



Water as a hydrogen source in palladium-catalyzed reduction and reductive amination of nitroarenes mediated by diboronic acid



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ARTICLE INFO

Article history:

Received 10 April 2017

Received in revised form

13 May 2017

Accepted 15 May 2017

Available online 16 May 2017

Keywords:

Reduction

Reductive amination

Nitroarenes

Diboronic acid

Hydrogen source

ABSTRACT

An unprecedented palladium-catalyzed chemoselective reduction and reductive amination of nitroarenes with water as a hydrogen source mediated by diboronic acid have been discovered. A series of aryl amines containing various reducible functional groups were obtained in good to excellent yields.

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1. Introduction

With the merits of environment benign, safety and cost-benefit, water has been applied as an ideal hydrogen source for transfer hydrogenation in recent years. In 2006, the first example using water as a hydrogen source in the reduction of epoxides, alkenes, and alkynes catalyzed by titanocene was reported.¹ In 2016, the palladium-catalyzed hydrogen/deuterium transfer from H₂O/D₂O to alkenes and alkynes mediated by diboronic acid has been discovered.² And then diboron-promoted transfer hydrogenation of *N*-heteroarenes with water as a hydrogen source catalyzed by palladium or under metal-free conditions has also been achieved.³ Lately, the palladium-catalyzed enantioselective reductive Heck reactions with water as a hydride source was reported by Zhu and coworkers.⁴ Except for the above examples, the application of water as a hydrogen source was less investigated.⁵

Aryl amines are important building blocks and key intermediates in the synthesis of bioactive natural products, pharmaceuticals, dyes, agrochemicals, polymers, and photographic materials.⁶ The reduction and reductive amination of nitroarenes are straightforward methods to prepare such compounds. Followed

by the classical reduction methods using a large excess of Zn, Fe, or SnCl₂ in acid conditions,⁷ a variety of reducing reagents including H₂,⁸ NaBH₄,⁹ HCOOH,¹⁰ 9,10-dihydroanthracene,¹¹ 1,4-dihydropyridine,¹² thiols,¹³ (2-pyridyl)-phenyl-methanol,¹⁴ vasicine,¹⁵ hydrazine hydrate,¹⁶ HSiCl₃,¹⁷ alcohol, and etc.¹⁸ have been applied in the reduction of nitroarenes. However, most of these methods suffer from several defects including lack of chemoselectivity, the use of high pressure equipment, hazardous or pyrophoric reagent. Herein, we report a palladium-catalyzed chemoselective reduction and reductive amination of nitroarenes with water as a hydrogen source mediated by diboronic acid under mild conditions.

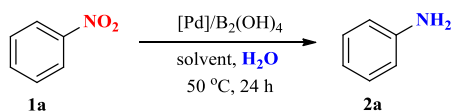
2. Results and discussion

The reduction of nitrobenzene (**1a**) with 2.5 equivalents of diboronic acid and 10 equivalents of water in acetonitrile at 50 °C for 24 h was chosen as a model reaction. As shown in Table 1, the aniline (**2a**) was obtained with 73% yield in the presence of 0.5 mol % palladium on carbon (5 wt% Pd/C) (entry 1). Control experiments showed that the reaction could not proceed without either the Pd/C catalyst or the diboronic acid (entries 2, 3). Trace amount of **2a** was detected by GC in the absence of stoichiometric water (entry 4, 5% yield), which is very different from Yoon's work, where the decaborane itself acted as a reducing agent in the presence of Pd/C.¹⁹ By

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Table 1
Screening of reaction conditions for the reduction of nitrobenzene ^a.



Entry	[Pd]	B ₂ R ₂	Solvent	H ₂ O	Yield % ^b
1	Pd/C	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	73
2	—	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	0
3	Pd/C	—	CH ₃ CN	10 eq.	0
4	Pd/C	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	0 eq.	5
5	Pd/C	2.5 eq. B ₂ (OH) ₄	Toluene	10 eq.	62
6	Pd/C	2.5 eq. B ₂ (OH) ₄	THF	10 eq.	58
7	Pd/C	2.5 eq. B ₂ (OH) ₄	CHCl ₃	10 eq.	0
8	Pd/C	2.5 eq. B ₂ (OH) ₄	MeOH	0 eq.	55
9	Pd(OAc) ₂	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	64
10	Pd(CF ₃ COO) ₂	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	66
11	Pd(PPh ₃) ₄	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	43
12	Pd(acac) ₂	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	33
13	Pd(PPh ₃) ₂ Cl ₂	2.5 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	0
14	Pd/C	2.5 eq. B ₂ pin ₂	CH ₃ CN	10 eq.	53
15	Pd/C	2.5 eq. B ₂ (cat) ₂	CH ₃ CN	10 eq.	30
16	Pd/C	3.3 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	99
17 ^c	Pd/C	3.3 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	85
18	Pd/C	3.3 eq. B ₂ (OH) ₄	CH ₃ CN	5 eq.	83
19 ^d	Pd/C	3.3 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	89
20 ^e	Pd/C	3.3 eq. B ₂ (OH) ₄	CH ₃ CN	10 eq.	95

^a Reaction conditions: nitrobenzene (0.6 mmol), 0.5 mol % [Pd], 1.0 mL solvent, 50 °C, 24 h.

^b Determined by GC analysis with an internal standard (mesitylene).

^c 0.25 mol % Pd/C was used.

^d 40 °C, 24 h.

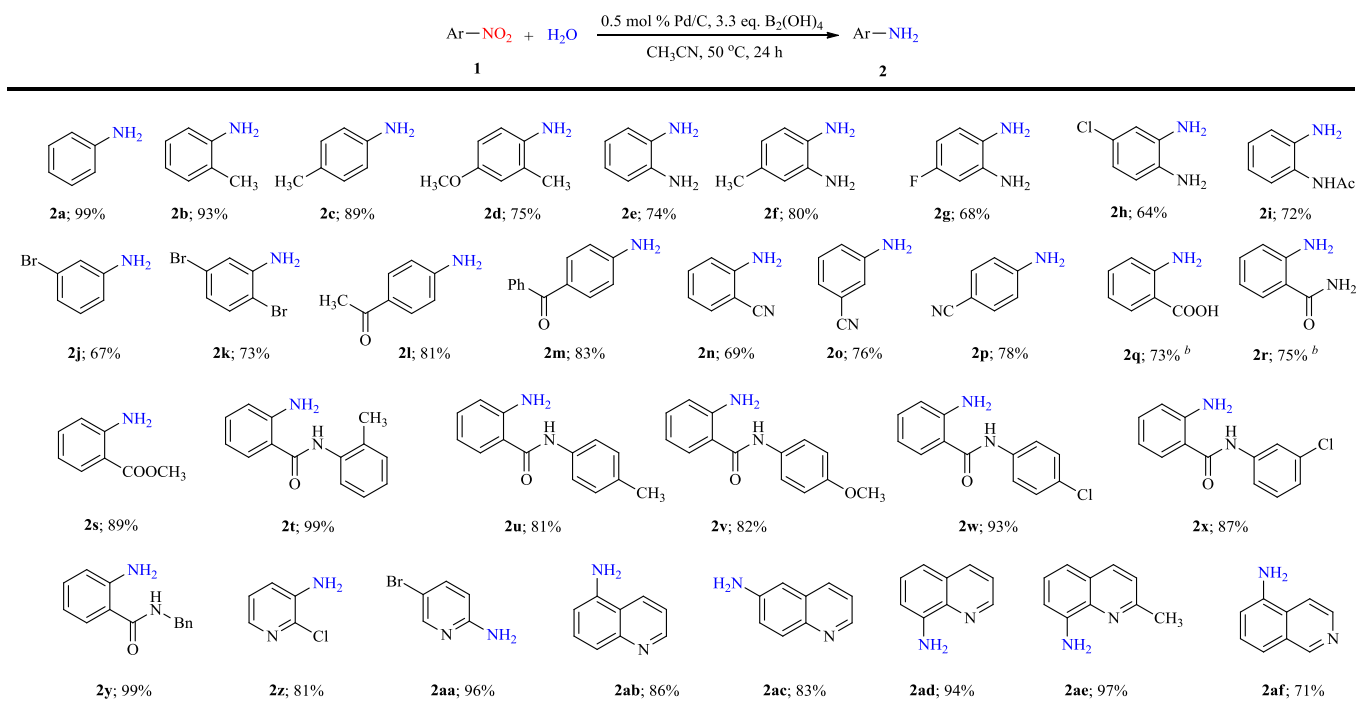
^e 60 °C, 18 h.

screening the solvents, it was found that **2a** was obtained with 62% and 58% yields in toluene and tetrahydrofuran respectively,

whereas no reaction occurred in chloroform (entries 5–7). The reaction proceeded as well in anhydrous methanol to give **2a** in 55% yield, meaning that the alcohol can also serve as solvent and hydrogen source (entry 8). Other palladium catalysts including Pd(OAc)₂, Pd(CF₃COO)₂, Pd(PPh₃)₄, Pd(acac)₂ were also applicable in this transformation except for Pd(PPh₃)₂Cl₂ (entries 9–13).

Other boron reagents including bis(pinacolato)diboron and bis(catecholato)diboron showed less effective, while boronic acid and phenylboronic acid furnished no product at all (entries 14–15, and Supporting Information). The yield of **2a** reached to 99% by increasing the amount of diboronic acid from 2.5 to 3.3 equivalents (entry 16). The starting material **1a** was not completely consumed if reducing the amount of catalyst loading and water, shortening the reaction time, lowering the reaction temperature (entries 17–18, and Supporting Information). The control reactions at different temperature were also tested (entries 19–20). Finally, 0.5 mol % of Pd/C, 3.3 equivalents of diboronic acid, 10 equivalents of water, 1.0 mL of CH₃CN, 50 °C, and 24 h were set as the optimal reaction parameters.

As shown in Scheme 1, with the optimal reaction conditions in hand, the scope of nitroarenes was evaluated. In general, the reduction of nitroarenes with electron-withdrawing or electron-donating groups proceeded smoothly to give the corresponding aryl amines in good to excellent yields. In the case of nitroarenes bearing labile halogens (F, Cl, and Br), the chemoselective reduction of nitro groups took place exclusively to give the corresponding anilines **2g**, **2h**, **2j**, and **2k** in 64–73% yields without dehalogenation. As for the nitroarenes **1l–1p**, the nitro groups were reduced selectively in the presence of reducible carbonyl and nitrile groups, giving the corresponding anilines **2l–2p** with 69–83% yields. However, the nitro compounds **1q** and **1r** containing carboxyl and amide substituents exhibited lower reactivity, affording the anilines **2q** and **2r** in moderate yields even if increasing the catalyst loading to 2 mol %. Compared with 2-nitrobenzamide, the reduction of *N*-phenyl-2-nitrobenzamides **1t–1x** afforded the



^a Reaction Conditions: Nitroarene (0.6 mmol), 0.5 mol % Pd/C, H₂O (6.0 mmol), B₂(OH)₄ (2.0 mmol), 1.0 mL of CH₃CN, 50 °C, 24 h, isolated yield.

^b 2 mol % Pd/C was used.

Scheme 1. Scope of the Reduction of Various Nitroarenes ^a.

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