



Electrocatalysis

Direct Arylation of α-Amino C(sp³)-H Bonds by Convergent Paired Electrolysis

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Abstract: A metal-free convergent paired electrolysis strategy to synthesize benzylic amines through direct arylation of tertiary amines and benzonitrile derivatives at room temperature has been developed. This TEMPO-mediated electrocatalytic reaction makes full use of both anodic oxidation and cathodic reduction without metals or stoichiometric oxidants, thus showing great potential and advantages for practical synthesis. This convergent paired electrolysis method provides a straightforward and powerful means to activate C–H bonds and realize cross-coupling with cathodically generated species.

Benzylic amines are ubiquitous structural motifs among natural products and medicinal agents.^[1] An ideal method to construct the building blocks is the direct cross-coupling of aryl compounds and amines.^[2-4] Among the existing methods, transition-metal catalysis or stoichiometric oxidants are utilized to active the inert α -amino sp³ C–H bonds. In 2011, MacMillan and co-workers disclosed a breakthrough method involving photoredox-catalyzed α -amino C–H arylation for the construction of benzylic amines from readily available tertiary amines and cyanoaromatics.^[2a] Inspired by this pioneering work, highly efficient photoredox catalysis methods were successively developed for diverse C–H bond arylation reactions.^[2b-g]

Different metal-catalysis strategies were successfully developed by the groups of Li,^[3a] Sames,^[3b] Chen,^[3c] Maes,^[3d] Yu,^[3e,f] Glorius,^[3g] and Gong,^[3h] using oxidative cross-dehydrogenative coupling, directed C–H bond activation, and deprotonation–transmetalation. Impressively, chiral benzylic amines have been constructed through asymmetric deprotonation,^[3c] and chiral phosphorus ligands enabled enantioselective C–H activation by palladium^[3f,h] or rhodium catalysis.^[3g] Recently, Shirakawa et al. discovered that the metal-free arylation of alkylamines with aryl halides can be promoted by an equivalent *tert*-butoxy radical precursor at 60 or 120 °C.^[4] Despite these important and elegant advances, the metal- and stoichiometric-oxidant-free methods for the

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direct arylation of amines are unavailable, and remain a great challenge in organic synthesis. Therefore, novel and environmentally friendly approach to α -amino sp³ C–H arylation by using clean energy are urgently needed.

As a direct and powerful tool to provide and transfer electrons, electrolysis can trigger various transformations and afford interesting and unexpected products.^[5] In contrast to normal electrochemical process, which only involve either the anodic or cathodic reaction, paired electrolysis simultaneously matches the two desirable half reactions, thus furnishing one or more products.^[6] In partucular, convergent paired electrolysis,^[6f-h] in which the intermediates formed at anode and cathode interact with each other to yield the final product, is an efficient approach to perform cross-coupling reactions. From the perspective of retrosynthesis for the arylation of α -amino sp³ C–H bonds, we can divide the coupling produces into two parts: dehydrogenation of amines and reduction of aryl precursors, such as halogenated aromatics and benzonitriles. Therefore, we speculated that the cross coupling of tertiary amines and arenes could be achieved through convergent paired electrolysis, in which the anodically generated α -amino radicals react with the arene radical anions formed at the cathode, giving arise to the final products (Scheme 1).



Scheme 1. Convergent paired electrolysis for the arylation of tertiary amines. EWG = electron-withdrawing group.

Generally, the compatibility of the two desired half reactions and its reactive species are the major factors in developing convergent paired electrolysis. Hence, at the outset, optimizing suitable partners was carried out. Under direct electrolysis with an electrolyte solution of nBu_4NClO_4 in CH₃CN and pyridine as an additive base, combinations of a variety of tertiary amines and arenes were tested, such as 1phenylpyrrolidine (**1a**), 1-methylpyrrolidine, *N,N*-dimethylaniline, 2-chlorobenzothiazole, 4-cyanopyridine, and 1,4-dicyanobenzene (**2a**). Only the pairing of **1a** and **2a** afforded the desired product (**3a**) in 8% yield. Thus, they were chosen as the model reactants to screen for optimal conditions, including solvents, mediators, and electrode materials. The result showed that the outcome of the process can be improved in the presence of 2,2,6,6-tetramethylpiperidinooxy (TEMPO),

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Table 1: Optimization of reaction conditions [a]



Entry	Deviation from standard conditions	Yield [%] ^[b]
1	none	78(10) ^[c]
2	No mediator	35
3	II instead of I	46
4	III instead of I	40
5	IV instead of I	34
6	no base	39
7	under air atmosphere	45 (20)
8	DMF as solvent	66
9	acetone as solvent	32
10	CH ₃ CN as solvent	47
11	RVC(+)-CF(-) instead of RVC(+)-RVC(-)	45
12	RVC(+)-Pt(-) instead of $RVC(+)$ -RVC(-)	64

[a] Reaction condition: reticulated vitreous carbon RVC anode, RVC cathode, 0.4 mmol **1 a**, 0.2 mmol **2 a**, 0.02 mmol **I**, 0.4 mmol 2,6-lutidine, 0.4 mmol *n*Bu₄NClO₄, 4 mL DMA, N₂, constant current = 5 mA, 25 °C, 8 h, 7.5 Fmol⁻¹. [b] Yield of isolated **3 a**. [c] Yield of isolated **4**.

which is a normal mediator in electrochemistry.^[5f, 7] In an undivided cell equipped with reticulated vitreous carbon (RVC) as the anode and cathode, 3a was afforded in 78% yield with 10 mol% TEMPO in N,N-dimethylethanamide (DMA) under a constant current of 5 mA (Table 1, entry 1). It is also interesting to note that the α -cyanation product 4, a byproduct generated from the addition of CN- to an iminium ion, was also obtained in 10% yield.^[7d,8] Upon removing TEMPO or replacing TEMPO with analogues II-IV, the yields dramatically descended to 34–46% (Table 1, entries 2-5). Since the deprotonation of 1a could be facilitated under basic condition, 3a was only obtained in 39% yield in the absence of 2,6-lutidine (Table 1, entry 6). Considering that the α -amino carbon radical is prone to be oxidized and transformed into imine nitrenium ions,^[7d,8,9] the electrolysis under air atmosphere was tested and gave 3a and 4 in 45% and 20% yields, respectively (Table 1, entry 7). The survey of polar solvents, such as DMA, N,N-dimethylamide (DMF), CH₃CN, and acetone, indicated that DMA was the best (Table 1, entries 8-10). By contrast, no desired product was obtained in protic or nonpolar solvents. When the RVC cathode was replaced with carbon felt (CF) or Pt plate, 3a was afforded in 45% and 64% yields, respectively (Table 1, entries 11,12).

With the optimal conditions in hand, the scope with respect to tertiary amines and benzonitrile derivatives under the standard conditions was explored. A variety of tertiary arylamines bearing electron-donating groups, such as methyl, methoxyl, tertiary butyl, phenoxyl, acetoxyl, and acetamino, were examined with moderate to excellent yields groups (Scheme 2. 3b-3j, 42–92%). The interaction between 2a and



Scheme 2. Substrate scope. Reaction conditions: RVC anode, RVC cathode, 0.4 mmol 1, 0.2 mmol 2, 0.02 mmol I, 0.4 mmol 2,6-lutidine, 0.4 mmol *n*Bu₄NClO₄, 4 mL DMA, N₂, constant current = 5 mA. [a] Yield of isolated products. [b] The yield from 10 mmol scale electrolysis. [c] Catalyzed by IV. [d] NaAcO (0.4 mmol) as the additive base, 40 °C, constant current = 10 mA. [e] The yield was obtained with the standard conditions. [f] Pyridine (0.4 mmol) as the additive base, DMF as the solvent, constant current = 10 mA. [f] NaHCO₃ (0.4 mmol) as the additive base, DMF as the solvent, constant current = 10 mA.

amines substituted with weakly electron-withdrawing groups (F, Cl, Br and OCF₃) afforded the desired products in 62% to 86% yields under the optimal conditions (Scheme 2. 3k-3n). Additionally, the coupling of 2a with ortho-, meta-, or multisubstituted amines also smoothly proceeded with yields of 62-92% (Scheme 2. 3h-3j, 3o-3p). However, when amine substrates with strongly electron-withdrawing groups were used, the arylated adducts were not detected,^[10] mainly due to their poor electronic effect on oxidation potential (1q $E_{p/2}$ = 1.02 V; $\mathbf{1r} E_{p/2} = 0.99 \text{ V}$).^[11] The reactions between $\mathbf{1q} - \mathbf{1r}$ and 2a did not occur even upon performing the electrolysis at higher temperatures, for longer times, or mediated by IV. By contrast, the reaction proceeded when the strongly electronwithdrawing groups were not directly linked to the phenyl group (1s $E_{p/2} = 0.74 \text{ V}$; 1t $E_{p/2} = 0.72 \text{ V}$), as demonstrated by the formation of 3s-3t when the strongly electron-withdrawing groups were not directly linked to the phenyl group (1s $E_{p/2} = 0.74 \text{ V}$; **1t** $E_{p/2} = 0.72 \text{ V}$). Notably, β -naphthyl amine was also compatible in the electrolysis protocol (Scheme 2, 3u). Due to the impaired stereoelectronic overlap between the amino lone pair and carbon radical, ^[2c] the arylation of

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acyclic amine and six-membered piperidine was inefficient under standard conditions. Thus modified conditions were provided to perform the arylation (Scheme 2, 3v-3w).

Tertiary aliphatic amines were also viable substrates and their selective arylation, thus further highlighted the synthetic utility of this electrochemical approach, although satisfactory yields were not obtained (Scheme 2, **3x-3ad**). Direct arylation of triethylamine furnished **3x** in 44 % yield. Compound **3y** was also produced as a 4:1 mixture of regioisomers. It is worth noting that an aryl group was regioselectively incorporated into N-benzyl aliphatic amines while the benzylic methylene remained intact (Scheme 2. **3z-3ab**). For cyclic aliphatic amines, the arylation occurred preferentially at the tetrahydropyrrole ring, as illustrated by **3ab-3ad**.

Additionally, the scope with respect to analogues of 2a as the aromatic partner was tested. Dicyano aromatic compounds, including 1,4-dicyanobenzene, 2,5-dicyanotoluene, and 4,4'-biphenyldicarbonitrile, readily underwent the coupling with 1a to furnish corresponding products in moderate to good yields (Scheme 2. 3ae-3ag). Since the elimination of CN^- in 2,5-dicyanotoluene lacks regioselectivity, 3af is produced as a 1:1 mixture of the two isomers. Benzonitriles bearing ester and amide groups are also suitable substrates in this electrochemical arylation (Scheme 2. 3ah-3ai). However, some electron-deficient heteroaromatic compounds, such as 4-cyanopyridine, 1-isoquinolinecarbonitrile, 2-chlorobenzoxazole, and 2-chlorobenzothiazole, were not compatible with this convergent paired electrolysis (see the Supporting Information for details).

Compared with normal electrolysis, convergent paired electrolysis is more dependent on mass transfer of reactive species from the surface of electrodes to bulk solution. This became the crucial factor in scale-up experiments. In order to increase the concentration of α -amino radicals at the anode and the collision frequency of anodic and cathodic intermediates, a three-electrode system RVC(+)-RVC(-)-RVC(+) was used and the distance between each electrode was as close as possible. In this way, the gram-scale electrochemical arylation was performed on a 10 mmol scale and gave 1.52 g **3a** in synthetically useful yield (see the Supporting Information for details).

In order to investigate the anodic and cathodic processes, a series of cyclic voltammetry (CV) studies were conducted. First, the electrochemical behavior of **2a** was studied in 0.1m nBu_4NCIO_4/DMA at 100 mV s⁻¹. A couple of reversible redox peaks were observed at -1.65 V, which corresponds to the reduction of **2a** to anion radical species **5**, and -1.34 V, which corresponds to the oxidation of anion radical species **5** to **2a** (Figure 1 A).

Then the CV curves of TEMPO and 1 m were recorded. The anodic peak of TEMPO was slightly increased but the cathodic peak disappeared with the inclusion of 1 m (Figure 1B), thus demonstrating that anodic formed TEMPO⁺ reacted with 1 m to generate the amino radical cation 6. The involvement of 2,6-lutidine, which facilitates the deprotonation of amino radical cation 6, shifted the electron transfer equilibrium to TEMPO and greatly increased the catalytic current (Figure 1F).^[5d] The important role of 2,6-lutidine was also shown in Table 1, entry 6. As depicted in Figure 1C,



Figure 1. Cyclic voltammetry studies in 3 mL DMA (A) and CH₃CN (B, C, D, E; 0.1 M *n*Bu₄NClO₄). A) 0.06 mmol 2 a, 100 mVs⁻¹;
B) 0.06 mmol 1 m, 0.03 mmol I, 0.06 mmol 2,6-lutidine, 20 mVs⁻¹;
C) 0.06 mmol 1 q, 0.03 mmol I, 0.06 mmol 2,6-lutidine, 20 mVs⁻¹;
D) 0.06 mmol 1 m, 0.03 mmol I; E) 0.06 mmol 1 q, 0.03 mmol I.

a similar interaction between 1q and TEMPO was also detected at the same scanning rate (Figure 1 C). However, the cathodic peak gradually appeared as the scanning rate increased from 10 to 200 mV s⁻¹ (Figure 1 D). By contrast, the cathodic peak did not appear even at a scanning rate of 200 mV s⁻¹ when testing the interaction between TEMPO⁺ and 1m (Figure 1 E). We thus presumed that the reaction rate of TEMPO⁺ with 1q is much lower than that with the 1m DCB anion radical.^[12]

To further assess the convergent process of the electrolysis reaction, a divided-cell experiment was carried out. Compound **3a** was not detected in the anode or cathode chambers. However, the dimerization occurred and gave **8** in the anode chamber (Scheme 3a). Next, under the standard conditions, the electrolysis was carried out in the presence of 2.0 equiv of **9**, which is used as a radical acceptor. This led to the formation of **10** in 17% yield and impeded the generation of **3a** (Scheme 3b), thus indicating the existence of α -amino radical **7**.^[13] In the absence of anion radical **5**, α -amino radical **7** could be oxidized to iminium ion **12**, which reacted with enamine intermediate to afford **8**.^[14]

On the basis of the experimental studies above, a plausible mechanism for the TEMPO-catalyzed arylation of α -amino sp³ C–H was proposed (Scheme 4). TEMPO is known to undergo single-electron oxidation to afford TEMPO⁺,^[7e-g] which reversibly oxidizes the tertiary arylamine to TEMPO

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Scheme 3. Mechanistic experiments.

and amino radical cation **6**. The oxidation rate is inversely associate with the oxidation potential of the substrates. The α -C(sp³)-H of **6** is activated and undergoes deprotonation by 2,6-lutidine to provide amino radical **7**.^[15] On the one hand, **7** couples with the anodic formed anion radical **5** to generate the key intermediate **11**, which undergoes subsequent elimination of CN⁻ and aromatization to give the final product. On the other hand, it proceeds through further oxidation and deprotonation to give imine nitrenium ion **12**, which is then attacked by the eliminated CN⁻ to yield the byproduct **4**.^[8]



Scheme 4. Proposed mechanism for the convergent paired electrolysis.

In summary, we have developed a metal-free convergent paired electrolysis method to synthesize a variety of benzylic amines through direct arylation of tertiary amines and benzonitrile derivatives. Both the anodic and cathodic reactions are fully utilized. Moreover, metals and stoichiometric oxidants are not required. A new perspective for the construction of carbon–carbon bonds through cross-coupling between anodically and cathodically generated species has been provided. This could greatly enrich the application of convergent paired electrolysis in organic synthesis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arylation \cdot cross-coupling \cdot C–H activation \cdot electrocatalysis \cdot tertiary amines

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Direct Arylation of α -Amino C(sp³)-H Bonds by Convergent Paired Electrolysis



It's electrifying! A convergent paired electrolysis method to synthesize benzylic amines through direct arylation of tertiary amines and benzonitrile derivatives without stoichiometric oxidants and metals is reported. This electrocatalytic

approach makes full use of the anodic and cathodic reactions and provides a new perspective for the cross-coupling of anodically and cathodically generated species.

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