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# Ag/Cu-mediated decarboxylative cyanation of aryl carboxylic acids with K<sub>4</sub>Fe(CN)<sub>6</sub> under aerobic conditions

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#### ABSTRACT

A method for facile synthesis of aryl nitriles has been well established via Ag/Cu-mediated decarboxylative cyanation of benzoic acids with  $K_4$ Fe(CN)<sub>6</sub> under aerobic conditions. The approach of using readily accessible aryl carboxylic acids and green  $K_4$ Fe(CN)<sub>6</sub> as starting material provides a feasible alternative to previous cyanation protocols. Control experiments revealed the key role of Cu for the process and excluded the possibility of a radical mechanism for the transformation.

#### **GRAPHICAL ABSTRACT**



# ARTICLE HISTORY

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#### **KEYWORDS**

Aerobic conditions; aryl carboxylic acids; aryl nitriles; Ag/Cu bimetallic system; decarboxylation

# Introduction

Nitrile serves as a versatile synthetic platform that can be facilely converted into a wide variety of functional groups in organic synthesis, including amine, amide, aldehyde, tetrazole and others.<sup>[1]</sup> Moreover, aryl nitriles are widely found as core structural motifs in value-added pharmaceuticals, agrochemicals, dyes and materials.<sup>[2]</sup> Conventionally, Sandmeyer reaction and Rosenmund-von Braun transformation are the common synthetic routes to access aryl nitriles;<sup>[3]</sup> nevertheless, the methods typically hinge on the laborious pre-preparation of unstable aryldiazonium salt and use of stoichiometric amounts of cuprous cyanide under drastic conditions. From the standpoint of the employment of both available aryl donor and safe cyano source, there is significant room for improvement with respect to practical and efficient cyanation procedure.

Transition-metal-mediated reaction for cost-effective and environmentally friendly synthesis of aryl nitriles is a significant topic of current interest in organic chemistry, in this context, transition-metal-promoted cyanation of aryl halides C–X bonds or arenes

(2) Supplemental data (full experimental detail, <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra data and references for all the products) for this article can be accessed on the publisher's website.

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| NO2 +    | K <sub>4</sub> Fe(CN) <sub>6</sub>  | Ag <sub>2</sub> SO <sub>4</sub> , Cu(OAc) <sub>2</sub><br>2,9-DMP | NO <sub>2</sub> |                    |
|----------|---|---|-----------------|--------------------|
| MeO COOH |   | "standard conditions"   | MeO 23          | CN                 |
| 10       |   | standard conditions   | 24              |                    |
| Entry    | Alteration from standard conditions   |   |                 | Isolated yield (%) |
| 1        | None  |   |                 | 85                 |
| 2        | Ag <sub>2</sub> O [instead of Ag <sub>2</sub> SO <sub>4</sub> ]               |   |                 | 77                 |
| 3        | Ag <sub>2</sub> CO <sub>3</sub> [instead of Ag <sub>2</sub> SO <sub>4</sub> ] |   |                 | 79                 |
| 4        | 5 mol% Ag <sub>2</sub> SO <sub>4</sub>  |   |                 | 74                 |
| 5        | Cu <sub>2</sub> O [instead  | of Cu(OAc) <sub>2</sub> ]   |                 | 56                 |
| 6        | Cul [instead o  | of Cu(OAc) <sub>2</sub> ]   |                 | 48                 |
| 7        | Cu(OTf) <sub>2</sub> [inst  | ead of Cu(OAc) <sub>2</sub> ]                                     |                 | 23                 |
| 8        | 0.5 equiv Cu(   | OAc) <sub>2</sub>   |                 | 47                 |
| 9        | 1,10-phen [in:  | stead of 2,9-DMP]   |                 | 72                 |
| 10       | 4,7-DPP [inste  | ad of 2,9-DMP]  |                 | 68                 |
| 11       | 15 mol% 2,9-[   | OMP   |                 | 77                 |
| 12       | 0.5 equiv K <sub>4</sub> Fe   | e(CN) <sub>6</sub>  |                 | 56                 |
| 13       | 2 mL DMSO   |   |                 | 60                 |
| 14       | DMF [instead  | of DMSO]  |                 | 48                 |
| 15       | N <sub>2</sub> [instead of  | f O <sub>2</sub> ]  |                 | 0                  |
| 16       | 120 °C [instea  | d of 140 °C]  |                 | 77                 |

Table 1. Selected results of screening the optimal conditions.<sup>a</sup>

<sup>a</sup>Standard conditions: **1a** (0.2 mmol),  $K_4$ Fe(CN)<sub>6</sub> (0.18 equiv.),  $Ag_2SO_4$  (0.1 equiv.),  $Cu(OAc)_2$  (1 equiv.), 2,9-DMP (0.3 equiv.), DMSO (4 mL),  $O_2$  (1 atm).

C-H bonds with various cyano source have been intensively investigated, respectively.<sup>[4]</sup> The cyano source used in the above reactions could be generated *in situ* from either an organic molecule (CH<sub>3</sub>NO<sub>2</sub>, DMF, AIBN)<sup>[5]</sup> or an organic/inorganic combination (DMF with NH<sub>3</sub> or an ammonium salt, DMSO with an ammonium salt);<sup>[6]</sup> additionally, cyano group transferred to an aromatic ring usually originated from CN-containing compounds with the whole cyanide unit, such as inorganic metal cyanides salts (KCN, NaCN, Zn(CN)<sub>2</sub> and CuCN)<sup>[7]</sup> and organic CN-containing compounds (cyanohydrin, TMSCN, CH<sub>3</sub>CN and malononitrile, N-cyanosuccinimide, N-cyano-N-phenyl-p-toluenesulfonamide (NCTS)).<sup>[8]</sup> However, the inherent toxicity of metal cyanides and irreversible deactivation of the metal catalysts with too much-dissolved cyanide ions are major concerns that restrict wide application of the reactions. In stark contrast to the aforementioned cyano source, potassium hexacyanoferrate(II)  $K_4$ Fe(CN)<sub>6</sub> is usually used as a nontoxic additive in the food industry for residual metal precipitation. Since  $K_4$ Fe(CN)<sub>6</sub> has high stability constant and low dissociation, thus, it can gradually deliver cyanide ions into reaction mixture and prevent transition-metal catalyst poisoning to a great extent. Based on its commercial availability, bench stability and cheapness, as reported, K<sub>4</sub>Fe(CN)<sub>6</sub> is a green cyanide source to synthesize aryl nitriles with Pd catalyst.<sup>[9]</sup>

Among various aryl donors in the preparation of aryl nitriles, aryl carboxylic acids are widely found in nature with innocuity and commercially available in a large variety. Because carboxylic acids can act as distinctly attractive alternatives to traditional electrophilic aryl halides or nucleophilic organometallic counterparts in coupling reactions to minimize waste products with loss of nontoxic CO<sub>2</sub> and enhance the synthetic utility of cross-coupling chemistry, it opens up novel perspective to employ a large pool of readily available aromatic carboxylic acids as arylating reagents.<sup>[10]</sup> During the last decade, a



Table 2. Ag/Cu-mediated coupling of benzoic acids with K<sub>4</sub>Fe(CN)<sub>6</sub> under aerobic conditions.<sup>a</sup>

Ag<sub>2</sub>SO<sub>4</sub>, Cu(OAc)<sub>2</sub>

aReaction conditions: 1 (0.2 mmol),  $K_4$ Fe(CN)<sub>6</sub> (0.18 equiv),  $Ag_2SO_4$  (0.1 equiv.),  $Cu(OAc)_2$  (1 equiv.), 2,9-DMP (0.3 equiv.), DMSO (4 mL),  $O_2$  (1 atm), 140 °C, 20 h.

blsolated yield by an average of two runs.

c0.2 equivalent of  $Ag_2SO_4$  used.

great contribution has been made to create C–C and C–Hetero bonds from the powerful tool of transition-metal-promoted decarboxylative coupling of aromatic carboxylic acids with various carbon- and heteroatom-based coupling partners, including alkenes,<sup>[11]</sup> aryl halides,<sup>[12]</sup> alkynes,<sup>[13]</sup> arenes,<sup>[14]</sup> organoboron compounds,<sup>[15]</sup> imines,<sup>[16]</sup> trifluoromethylating agents,<sup>[17]</sup> silicate esters,<sup>[18]</sup> *H*-phosphine oxides,<sup>[19]</sup> trifluoromethylthiolating reagents,<sup>[20]</sup> thiols and disulfides.<sup>[21]</sup>



Scheme 1. Control experiments to understand reaction mechanism.

Although employing electrophilic cyanating reagent NCTS as cyano source, Song developed metal-free catalyzed decarboxylative cyanation of alkyl carboxylic acids with strong base and Pd-catalyzed decarboxylative cyanation of aryl carboxylic acids;<sup>[22]</sup> in addition, another Song revealed a copper-catalyzed reaction between phenylacetic acids and urea under aerobic conditions to afford benzonitriles *via* a sequence of decarboxylation, dioxygen activation, C–H bond functionalization and nitrile formation with urea as the nitrogen source;<sup>[23]</sup> and Waser disclosed Ir-catalyzed transformation of  $\alpha$ -amino and  $\alpha$ -oxy acids to corresponding nitriles with cyanobenziodoxolones (CBX) as cyano donor under visible light irradiation.<sup>[24]</sup> To the best of our knowledge, it's a daunting challenge and very few examples of decarboxylative cyanation of aryl carboxylic acids have been reported with transition-metal promoters by far.<sup>[25]</sup> K<sub>4</sub>Fe(CN)<sub>6</sub> is a green and cheap cyanide source, in view of our continuing research pursuit in functionalization of aromatic carboxylic acids,<sup>[26]</sup> we herein first describe Ag/Cu-mediated decarboxylative conversion of a range of benzoic acids to aryl nitriles with K<sub>4</sub>Fe(CN)<sub>6</sub> under aerobic conditions.

### **Results and discussion**

We commenced our investigation by selecting decarboxylative cyanation of 5-methoxy-2-nitrobenzoic acid (1a) with  $K_4Fe(CN)_6$  as the model reaction for the optimization studies, and illustrative samplings of the impact of various parameters on the course of the reaction are presented in Table 1. Much to our delight, the desired product 5-methoxy-2-nitrobenzonitrile (2a) was successfully achieved in an excellent yield (85%) when the model reaction was treated with  $Ag_2SO_4$  (0.1 equiv.) and  $Cu(OAc)_2$  (1 equiv.) as bimetallic catalysts in the presence of 2,9-dimethyl-1,10-phenanthroline (2,9-DMP) (0.3 equiv.) as ligand in DMSO at 140 °C for 20 h under aerobic conditions (Table 1, entry 1). A slightly diminished yield was obtained when replaced  $Ag_2SO_4$  with  $Ag_2O$  or  $Ag_2CO_3$  under otherwise equal conditions, respectively (entries 2 and 3), furthermore, halving the loading of  $Ag_2SO_4$  gave a reduced yield (entry 4). The survey of Cu promoter demonstrated the conversion was significantly less efficient with other copper compounds (Cu<sub>2</sub>O, CuI and Cu(OTf)<sub>2</sub>) (entries 5–7), and the clue clearly implied Cu(OAc)<sub>2</sub> was the best choice. Nevertheless, decreasing the loading of Cu(OAc)<sub>2</sub> to 0.5 equivalent resulted in a remarkable drop in reaction activity under otherwise identical conditions (entry 8). Subsequently, other ligands including 1,10-phenanthroline and 4,7diphenyl-1,10-phenanthroline (4,7-DPP) were proved to be less effective compared with 2,9-DMP (entries 9-10), and the choice of 2,9-DMP showed the highest efficiency for this transformation (entry 11). Intriguingly, increasing the loading of  $K_4$ Fe(CN)<sub>6</sub> or reducing the volume of DMSO solvent had a detrimental effect on the transformation (entries 12-13), presumably owing to the poisoning of transition-metal Ag/Cu bimetallic mediators with relatively enhanced concentration of cyanide ions from the Fe(II) center. Solvent screening showed DMSO was the best one for the decarboxylative cyanation coupling (entry 14). A dioxygen atmosphere was crucial to accomplish the reaction since no desired product was detected under nitrogen atmosphere instead of oxygen atmosphere (entry 15). Finally, the yield of the product obviously decreased with reducing reaction temperature from 140 °C to 120 °C, indicating it was a temperature-dependent reaction (entry 16). Based on the aforementioned results, we decided to perform 5dimethoxy-2-nitrobenzoic acid (1a, 1 equiv.) with  $K_4Fe(CN)_6$  (0.18 equiv.) in DMSO at  $140 \,^{\circ}\text{C}$  for 20 h in the presence of Ag<sub>2</sub>SO<sub>4</sub> (0.1 equiv.) and Cu(OAc)<sub>2</sub> (1 equiv.) as bimetallic mediators as well as 2,9-DMP (0.3 equiv.) as the optimized conditions.

Subsequently, the optimal conditions inspired us to extensively explore the scope of aryl carboxylic acids substrates in this Ag/Cu-mediated decarboxylative cyanation reaction. As shown in Table 2, the transformation was similar to our recent observation,<sup>[26]</sup> which was effective for a diverse range of substituted ortho-nitrobenzoic acids (1a-j) and ortho-methoxybenzoic acid (1k). It is a suitable substrate of ortho-nitrobenzoic acid (1f) to swimmingly deliver the desired ortho-nitrobenzonitrile in 70% isolated yield. Because the diverse electronic nature of substituent on the ortho-nitrobenzoic acid substrate had some effect on the conversion, ortho-nitrobenzoic acid (1f) was the divide between electron-donating (methoxy and methyl) and -withdrawing (chloro, trifluoromethyl and bromo) groups on the aromatic ring of the 2-nitrobenzoic acid substrate. It is observed that ortho-nitrobenzoic acid-bearing electron-donating (methoxy and methyl) groups furnished corresponding products in satisfied yields, 5-methoxy-2-nitrobenzoic acid (1a) and its isomer 4-methoxy-2-nitrobenzoic acid (1b) as well as 4,5dimethoxy-2-nitrobenzoic acid (1c) were readily accommodated to smoothly afford the desired cyanation products. Likewise, a similar observation was consistent with good conversion for 4-methyl-2-nitrobenzoic acid (1d) rather than sterically hindered 2-methyl-6-nitrobenzoic acid (1e), indicative of the sensitivity of the transformation to steric hindrance. Unfortunately, 2-nitrobenzoic acids tolerated electron-withdrawing (chloro, trifluoromethyl and bromo) groups provided moderate yields in this protocol, 5-chloro-2-nitrobenzoic acid (1g) and its isomer 4-chloro-2-nitrobenzoic acid (1h) furnished the hoped-for products with the chloro moiety surviving from the standard conditions, furthermore, the chloro moiety could be used as a useful precursor for latestage modification via the activation of C-Cl bond, making further elaborations of the respective cyanation products possible. The substrates 4-trifluoromethyl-2-nitrobenzoic acid (1i) and 4-bromo-2-nitrobenzoic acid (1j) led to decreased yields with concomitant formation of protodecarboxylation products, respectively. Finally, it is noteworthy that electron-rich 2,4-dimethoxybenzoic acid (1k) was also compatible with this protocol to furnish expected product in the transformation, although the loadings of Ag was increased to 0.2 equiv. to provide 40% isolated yield under otherwise equal conditions.

Thereafter, some control experiments were performed to gain further insight into the underlying reaction mechanism. First, Cu-catalyzed decarboxylative cyanation (1a) with  $K_4$ Fe(CN)<sub>6</sub> provided corresponding product in 26% yield without Ag, whereas no desired product was detected in the absence of Cu under otherwise identical conditions (Scheme 1, A), thus, the results suggested that Cu was the key to the successful implementation of transformation, which is consistent with the literature reported by Hoover and coworkers.<sup>[27]</sup> Second, the reaction could not be suppressed in the presence of radical scavengers such as BHT (2,4-di-*tert*-butyl-4-methylphenol) or TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (Scheme 1, B), suggesting the radical pathways are unlikely.

# Conclusion

In conclusion, we have presented an Ag/Cu-mediated protocol for decarboxylative cyanation of broadly available aryl carboxylic acids with  $K_4Fe(CN)_6$  serving as a green cyanide source. The process provided products in moderate to good yields with high selectivity and exhibited a good functional compatibility with respect to both electrondonating and -withdrawing groups, which is a low-cost alternative to existing methods for the preparation of nitriles. Control experiments suggested Cu was essential for the reaction and radical mechanism might not be involved in the transformation. Ongoing investigations directed towards detailedly elucidate reaction mechanism and extend practical application of this method are currently in progress.

# Experimental

# **General information**

The reagents used for experiments were commercially available and were used as received unless otherwise noted. DMSO was distilled from  $CaH_2$  under reduced pressure and stored under nitrogen. All reactions were performed under dioxygen with the strict exclusion of moisture using Schlenk techniques. Column chromatography was performed on silica gel 300–400 mesh. The yields reported are the isolated yields and the average of two runs. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded at 400, 100 and 377 MHz with CDCl<sub>3</sub> as a solvent, respectively. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on Bruker Daltonics APEX II 47e Specification (ESI).

# Typical procedure for the synthesis of aryl nitrile

An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol),  $Ag_2SO_4$  (6.2 mg, 0.02 mmol, 0.1 equiv.),  $Cu(OAc)_2$  (36.3 mg, 0.2 mmol, 1 equiv.),  $K_4Fe(CN)_6$  (13.2 mg, 0.036 mmol, 0.18 equiv.) and 2,9-dimethyl-1,10-phenan-throlinium (12.5 mg, 0.06 mmol, 0.3 equiv.). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 140 °C for the indicated amount of time

(unless otherwise specified). After cooling to room temperature, the reaction mixtures were diluted with ether (10 mL) and filtered through a pad of silica gel that was then washed with ether (10 mL  $\times$ 3). The combined organic phase was washed with brine (20 mL  $\times$ 2), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The resulting residue was purified using flash column chromatography over silica gel to provide the corresponding product with ethyl acetate/hexane as eluent.

#### 5-Methoxy-2-nitrobenzonitrile (2a)

Yellow solid, mp 95–96 °C, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.31 (d, J=9.3 Hz, 1 H), 7.32 (d, J=2.6 Hz, 1 H), 7.21 (dd, J=2.6, 9.3 Hz, 1 H), 3.97 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.7, 141.4, 128.0, 120.6, 118.2, 115.1, 110.0, 56.7. Exhibited spectral data in accordance with the previous report.<sup>[29]</sup>

### **Disclosure statement**

We state that none of the authors have any conflict of interest in the context of this communication.

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