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Pd-Catalyzed Decarboxylative *Ortho*-Halogenation of Aryl Carboxylic Acids with Sodium Halide NaX Using Carboxyl as a Traceless Directing Group

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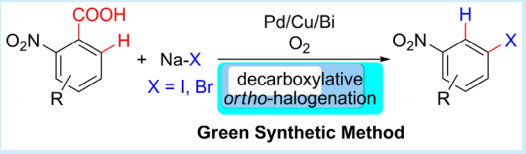
Supporting Information

ABSTRACT: A highly regioselective Pd-catalyzed carboxyl directed decarboxylative *ortho*-C−H halogenation of cheap *o*-nitrobenzoic acids with NaX (X = I, Br) under aerobic conditions has been established. The utility of the method has been demonstrated by the gram-scale reaction and derivatization of the product. Experimental results have confirmed Pd and Bi played critical roles in the transformation and indicated the transformation might proceed via 2-halo-6-nitrobenzoic acid derivative intermediate.



Aryl carboxylic acids are obviously advantageous choice for their wide availability and low cost, and the carboxyl groups are able to not only act as anchor points for *ipso*-functionalization through decarboxylative conversion but also direct *ortho*-functionalization via carboxyl-directed C−H activation at specific positions as well.[1] In this context, significant progress has been made in a range of decarboxylative transformations under Pd,[2] Cu,[3] Ag,[4] Rh,[5] Ni,[6] Fe,[7] and Mn[8] catalysis, including *ipso*-arylation,[2a−i,3a,5,4c,6b] alkenylation,[2j,6d] alkynylation,[4d,6c] alkylation,[7,6e] amination,[2k,3c] azidation,[4b] borylation,[6a] etherification,[4e] halogenation,[4f,8] silylation,[3b] and trifluoromethylthiolation.[4a] In addition, transition-metal-catalyzed carboxyl-directed *ortho*-C−H functionalization of benzoic acids with various coupling partners has also been intensively investigated during the past decade.[1,9] Unfortunately, the strategy involving directing group suffers from the limitation to remove carboxyl with extra effort in many cases, since the directing group is not usually present in desired final molecule.

As an intrinsic part of the substrate, the traceless directing group can direct a target functional group into a specific position of the substrate and then be completely removed with no trace under transition-metal catalysis in a one-pot manner. In terms of atom and step economy, employing carboxyl as a traceless directing group is a state-of-the-art strategy in decarboxylative *ortho*-C−H functionlization. In this regard, Larrosa described exquisite control of regioselectivity in synthesizing *meta*-substituted biaryls through Pd-catalyzed *ortho*-C−H arylation of benzoic acids or salicylic aicds with iodoarenes using carboxyl as a traceless directing group;[10] additionally, this group revealed an interesting example for Pd-catalyzed one-pot *meta*-arylation of phenols, which consisted of a two-step synthetic sequence involving an initial Kolbe−Schmitt carboxylation and the following tandem arylation/decarboxylation reaction.[11] Moreover, the strategy utilizing carboxyl as a traceless directing group has great potential to prepare diversely substituted arenes, as a result, considerable efforts has been devoted to develop transition-metal-catalyzed regiospecific decarboxylative *ortho*-C−H alkenylation,[12] arylation,[13] alkylation,[14] and amidation[15] of aromatic carboxylic acids to create new C−C bonds. Although the group of Goossen established a method to construct a C−O bond through Ag/Cu-mediated *ortho*-C−H alkoxylation of aryl carboxylates with carboxylate substituents as cleavable directing groups,[16] to the best of our knowledge, decarboxylative *ortho*-C−H functionlization of aryl carboxylic acids to build other carbon−heteroatom bonds including carbon−halogen bonds has remained hitherto elusive.

In continuation of our interest in copper-mediated decarboxylative *ipso*-functionalization of aryl carboxylic acids,[17] we have reported decarboxylative *ipso*-halogenation of aryl carboxylic acids with CuX as both reaction promoter and halogen source.[17e] In view of the requirement for stoichiometric amounts of CuX, there is still significant room for improvement for decarboxylative *ipso*-halogenation transformation. Recently, our group has established Ag/Cu-catalyzed halodecarboxylation to generate versatile aryl halides using nontoxic sodium halide NaX as halogen donator.[17f,g] Furthermore, the realized decarboxylative *ipso*-halogenation of aryl carboxylic acids has inspired us to introduce a halo group into the *ortho*-C−H bond of benzoic acids and the following protodecarboxylation in a one-pot process via the aforementioned traceless directing group strategy. In order to reach the goal, the initial step of carboxyl-directed *ortho*-C−H halogenation of benzoic acids must be achieved prior to decarboxylation process to deliver *ortho*-halogenation, while undesired decarboxylative *ipso*-halogenation conversion needs to be completely suppressed. If all goes smoothly, the desired reaction will be synthetically complementary to our recently established decarboxylative *ipso*-halogenation transformation (Scheme 1).[17e−g]

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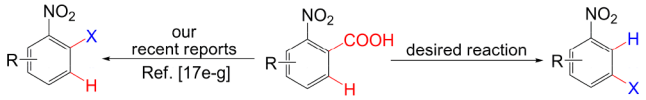
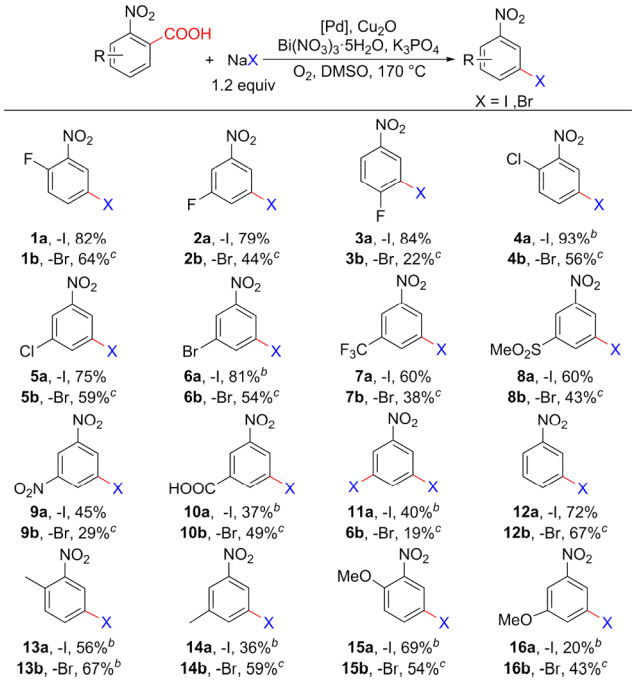
Scheme 1. Established and Desired Transformations in Our Group



We performed decarboxylative *ortho*-iodination of 2-nitrobenzoic acid **12** with NaI as the model reaction to identify the optimum reaction conditions (see the SI for details). Electrophilic Pd(II) was chosen as catalyst to promote *ortho*-C−H activation of benzoic acids with carboxyl as the directing group,[1,9] and a combination of Pd(II) with Lewis acid would improve the reactivity of the Pd(II) catalyst by decreasing the electron density at the Pd(II) center.[18] Hoover and our group have revealed that Cu(II) efficiently mediated decarboxylation of *o*-nitrobenzoic acids under aerobic oxidative conditions.[17,19−21] Thus, the later stage of decarboxylation in the desired reaction could also be promoted by Cu(II), which is generated in situ by the slow oxidation of the poorly soluble Cu_2O. To our delight, the model reaction was conducted in the presence of $Pd(OAc)_2$ (10 mol %) as catalyst with Cu_2O (1 equiv) and K_3PO_4 (0.5 equiv) as well as $Bi(NO_3)_3{\cdot}5H_2O$ (2 equiv) as additives to furnish desired *m*-nitroiodobenzene **12a** in 72% isolated yield under a dioxygen atmosphere in DMSO at 170 °C, whereas the decarboxylative *ipso*-iodination product was not detected in the crude reaction mixtures.

To evaluate the power of this methodology, we examined the scope of substituted benzoic acids for this novel Pd-catalyzed decarboxylative *ortho*-halogenation transformation (Scheme 2). Similar to our recent observation,[17] a variety of *o*-nitrobenzoic acids **1**−**16** were successfully transformed into the corresponding *m*-nitrohalobenzenes in moderate to excellent yields with no trace of decarboxylative *ipso*-halogenation regioisomer. It was observed that *o*-nitrobenzoic acid **12**, which was also the divide between electron-withdrawing (fluoro, chloro, bromo, trifluoromethyl, methylsulfonyl, nitro, and carboxyl) and electron-donating groups (methyl and methoxy) on the aromatic ring of 2-nitrobenzoic acid, was a viable substrate to afford the desired *m*-nitrohalobenzenes with NaX (X = I, Br) in good yields; thus, the range of the substituents was found to be broad in this protocol. It has been reported that *ortho*-substituted benzoic acids are inherently destabilized substrates compared with their *meta*- and *para*-substituted counterparts, while the presence of an *ortho*-electron-withdrawing group results in additional stabilization of the transition state. Thus, owing to the combination of steric and electronic effects, *o*-nitrobenzoic acids lead to much lower activation energy barriers for decarboxylation processes.[17f,22] For the process of decarboxylative *ortho*-iodination, albeit with moderate yields in the case of 2-nitrobenzoic acid bearing another nitro group **9** and carboxyl group **10**−**11**, *o*-nitrobenzoic acid with other electron-withdrawing groups **1**−**8** furnished target products at synthetically useful levels. For the substrates of 2-nitrobenzoic acid with a fluorine substituent in different positions, 3-fluoro-2-nitrobenzoic acid **1** and its isomers **2** and **3** were effective substrates to conveniently provide the corresponding products in good yields. It was found that the desired products were provided in good to excellent yields for the substrate 3-chloro-2-nitrobenzoic acid **4** and its isomeric compound **5** with a chloro substituent at the *meta*-position of nitro group. Likewise, *o*-nitrobenzoic acids with a bromo **6** or trifluoromethyl **7** substituent at the *meta*-position of the nitro group were qualified substrates to furnish target products. Interestingly, for the cases of the decarboxylative *ortho*-halogenation of 2-nitrobenzoic acid tolerated another carboxyl group, *ortho*-diiodination occurred directly for the case of 2-nitroisophthalic acid **11** with two carboxyls at the *ortho*-position of nitro group, whereas 2-nitroterephthalic acid **10** afforded the monoiodinated product with the *m*-carboxyl substituent to the nitro group intact. It is worth noting that *o*-nitrobenzoic acid with methyl and methoxy groups also participated in the transformation, for example, 3-methyl-2-nitrobenzoic acid **13** and 3-methoxy-2-nitrobenzoic acid **15** proceeded well to undergo the conversion. Compared with their isomers, 4-methyl-2-nitrobenzoic acid **14** and 4-methoxy-2-nitrobenzoic acid **16** were less amenable to the process with relatively low transformation efficiency. Apart from *o*-nitrobenzoic acid bearing carboxyl, methyl, and methoxy groups (**10**, **13**−**14**, and **16**), the efficiency of decarboxylative *ortho*-iodination was superior to that of decarboxylative *ortho*-bromination in this protocol, which could be explained as a result of the order of electron-withdrawing ability of the halogen. To solve this problem, regulating reaction conditions with the use of $Pd(PPh_3)_4$ as catalyst led to smooth decarboxylative *ortho*-bromination at the position *meta* to the nitro group.

Scheme 2. Scope of the Reaction[a]



[a]Conditions: acid (0.2 mmol), NaI (1.2 equiv), $Pd(OAc)_2$ (0.15 equiv), Cu_2O (1 equiv), $Bi(NO_3)_3{\cdot}5H_2O$ (2 equiv), K_3PO_4 (0.5 equiv), DMSO (2 mL), O_2, 170 °C, 10 h. [b]$Pd(TFA)_2$ (0.1 equiv) instead of $Pd(OAc)_2$ (0.15 equiv). [c]$Pd(PPh_3)_4$ (0.2 equiv) instead of $Pd(OAc)_2$ (0.15 equiv).

To further prove the effectiveness and practicality of this method, a large-scale decarboxylative *ortho*-iodination of 4-chloro-2-nitrobenzoic acid **5** was run under the optimized conditions, and the desired **5a** was obtained on a gram scale in 50% isolated yield (1.1 g) (Scheme 3A). Additionally, derivatization of **5a** was also tested, and the compound **5a**

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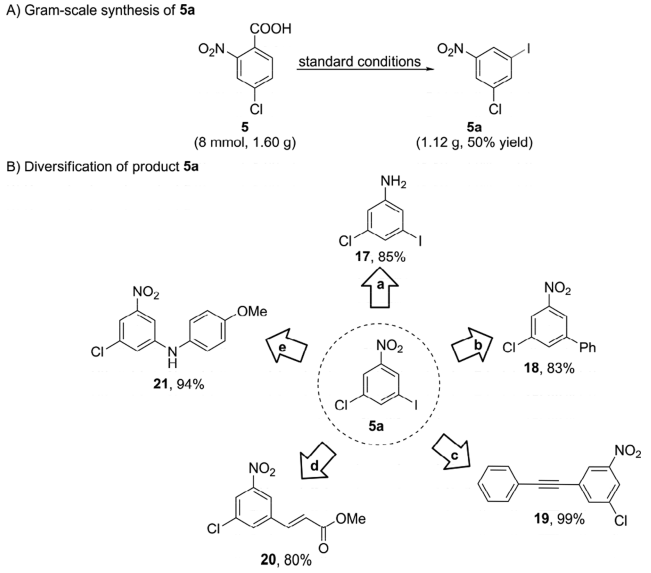
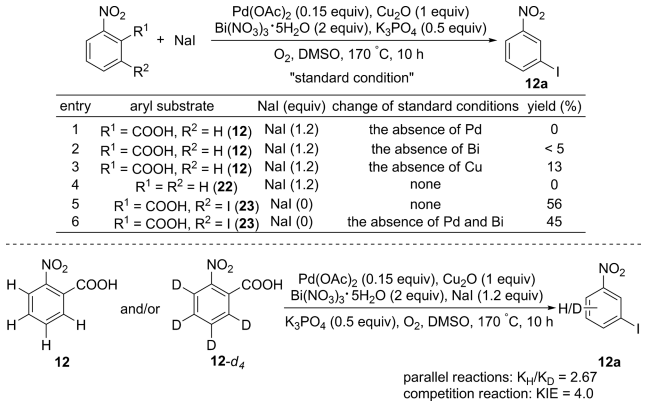
Scheme 3. Gram-Scale Synthesis of Product 5a and Derivatization of 5a



was efficiently transformed into various products **17**−**21** in good to excellent yields with high chemoselectivity under different conditions (Scheme 3B; see the SI for the details).

Some experiments were carried out to elucidate reaction mechanism, as shown in Scheme 4. First, control experiments

Scheme 4. Experimental Mechanistic Studies

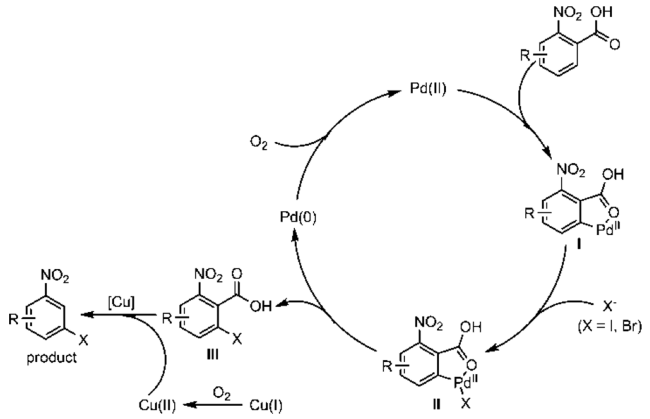


entry	aryl substrate	NaI (equiv)	change of standard conditions	yield (%)
1	R^1 = COOH, R^2 = H (**12**)	NaI (1.2)	the absence of Pd	0
2	R^1 = COOH, R^2 = H (**12**)	NaI (1.2)	the absence of Bi	< 5
3	R^1 = COOH, R^2 = H (**12**)	NaI (1.2)	the absence of Cu	13
4	R^1 = R^2 = H (**22**)	NaI (1.2)	none	0
5	R^1 = COOH, R^2 = I (**23**)	NaI (0)	none	56
6	R^1 = COOH, R^2 = I (**23**)	NaI (0)	the absence of Pd and Bi	45

were performed to investigate the influence of Pd catalyst and additives ($Bi(NO_3)_3{\cdot}5H_2O$ and Cu_2O) on the transformation under otherwise equal conditions. In the absence of Pd catalyst, the transformation gave some protodecarboxylation product instead of desired product **12a** (entry 1). As for the lack of $Bi(NO_3)_3{\cdot}5H_2O$, the conversion furnished a trace amount of target product **12a** along with decarboxylative methylthiolation,[17a] protodecarboxylation,[17b] and some unidentified byproducts (entry 2). Furthermore, a low yield of **12a** was observed without Cu_2O (entry 3). Therefore, the control experiments demonstrated Pd catalyst and $Bi(NO_3)_3{\cdot}5H_2O$ additive were crucial to the transformation, while Cu_2O played an important role in the conversion. Second, none of desired product **12a** was detected when nitrobenzene **22** was mixed with NaI under standard conditions, so the possibility of nitrobenzene as an intermediate was ruled out, while it was suggested the likelihood of the *ortho*-C−H iodination step was prior to decarboxylation process (entry 4). Moreover, 2-iodo-6-nitrobenzoic acid **23** was prepared to test whether the compound was an intermediate to form **12a** via protodecarboxylation, significantly, the obtainment of **12a** (56% yield) under standard conditions highlighted that 2-iodo-6-nitrobenzoic acid **23** was very probably the intermediate in this decarboxylative *ortho*-iodination transformation (entry 5). Additionally, 2-iodo-6-nitrobenzoic acid **23** was converted into **12a** in 45% yield without Pd catalyst and Bi additive (entry 6), and it was presumed that Cu acted as the promoter of protodecarboxylation in this method. The transformation exhibited an intermolecular kinetic isotope effect (KIE) both in the competitive experiment (k_H/k_D = 4.0) and in parallel reactions (k_H/k_D = 2.67), so the C−H bond-cleavage process might be involved in the rate-limiting step of the conversion, which was consistent with *ortho*-C−H functionalization of benzoic acids using carboxyls as directing groups.[13b,23]

In light of the above results, although the detailed mechanism is not clear, a plausible mechanism for decarboxylative *ortho*-halogenation conversion is proposed in Scheme 5.

Scheme 5. Proposed Mechanism



Initially, Pd(II) species underwent a carboxyl-directed cyclometalation reaction to form five-membered palladacycle intermediate **I** with the assistance of Bi additive.[9] Due in part to the electron deficiency of *o*-nitrobenzoic acids, in this regard, Bi additive was proposed to act as a Lewis acid to increase the electrophilicity of the Pd(II) catalyst.[18,24] Subsequently, the coordination of halogen X (X = I, Br) with the Pd of intermediate **I** to generate Pd(II) complex **II** and then the formation of 2-halo-6-nitrobenzoic acid derivative **III** via reductive elimination with the simultaneous release of Pd(0) species occurred. Afterward, catalytic species Pd(II) was regenerated under aerobic oxidative conditions to complete the catalytic cycle.[25] Finally, the resulting 2-halo-6-nitrobenzoic acid derivative **III** underwent a protodecarboxylation to provide the desired *m*-nitrohalobenzene derivative product in the presence of Cu(II) that originated from stoichiometric amounts of Cu(I) under aerobic conditions.[17,19]

In summary, we have represented an approach to prepare *m*-nitrohalobenzenes via Pd-catalyzed decarboxylative *ortho*-halogenation coupling of easily available *o*-nitrobenzoic acids with abundant NaX (X = I, Br) under aerobic conditions. Gram-scale reaction and derivatization of the product were performed to assess advantage of the method. Supported by preliminary mechanistic studies, Pd and Bi were essential for the conversion, and 2-halo-6-nitrobenzoic acid derivative was

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an intermediate in the transformation. Efforts are currently underway to improve reaction efficiency, and the result will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00460.

Experimental procedures and spectral data for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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