Cross-Coupling

DOI: 10.1002/anie.201408630

Silver-Catalyzed Arylation of (Hetero)arenes by Oxidative Decarboxylation of Aromatic Carboxylic Acids**

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Abstract: *A long-standing challenge in Minisci reactions is achieving the arylation of heteroarenes by oxidative decarboxylation of aromatic carboxylic acids. To address this challenge, the silver-catalyzed intermolecular Minisci reaction of aromatic carboxylic acids was developed. With an inexpensive silver salt as a catalyst, this new reaction enables a variety of aromatic carboxylic acids to undergo decarboxylative coupling with electron-deficient arenes or heteroarenes regardless of the position of the substituents on the aromatic carboxylic acid, thus eliminating the need for ortho-substituted aromatic carboxylic acids, which were a limitation of previously reported methods.*

The importance of aryl–aryl scaffolds in materials science and medicinal chemistry is a great impetus to the development of catalytic methods for constructing such structures. Among these established methods, the catalytic direct arylation of aromatic C–H bonds is one of the most attractive approaches to biaryl compounds because such a reaction proceeds in a step- or atom-economical fashion.[1,2] In spite of the progress in this area, the catalytic C–H arylation of electron-deficient arenes or heteroarenes, such as pyridines, has remained a challenging goal. Only recently have pioneering studies on the arylation of pyridines been reported,[3–6] including silver-catalyzed coupling with arylboronic acids through aryl radical formation,[3a] nickel-catalyzed coupling with arylzinc reagents by 1,2-addition of a nucleophile,[4] palladium-[5a–c] or rhodium-catalyzed[5d] coupling with aryl halides, and palladium-[6a–c] or rhodium-catalyzed[6d] C–H/C–H cross-coupling with electron-rich heteroarenes. However, significant room still exists for improvement of these reactions with regard to generality, catalytic efficiency, and reaction conditions.

In contrast, the palladium/silver- or palladium/copper-catalyzed decarboxylative cross-coupling of aromatic carboxylic acids to synthesize biaryl compounds has captured considerable interest because aromatic carboxylic acids are readily available, stable, and low-cost.[7] Based on sivler- or copper-promoted decarboxylation to generate in situ aryl–silver or aryl–copper intermediates, aromatic carboxylic acids can cross-couple with aryl halides,[8] electron-rich heteroarenes,[9] polyfluorobenzenes,[10] and even other aromatic carboxylic acids[11] by using palladium catalysts. However, such decarboxylative cross-coupling reactions are usually limited to *ortho*-substituted aromatic carboxylic acids[12] because *ortho* substituents are necessary for silver- or copper-promoted decarboxylation to occur.[13] Besides, these reactions are not amenable to the C–H arylation of electron-deficient (hetero)arenes. To expand the substrate scope of decarboxylative cross-coupling reactions, a new decarboxylation approach needs to be identified. As a powerful synthesis tool, Minisci reactions effect the C–H alkylation of electron-deficient (hetro)arenes by silver-catalyzed oxidative decarboxylation of alkyl carboxylic acids to generate alkyl radicals.[14] Unfortunately, previous studies illustrated that the Minisci conditions failed to work for aromatic carboxylic acids,[3a,14e] probably because it was either difficult for aromatic carboxylic acids to undergo oxidative decarboxylation to generate aryl radicals, or the aryl radicals generated were too reactive to be captured by electron-deficient (hetero)arenes. Very recently, silver-catalyzed oxidative protodecarboxylaton of aromatic carboxylic acids via aryl radical generation and the related silver-catalyzed intramolecular decarboxylative arylation of benzoylbenzoic acid have been successfully achieved,[15] and encouraged us to reexamine the Minisci reaction of aromatic carboxylic acids. Herein, we report the first example of silver-catalyzed[16] intermolecular decarboxylative arylation of electron-deficient (hetero)arenes with aromatic carboxylic acids, thus providing a solution to the long-standing challenge of Minisci reactions (Scheme 1). This catalytic protocol enables a variety of aromatic carboxylic acids to act as arylating reagents without the need for *ortho* substituents, and is compatible with a broad range of functional groups.

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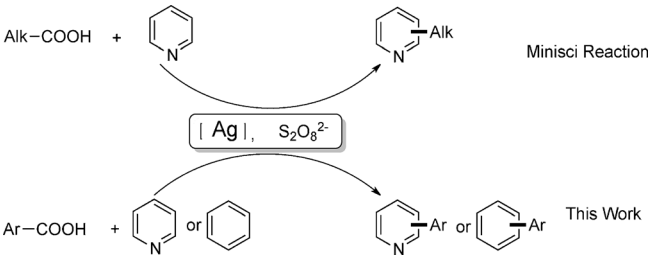
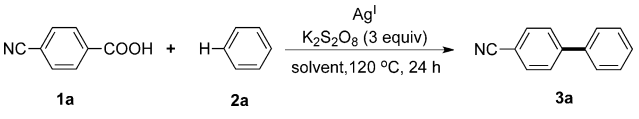
[**] Financial support from the 973 Program (Nos. 2011CB932404, 2011CBA00501), NSFC (Nos. 21332001, 21431008, 21301173) and the CAS/SAFEA International Partnership Program for Creative Research Teams is greatly appreciated.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408630.



Scheme 1. Silver-catalyzed C–H functionalization with (hetero)arenes by oxidative decarboxylation to generate radicals.

Table 1: Selected results for the screening of reaction conditions.[a]



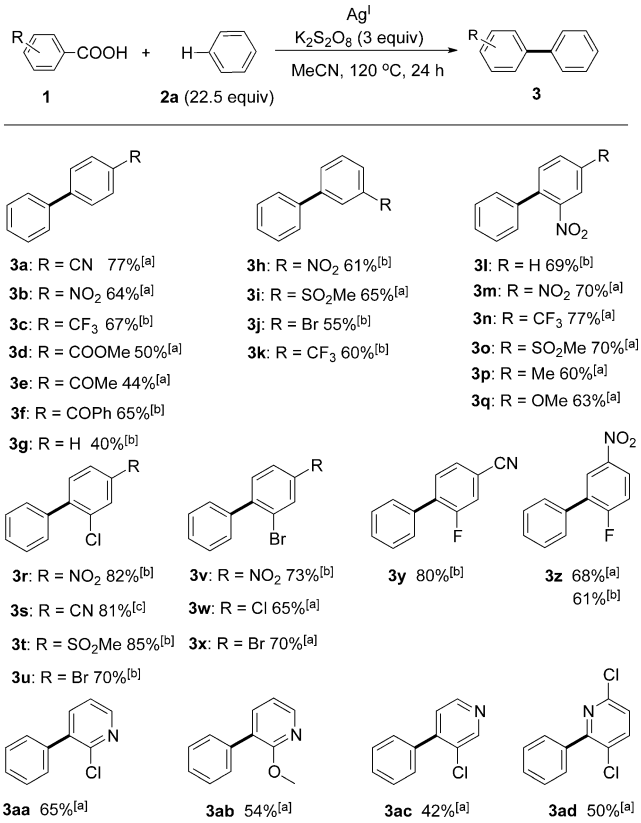
1a 2a 3a

Entry	AgX (mol%)	**2a** (mL)	MeCN (mL)	Yield [%][b]
1	AgOAc (20)	2 (90 equiv)	2	34
2[c]	AgOAc (20)	2	2	21
3[d]	AgOAc (20)	2	2	< 5
4	AgOAc (100)	2	2	< 5
5	AgOAc (5)	2	2	43
6	Ag_2SO_4 (2.5)	2	2	58[e]
7	Ag_2SO_4 (2.5)	1 (45 equiv)	1	71[f]
8	Ag_2SO_4 (2.5)	0.5 (22.5 equiv)	0.5	72[g]
9	$AgNO_3$ (5)	0.5	0.5	76
10	AgTFA (5)	0.5	0.5	80
11	Ag_2SO_4 (10)	0.5	0.5	81 (77)[h]
12[i]	Ag_2SO_4 (2.5)	0.5	0.5	< 5

[a] Reaction conditions: **1a** (0.25 mmol), **2a**, silver(I) salt, $K_2S_2O_8$ (0.75 mmol), 120°C, 24 h, N_2. [b] Yield determined by GC. [c] $(NH_4)_2S_2O_8$ (0.75 mmol) instead of $K_2S_2O_8$. [d] $Na_2S_2O_8$ (0.75 mmol) instead of $K_2S_2O_8$. [e] 36% of **1a** was recovered and 1.6% cyanobenzene and trace biphenyl were detected by GC. [f] 21% of **1a** was recovered and 3.8% cyanobenzene and trace biphenyl were detected by GC analysis. [g] 16% of **1a** was recovered and 3.5% cyanobenzene and trace biphenyl were detected by GC. [h] Yield of isolated product. [i] 20 μL H_2O was added. TFA = trifluoroacetate.

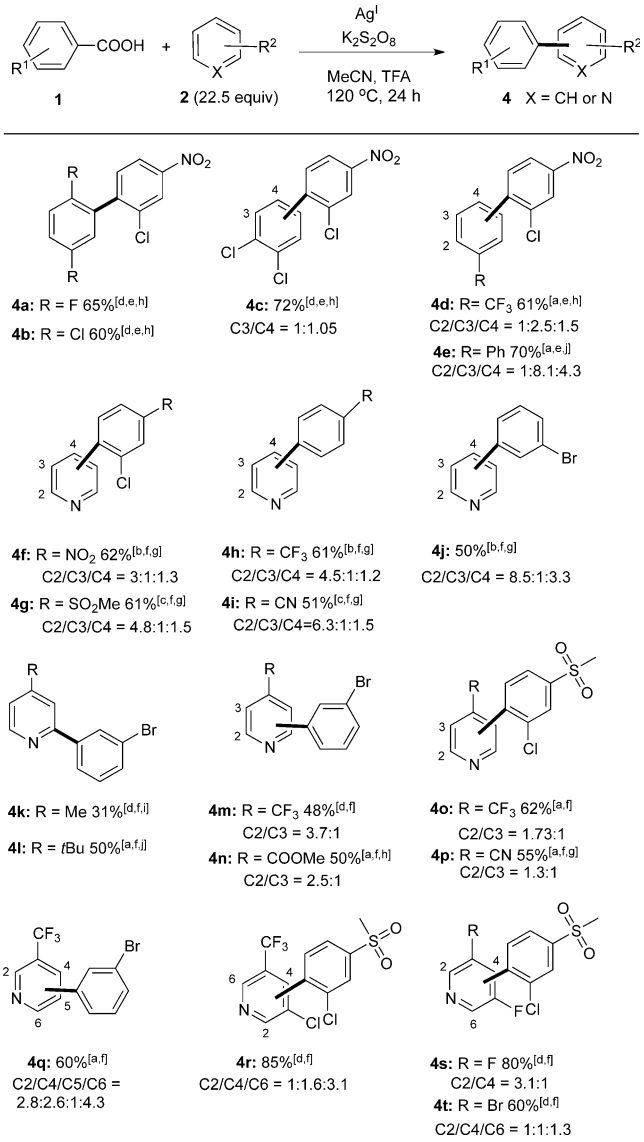
The decarboxylative cross-coupling between 4-cyanobenzoic acid (**1a**) with benzene (**2a**) was selected as a model reaction for optimization studies (Table 1). At the very beginning, the reaction of 0.25 mmol of **1a** with a large excess of **2a** (2 mL), conducted in 2 mL MeCN at 120°C in the presence of AgOAc (0.2 equiv) and $K_2S_2O_8$ (3 equiv), gave the arylated product **3a** in 34% yield after 24 hours (entry 1). When using $Na_2S_2O_8$ or $(NH_4)_2S_2O_8$ as the oxidant instead of $K_2S_2O_8$, the yields of **3a** dropped to 21% (entry 2) and less than 5% (entry 3), respectively. To our surprise, increasing the AgOAc loading to 1.0 equivalent give only a trace amount of **3a** along with a lot of the protodecarboxylation side-product and toluene (in 8% yield relative to AgOAc; entry 4), whereas reducing the AgOAc loading to 0.05 equivalents increased the yield to 43% (entry 5). After that, the efficacy of this arylation reaction in the presence of other sliver sources was examined. Several silver slats, such as $AgNO_3$, AgTFA and Ag_2SO_4 proved to be effective catalysts and led to better conversion (see the Supporting Information). Reducing the volumes of both benzene and MeCN significantly improved the yields (entries 7 and 8). The positive effect observed in entries 7 and 8 may result from the increase in the concentration of the silver(II) complex generated from oxidation of Ag_2SO_4 by $K_2S_2O_8$, a step which should accelerate decarboxylation of aryl carboxylic acid and improve conversion of aryl carboxylic acid.[17] By using 0.5 mL benzene and 0.5 mL MeCN, the yield increased to 80% when using 5 mol% AgTFA and to 81% when using 10 mol% Ag_2SO_4 (entries 9–11). Additionally, the addition of a minute amount of water to the reaction system sharply diminished the yield of **3a** (entry 12). The success of this method is to a large extent attributed to removal of water from the reaction system as compared to the Minisci reaction of boronic acids reported by Baran and co-workers.[3a]

With the optimized reaction conditions in hand, we next evaluated the substrate scope with respect to aromatic carboxylic acids (Scheme 2). Various *ortho*-, *meta*-, *para*-substituted, as well as disubstituted aromatic carboxylic acids provided the desired cross-coupling products in good yields. The reaction tolerated a variety of electron-withdrawing substituents such as nitro (**3b**, **3h**, **3l–q**, **3r**, **3v, 3z**), mesyl (**3i**, **3o**, **3t**), trifluoromethyl (**3c**, **3k**, **3n**), fluoro (**3y**, **3z**), chloro (**3r–u**, **3w**, **3aa**, **3ac**, **3ad**), bromo (**3j**, **3u**, **3v–x**), cyano (**3a**, **3s**, **3y**), ester (**3d**), acetyl (**3e**) and benzoyl (**3f**) groups. Although the *ortho* substituents were not necessary in this protocol, benzoic acids containing *ortho* substituents gave higher yields (**3l** versus **3b**, **3h**).



Scheme 2. Scope of aromatic carboxylic acids. Reaction conditions: aromatic carboxylic acid (0.25 mmol), benzene (0.5 mL), silver(I) salt (5–10 mol%), $K_2S_2O_8$ (0.75 mmol), MeCN (0.5 mL), 120°C, 24 h, N_2. Yields are those of isolated products. [a] 10 mol% $AgSO_4$ (0.025 mmol). [b] 5 mol% $AgNO_3$ (0.0125 mmol). [c] 5 mol% AgTFA (0.0125 mmol).

Picolinic acid, which can stabilize high-valent silver species,[18] also participated in the decarboxylative cross-coupling reaction and gave reasonable yields (**3aa–ad**; Scheme 2). Notably, the substituents influenced the efficiency of the decarboxylative cross-coupling reaction because of the difference in decarboxylation rates. For example, benzoic acids bearing an *ortho*-chloro substituent gave better results compared with *ortho*-nitro- and *ortho*-bromo-substituted



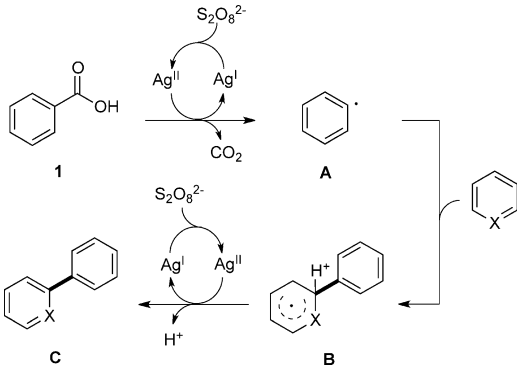
Scheme 3. Scope of (hetero)arenes. Reaction conditions: aromatic carboxylic acid (0.25 mmol), (hetero)arenes (5.625 mmol), silver(I) salt (5–25 mol%), $K_2S_2O_8$, 120°C, 24 h, N_2. Yields are those of isolated products and the relative ratio of regioisomers was calculated using GC-MS data. [a] 10 mol% Ag_2SO_4 (0.025 mmol). [b] 5 mol% $AgNO_3$ (0.0125 mmol). [c] 5 mol% AgTFA (0.0125 mmol). [d] 25 mol% Ag_2SO_4 (0.0625 mmol). [e] $K_2S_2O_8$ (0.75 mmol), without TFA. [f] $K_2S_2O_8$ (1.5 mmol), TFA (5.625 mmol). [g] MeCN (0.5 mL). [h] MeCN (0.75 mL). [i] MeCN (1 mL). [j] MeCN (1.5 mL).

benzoic acids. The latter produced more of the protodecarboxylation side-products.

The decarboxylative arylation reaction was applicable to benzenes bearing electron-withdrawing groups and pyridines (Scheme 3), but reaction conditions needed to be adjusted slightly to obtain satisfying yields and depended on the (hetero)arenes (see the Supporting Information for details). Although an excess of (hetero)arene (22.5 equiv) was used, more than 90% starting materials could be recovered through column chromatography. 1,4-Dichloro- and 1,4-difluoro-substituted benzenes offered pure products (**4a**, **4b**) while 1,2-disubstituted benzenes and monosubstituted benzenes formed a mixture of isomers (**4c–e**). Unfortunately, arenes bearing electron-rich substituents did not work well in this reaction. In the case of pyridines, trifluoroacetic acid (TFA) was essential for the decarboxylative arylation, presumably because the introduction of TFA enhances the reactivity of the pyridines towards capturing nucleophilic aryl radical intermediates generated from decarboxylation.[14e] Similar to Minisci reactions with alkyl carboxylic acids, arylation occurred preferentially at the C2-position of pyridines over the C3- and C4-positions (**4f–j**). For 4-*tert*-butylpyridine and 4-methylpyridine, only the C2-arylated products were formed as a result of steric and electronic effects (**4k**,**l**). In contrast, electron-withdrawing groups such as CF_3, CN, and an ester obviously reduced the reaction selectivity (**4m–p**). Pyridines containing two electron-withdrawing groups at C3 and C5 were observed to afford higher yields (**4q–t**). With the exception of CF_3-substutied pyridines, the reaction selectivity exhibited by all substituted pyridines can be predicted using guidelines put forward by Baran, Blackmond, et al.[3d]

The previous studies on silver-catalyzed Minisci reactions[14,17] revealed that these reactions involved silver(II)-promoted oxidative decarboxylation of alkyl carboxylic acids to generate alkyl radicals. The reactivity and selectivity observed in the silver/persulfate-catalyzed arylation reaction of electron-deficient heterocycles with arylboronic acids points to the possibility that this reaction involves the generation of an aryl radical.[3a] To gain mechanistic insights, additional experiments were performed. When the reaction was conducted in the presence of radical scavengers, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT), none of decarboxylative cross-coupling products were observed. Competition experiments between benzene and [D_6]benzene showed a negligible kinetic isotope effect ($k_H/k_D = 1.3$), thus suggesting that the rate-limiting step does not involve C–H bond cleavage of benzene.

On the basis of the preliminary results and previous reports, a possible mechanism is proposed (Scheme 4). At the beginning of the reaction, the silver(I) salt is oxidized to a silver(II) species by the persulfate anion. Then, the silver(II) species oxidizes the aromatic carboxylic acids **1**, thus leading to decarboxylation and aryl radical (**A**) generation. The aryl radical subsequently adds to benzene or pyridine to generate



Scheme 4. The proposed mechanism for silver-catalyzed decarboxylative arylation.

the cyclohexadienyl radical intermediate **B**. Finally, **B** is oxidized by the silver(II) species to rearomatize and produce the arylated product **C**.

In summary, the silver-catalyzed intermolecular decarboxylative arylation of electron-deficient (hetero)arenes has been successfully developed using aromatic carboxylic acids as arylating reagents, as well as a catalytic amount of a silver salt and a cheap inorganic oxidant. The reaction demonstrates a broad substrate scope and excellent functional-group tolerance. This catalytic method should be valuable in the synthesis of aryl-(hetero)aryl motifs.

Received: August 28, 2014
Revised: November 16, 2014
Published online: December 23, 2014

Keywords: C–H activation · heterocycles · oxidation · radicals · silver

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