



Montmorillonite K10 as Highly Efficient Catalyst for the Synthesis of Phenols from Arylboronic Acids

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ABSTRACT

A simple, efficient and green Montmorillonite K10 catalyzed method for the ipso-hydroxylation of arylboronic acid to phenol has been developed using aqueous hydrogen peroxide as an oxidizing agent. The versatility of this protocol is that the reactions were performed at room temperature in short reaction time under metal-, ligand- and base-free conditions.

Keywords: Arylboronic acid, Phenols, Montmorillonite K10, catalysis, green synthesis.

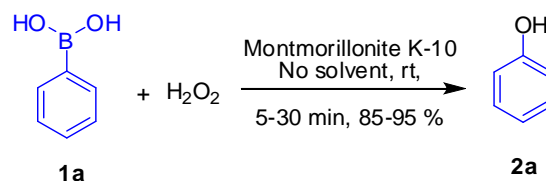
1. INTRODUCTION

Phenols and their derivatives are present in numerous natural products in monomeric or polymeric forms. Phenols have wide range of applications as a key synthetic precursor for the construction of pharmaceuticals, polymers and naturally occurring compounds [1]. Phenols are commonly prepared by nucleophilic aromatic substitution of aryl halides, Cu-catalyzed transformation of diazoarenes and benzyne protocols [2]. However, these methods suffer from major drawbacks such as harsh reaction conditions and diazotization of amino groups to diazoarenes, which is often not compatible with many other functional groups. In addition to it, some literature reported the conversion of aryl halides such as aryl bromides and chlorides into phenols in the presence of Pd-based catalyst and phosphine ligands [3] and aryl iodides into the corresponding phenols in the presence of Cu-catalyst using non-phosphine ligands [4] at high temperature.

Over the last decade, arylboronic acids and their derivatives have emerged as an important moiety in a wide range of organic reactions [5]. Although phenols have been reported as byproducts in many metal catalyzed reactions of arylboronic acids [6]. Recently several researchers were demonstrated the efficient conversion of arylboronic acids into phenols. Arylboronic acids are considered as a suitable precursor for the synthesis of phenols because they are safe, stable to heat, moisture, air and also commercially available with many substituted functional groups. According to

the literature, hydroxylation of arylboronic acids to phenols is reported using MCPBA- H₂O-EtOH [7], acidic Al₂O₃-H₂O₂ [8], I₂-H₂O₂ [9], CuSO₄-phenanthroline [10], H₂O₂-poly(N-vinyl pyrrolidone) [11], Amberlite IR-120-H₂O₂ [12] NH₂OH.HCl:NaOH [13], Potassium peroxy monosulfate [14], or aqueous H₂O₂ [15], etc.

Aqueous hydrogen peroxide is an environmentally benign oxidant that shows a high efficiency per weight of oxidant and it is relatively easy to handle [16]. On the other hand Montmorillonite K-10 clay has been using as catalyst for number of synthetic organic transformations and provides several advantages over classical acids, for example, strong acidity, non-corrosiveness, low cost, mild reaction conditions, good yields, selectivity, and ease of workup. [17] In this communication, we wish to report the use of easily available, cheap and environment friendly Montmorillonite K-10 clay as an excellent promoter to convert arylboronic acids (**1**) to phenols (**2**) using aqueous H₂O₂ as an oxidizing



Scheme 1: Montmorillonite K-10 mediated preparation of phenols (**2**) from arylboronic acids (**1**).

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Table 1: Optimization of reaction conditions for Montmorillonite K-10 mediated *ipso*-hydroxylation of **1a**^a

Entry	Catalyst (amount)	Oxidant	Solvent ^a	Time (min)	Yield ^b (%)
1.	-	H ₂ O ₂	-	60	05
2.	-	H ₂ O ₂	MeCN	60	08
3.	Montmorillonite K-10 (20 mg)	H ₂ O ₂	MeCN	30	82
4.	Montmorillonite K-10 (20 mg)	H ₂ O ₂	MeOH	30	80
5.	Montmorillonite K-10 (20 mg)	H ₂ O ₂	THF	30	76
6.	Montmorillonite K-10 (20 mg)	H ₂ O ₂	DCM	60	74
7.	Montmorillonite K-10 (20 mg)	H ₂ O ₂	MeCN-H ₂ O (1:1)	30	84
8.	Montmorillonite K-10 (20 mg)	H ₂ O ₂	THF-H ₂ O (1:1)	30	86
9.	Montmorillonite K-10 (20 mg)	H ₂ O ₂	MeOH-H ₂ O (1:1)	30	86
10.	Montmorillonite K-10 (15 mg)	H ₂ O ₂	-	5	95
11.	Montmorillonite K-10 (30 mg)	H ₂ O ₂	-	5	91
12.	Montmorillonite K-10 (10 mg)	H ₂ O ₂	-	5	89 ^c
13.	-	H ₂ O ₂	-	40 h	82 ^c
14.	Montmorillonite K-10 (15 mg)	Oxone	MeCN	60	Trace ^d
15.	Montmorillonite K-10 (15 mg)	t-BuOOH	-	60	45 ^e

^aReagents and conditions: phenylboronic acid (1 mmol), H₂O₂ (30% aq, 2 mL), Montmorillonite K-10 (15 mg), solvent (2 mL), ca 30 °C.

^bIsolated yields.

^cThe reaction did not reach to completion.

^dReagents and conditions: phenylboronic acid (1 mmol), Montmorillonite K-10 (15 mg), ca 30 °C. ^eReagents and conditions: phenylboronic acid (1 mmol), t-BuOOH (70% aq, 2 mL), Amberlite IR-120 (15 mg), ca 30 °C.

agent at room temperature under metal-, ligand- and base-free conditions.

2. EXPERIMENTAL

To study the role of H₂O₂ (30% aqueous) in the present reaction, phenylboronic acid (**1a**; 1 mmol) was chosen as a model substrate to perform the reactions under open vessel conditions at room temperature. The results are summarized in Table 1. When a mixture of **1a** (1 mmol) and aqueous hydrogen peroxide (2 mL) was stirred at room temperature in the absence of any organic solvent for 60 min, only a trace amount of phenol (**2a**) was obtained (Table 1, entry 1). The use of an organic solvent e.g. acetonitrile did not improve the product yield (Table 1, entry 2).

Surprisingly, the yield of **2a** was increased dramatically to 82% when the same reaction was performed in the presence of Montmorillonite K-10 for 30 min (Table 1, entry 3). The use of other solvents e.g. MeOH, THF, and DCM was examined and found to be effective (Table 1, entries 4-6). Notably, the reaction was found to be not sensitive to the presence of large volume of water as the use of 1:1 aqueous acetonitrile, aqueous THF, and aqueous MeOH was successful (Table 1, entries 7-9). Nevertheless, the best results were achieved when the reaction was performed in the absence of any solvent (Table 1, entry 10).

3. RESULT AND DISCUSSION

The increase of quantity of Montmorillonite K-10 did not improve the product yield whereas decrease in quantity lowered the yield (Table 1, entries 11-12). The reaction was found to be abnormally slow

in the absence of Montmorillonite K-10 indicating its key role in propagating the reaction (Table 1, entry 13). When the reaction was carried out using t-BuOOH or Oxone as an oxidant moderate yields were observed. (Table 1, entry 14 and 15). Based on the observation of entries 1, 10 and 13 it was evident that a combination of Montmorillonite K-10 and H₂O₂ was necessary for the quick and effective conversion of phenylboronic acid to phenol.

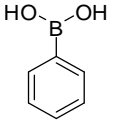
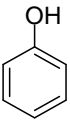
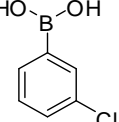
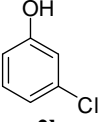
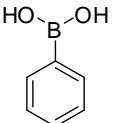
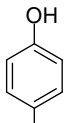
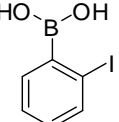
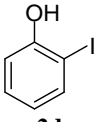
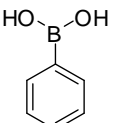
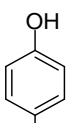
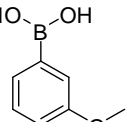
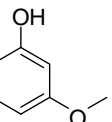
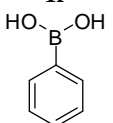
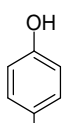
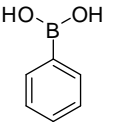
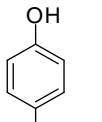
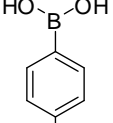
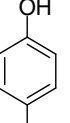
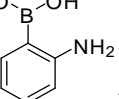
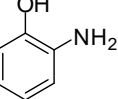
To understand the versatility of the current methodology, a wide array of diverse arylboronic acids were treated with Montmorillonite K-10/H₂O₂ as catalyst under the condition of entry 10 of Table 1. The results were presented in Table 2. In general, arylboronic acids with either electron-withdrawing or electron-donating substituents such as Cl, F, I, OMe, COOH, CHO, NH₂ (Table 2, entries 2-10) underwent the *ipso*-hydroxylation reaction in good yields (85-95%). It was observed that a variety of substituents on the aromatic ring were well tolerated. The reaction was also compatible with naphthylboronic acids (Table 2, entry 11 and 12).

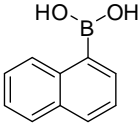
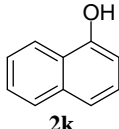
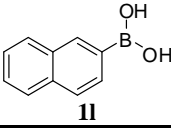
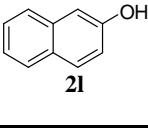
Recyclability of the Montmorillonite K-10 catalyst was examined. For this reason, the catalyst used was recovered from the reaction of phenyl boronic acid (**1a**) to phenol (**2a**) via filtration, dried and reused for the same reaction. This procedure was repeated for four times and results are summarized in Table 3.

4. CONCLUSIONS

In summary, we have developed a clean process for the synthesis of phenols starting from arylboronic

Table 2. Montmorillonite K-10 mediated synthesis of phenols (2)^a

Entry	Boronic acid (1)	Product (2)	Time (min)	Yield (%)
1	 1a	 2a	2	95
2	 1b	 2b	5	92
3	 1c	 2c	5	90
4	 1d	 2d	5	91
5	 1e	 2e	5	92
6	 1f	 2f	5	89
7	 1g	 2g	5	90
8	 1h	 2h	10	94
9	 1i	 2i	12	95
10	 1j	 2j	20	92

111	 1k	 2k	12	85
112	 1l	 2l	18	90

^aReagents and conditions: phenylboronic acid (1 mmol), H₂O₂ (30% aq, 2 mL), Montmorillonite K-10 (15 mg), ca 30 °C.

Table 3 Recycle of the Montmorillonite K-10 clay.

Cycle	Montmorillonite K-10, mg	%Yield
1	15	95
2	15	94
3	14	92

acids with aqueous hydrogen peroxide using a commercially available, strongly acidic cross-linked Montmorillonite K-10 as a recyclable catalyst. The features of this process include (a) an almost waste-free procedure, except for the regeneration of the resin catalyst at its first use; (b) the acidic ion-exchange-resin catalyst could be readily separated from the products by simple filtration and directly reused at least four times without any reactivation, whilst showing no significant loss of activity; (c) the technique is effective with a wide range of substituted aryl and heteroarylboronic acids giving *phenols as* products in good to excellent yields.

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*Bibliographical Sketch



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