsuitable for environment.^{4–8} The oxidation of boronic acid to phenol compounds is favourable functional group reactions in the organic chemistry. Therefore, replacement of aryl/alkyl halides with boronic acids is a good alternative as they are inexpensive, stable, safe to use and key reagent found in synthetic chemistry.^{9,10} Ample oxidizing systems have been reported for this oxidation purpose. The oxidation of boronic acids using a suitable oxidizing agent is the simplest route for the synthesis of these phenols.

Oxidation of boronic acids was carried out in the presence of metals such as Cu and Ru.^{11,12} Conventionally, this oxidation was performed with the help of several non-metals.^{13–19} This type of oxidation was also reported in presence of H_2O_2 .^{20–25} An electro-mediated technique under an air atmosphere was also applied for this type of oxidation.²⁶ These oxidation reactions are quite useful but these oxidants are expensive, hazardous or toxic. Moreover, toxic reagents are usually used to dissolve oxidizing agents and a large amount of inorganic wastes are generated after

workup. Hence, due to economical and environment concern, oxidation processes with inexpensive and environmental-friendly oxidants are very much required. Therefore, by acknowledging all reported work in this field, it is demanding need to develop an eco-friendly method for oxidation of boronic acids. Thus, developing a simple, highly efficient method for this type of oxidation is still a stimulating task.

Dimethyl carbonate (DMC) is an exigent green reagent, which used as an alternative in organic synthesis.^{27–29} The biodegradability and non-toxic nature of DMC makes it economical and environmentally attractive in both academic and industrial applications. The use of hydrogen peroxide as a green oxidant is safe, cheap with water as a byproduct. Recently, we have reported oxidation of arylboronic acid to phenol compounds using silica chloride as an efficient promoter with H_2O_2 as an oxidant.³⁰ Even though the said reaction was carried out in presence of silica chloride as a heterogeneous catalyst. Since it was easy to remove from reaction mixture but preparation method for silica chloride from $SOCl_2$ was hazardous because of evolution of SO_2 in environment causes pollution. Thus, as continuation of our research work to develop eco-friendly conditions for oxidation of organic compounds.^{31,32} Herein, we report oxidation of boronic acids by using DMC as solvent with H_2O_2 as an oxidant at room temperature. This method is purely based on principle of green chemistry with objective of designing chemical process, which is harmless to human health and environment. To the best of our knowledge, this is the first DMC/Solvent based oxidation system that is an alternative for transitional metal catalyst, toxic organic reagents and oxidants.

The reaction conditions were optimized by using phenylboronic acid **1a** (PBA) as key substrate. Oxidation of **1a** to **2a** was studied as

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a model reaction (Table 1) with H₂O₂ as an oxidant at room temperature. When mixture of **1a** (1 mmol) and H₂O₂ (2.0 equiv.) were stirred at room temperature for about 7 h only 9% conversion was observed due to insolubility of reaction mixture (Table 1, entry 1). Therefore, we have decided to carry out this oxidation using various solvents considering solubility issue of **1a** with H₂O₂. Thus, we have tried oxidation of **1a** to **2a** with different solvents such as Methanol (MeOH), Acetone, Acetonitrile (MeCN), Dimethyl carbonate (DMC), H₂O, Toluene, Pet ether, Chloroform (CHCl₃) and Dichloromethane (DCM) (Table 1, entries 2–10). Among the solvent studies, we found that 100% conversion was highest and observed only with DMC in 5 h (Table 1, entry 5). While in the case of other solvents such as MeOH, acetone, MeCN less conversion of **1a** to **2a** was observed in 7 h (Table 1, entries 2–4). We have tried oxidation of **1a** to **2a** in green solvent such as H₂O but insolubility of reaction mixture causes incomplete conversion 29% of **1a** to **2a** in 7 h (Table 1, entry 6). Additionally, with nonpolar solvents such as toluene and pet ether, 23% and 35% conversion for **2a** was observed in 7 h (Table 1, entries 7–8). Oxidation of **1a** to **2a** using halogenated solvents such as CHCl₃ and DCM resulted in 39% and 36% conversion respectively in 7 h (Table 1, entries 9–10). This indicates that the reaction is sensitive to solvents. It was further concluded that higher conversion for oxidation of **1a** to **2a** is solubility dependent and excellent under homogenous conditions. DMC helps the reaction to proceed in homogeneous phase which provides proper mixing of substrate with H₂O₂. Considering the hazards of using above organic solvents, we decided DMC as the best solvent for this oxidation as it is devoid of any mutagenic effect.

During the solvent study, we observed that when DMC was used as solvent, 100% conversion of product was obtained. We have further study the oxidation of **1a** to **2a** with different H₂O₂ quantities ranging from 0.5 to 2.1 equiv. (Table 1, entries 11–15). This showed that H₂O₂ turned out to be the best oxidant as it gave 100% conversion of the product (Table 1, entry 5,15) at room temperature in 5 h. Therefore, 2.0 equiv. of H₂O₂ is enough for complete conversion of **1a** to **2a** (Table 1, entry 5). When the

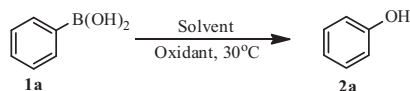
oxidation of PBA was carried out using less quantities of H₂O₂ differing from 0.5 to 1.7 equiv. of oxidant, the reaction was incomplete (Table 1, entries 11–14). However, absence of H₂O₂ in model reaction showed no conversion of product (Table 1, entry 16).

The optimized reaction conditions using DMC as a solvent with H₂O₂ as an oxidant were further applied to investigate the effect of different oxidant and temperature on the oxidation of **1a** to **2a** (Table 2). Screening other oxidants in present reaction conditions, We are pleased to find that H₂O₂ provided finer results than other oxidants (Table 2, entries 1–4). It was observed that other oxidants such as 70% TBHP, Oxone and m-CPBA gave 77%, 65% and 82% conversion for **2a** in 7 h respectively (Table 2, entries 1–3). In the case of UHP, we could get conversion only up to 48% in 7 h. This shows that other oxidants gave insufficient conversion of **1a** to **2a** even after keeping the reaction at room temperature for 7 h. H₂O₂ is excellent than other oxidants with its eco-friendly ability of improving oxidation performance. Furthermore, oxidation of **1a** under different temperatures was also investigated in this method. It was observed that reaction was incomplete at lower temperature, thus prolonging the reaction time (Table 2, entry 5–7). Hence, room temperature (30 °C) was chosen for further work as a clean method.

Therefore, the optimized reaction conditions found for the oxidation of **1a** to **2a** (1 mmol of substrate, 1.0 mL of DMC as a solvent, 2.0 equiv. of 30% H₂O₂ as an oxidant and 30 °C (room temperature)) were chosen as model reaction conditions for the studies.³⁴ Moreover, this oxidation method is free from catalyst such as metal, ligand or alkali. No significant amounts of byproducts were formed in this reaction. In order to generalize the scope of this protocol, we have carried out first oxidation of arylboronic acids with various functional groups present on it under optimized reaction conditions and the results are presented in Scheme 1. The influence of electron donating or withdrawing group on substrate was not significant in this method. The substrates bearing electron donating, withdrawing or halo groups were easily oxidized to respective phenols with excellent yields (Scheme 1, **2b–2k**). Interestingly, similar results were obtained upon subjecting naphthylboronic acid substrates, which gave good yields with high purity (Scheme 1, **2l–2m**). We have further carried out oxidation of heteroarene derivative such as pyridin-3-ylboronic acid that smoothly undergoes oxidation to give corresponding product (Scheme 1, **2n**) to the reaction conditions.

Encouraged by these results, we further applied this optimized reaction conditions to alicyclic and alkyl boronic acids which are presented in Scheme 2. The cyclohexylboronic acid efficiently undergoes oxidation to give good yield of cyclohexanol (Scheme 2, **2o**). Finally, we investigated alkyl boronic acid under present optimized reaction condition. Alkyl boronic acid such as

Table 1
Optimization of reaction parameters for **1a**.



Entry	Solvent	Oxidant H ₂ O ₂ (equiv.)	Time (h)	Conv. ^a (%)
<i>Solvent study</i>				
1	–	2.0	07	09
2	MeOH	2.0	07	44
3	Acetone	2.0	07	40
4	MeCN	2.0	07	43
5	DMC	2.0	05	100
6	H ₂ O	2.0	07	29
7	Toluene	2.0	07	23
8	Pet Ether	2.0	07	35
9	CHCl ₃	2.0	07	39
10	DCM	2.0	07	36
<i>Oxidant loading</i>				
11	DMC	0.5	07	37
12	DMC	1.0	07	66
13	DMC	1.5	06	79
14	DMC	1.7	06	86
15	DMC	2.1	05	100
16	DMC	–	05	0

Reaction conditions: **1a** (1 mmol), solvent (1.0 mL), 30% H₂O₂ (equiv.), temperature (30 °C).

^a Conversion determined by GC with the area normalization method.

Table 2
Effect of different oxidants and temperature on **1a**.

Entry	Oxidant (equiv.)	Time (h)	Temperature (°C)	Conv. ^a (%)
<i>Oxidant study</i>				
1	TBHP (70%)	07	30	77
2	Oxone	07	30	65
3	m-CPBA	07	30	82
4	UHP	07	30	48
<i>Temperature study</i>				
5	H ₂ O ₂	06	15	40
6	H ₂ O ₂	05	20	65
7	H ₂ O ₂	05	25	84

Reaction conditions: **1a** (1 mmol), DMC (1.0 mL), oxidant (2.0 equiv.), temperature (°C).

^a Conversion determined by GC with the area normalization method.

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