

Electrochemical Dehydrogenative C(sp²)–H Amination

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Abstract: A transition-metal-free direct electrolytic C–H amination involving an electrochemically generated nitrenium ion intermediate has been developed. The electrosynthesis takes place in the absence of any organoiodine catalysts and is enabled by an in situ generated electrolyte. A novel, efficient intramolecular and intermolecular C–H amination has been demonstrated using a simple reaction setup.

Organic transformations using electricity as an alternative for redox reagents have been considered as green and sustainable methods in organic chemistry.^[1] While the indirect electrosynthesis uses a redox mediator to carry out the desired redox reaction, direct electrolysis of substrate eliminates the requirement of such mediators and hence tends to overcome the limitation of reaction dependence on such electrocatalysts.^[2] In recent years, various electrochemical oxidations induced chem-

ical transformations with and without the use of such redox mediators have been realized. Among them, the cross-dehydrogenative coupling reactions enabled by electrochemical oxidation demand special attention because of their greater environmental compliance.^[3] The long-standing interest of organic chemists in C–N bond formation *via* C–H functionalization can be attributed to the development of highly atom economic transformations.^[4] For instance, C–H amination of 2-amidobiaryls has long been the most atom economical route for the synthesis of carbazoles and their derivatives.^[5] In 2011, our group reported an organocatalytic C–H amination using hypervalent iodine catalysis (Scheme 1a).^[6] Later reports revealed that iodine reagents were oxidized by means of anodic oxidation, which can be used for electrochemical C–H aminations. However, in such *Ex cell* methods, the substrate is added to the already oxidized solution of iodine reagent without the application of any applied current. So it is necessary to use stoichiometric quantities of hypervalent iodine precursors and high concentrations of supporting electrolytes for the electrolysis to proceed (Scheme 1b).^[7] Koleda et al. realized the synthesis of benzoxazoles using electrochemically generated

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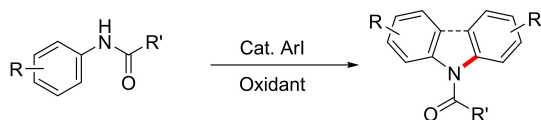
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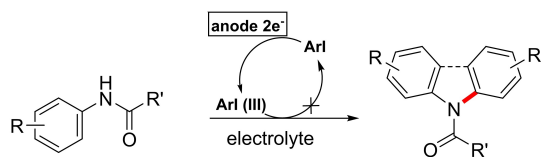
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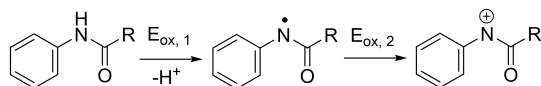
a) Previous work: hypervalent iodine catalyzed C–H amination



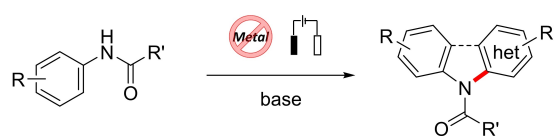
b) Organoiodine mediated electrochemical C–H amination



c) Chemistry of electrochemically generated nitrenium ion



d) This work: nitrenium ion mediated electrolytic C–H amination



• metal-free • electrocatalyst free • *in situ* electrolyte

Scheme 1. Direct metal-free C(sp²)–H aminations.

hypervalent iodine in presence of hexafluoroisopropanol.^[8] Very recently, Powers and co-workers addressed this challenge using iodine precursors as a redox mediator for C–N bond formations. Here the selective anodic oxidation of iodine catalyst is carried out in presence of the substrate and hence identified as *in cell* method of C–H amination.^[9] The electrochemistry with amidyl radical demonstrate new advancements and many novel transformations were discovered.^[10] While the generation of nitrenium ion intermediates is a key step in different chemical transformations, their electrochemical generation and applications in the synthesis of *N*-heterocycles are rare.^[11]

To our knowledge, the only example so far is a characteristic two-step oxidation of acetanilide derivatives reported by Waldvogel and co-workers. They demonstrated that amidoaryl substrates could be oxidized electrochemically to *N*-acyl radicals and then to the corresponding nitrenium ion intermediates leading to the corresponding benzoxazoles (Scheme 1c).^[12] Herein, we report a transition metal-free direct electrolytic approach for C(sp²)–H amination, involving an electrochemically generated nitrenium ion intermediate in the presence of an *in situ* generated supporting electrolyte in substoichiometric quantities (Scheme 1d). The attempts to reduce the use of additional supporting electrolytes has been a key area of research in electrochemistry as it considerably compliments the concept of green and sustainable chemistry.^[13] We investigated the direct electrolysis of 2-acetamidobiphenyl (**1a**) in 1,1,1,3,3,3-hexafluoroisopropanol (Table 1). The reaction did not proceed to give the desired product (**2a**), instead we observed the formation of the *N*–*N* dimer of **1a** (entry 1). Previous reports suggested that such products are formed by radical-radical couplings.^[14] This encouraged us to evaluate the effect of using graphite electrodes for electrolysis because of their known preference for two electron oxidations over the single electron

oxidation pathway (entry 2). To our delight, constant current electrolysis using graphite electrodes in presence of potassium *tert*-butoxide yielded 57% of the desired product **2a** (entry 3). Interestingly, the omission of tetrabutylammonium tetrafluoroborate from the reaction did not affect the outcome to a large extent and did not interrupt the electrolysis with a higher resistance as well (entry 4). Further screening of different solvents, inorganic and organic bases (entries 5–10) revealed sodium ethoxide as the better candidate under our electrolytic conditions (entry 11). It is noteworthy to mention that we consistently observed the formation of HFIP adducts of **1a** as side products throughout our optimization studies (see Supporting Information for details).

Afterwards we evaluated the substrate scope of the electro-oxidative intramolecular C–H amination using different 2-amidobiaryl derivatives. The substitutions on different positions of both rings were tolerated (scheme 2). Especially, different substitutions on 4-position of the aniline ring (**2c–2h**) as well as electron neutral and electron donating substituents on *para* position of the phenyl ring (**2i–2p**) were well compatible under our reaction conditions. Notably, for the first time, *N*-formyl-2-aminobiphenyl substrate was transformed to the corresponding carbazole derivative (**2b**) without the formation of a six membered ring (phenanthridin-6-one) as reported in previous studies.^[15]

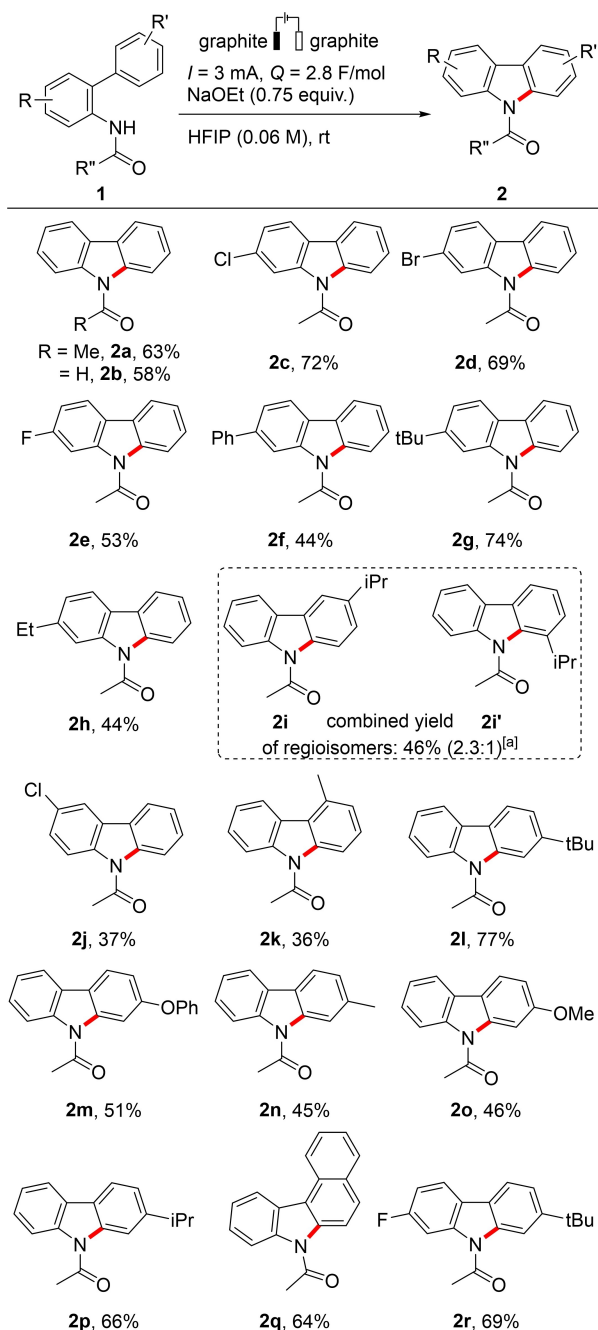
Substitution at 3' position leads to a mixture of regioisomeric products in a ratio of 2.3:1 (**2i** and **2i'**). In addition, biphenyl substrates with 5-chloro or 2'-methyl substitutions were transformed to the corresponding carbazoles (**2j** and **2k**) albeit in lower yields. To our delight, the substrates with a polyaromatic ring as well as substitutions on both rings yielded the corresponding carbazoles with moderate yields (**2q** and **2r**).

The general trend in substrate scope and observations made during the reaction studies (see Supporting Information for details) indicated the electro-oxidative formation of a nitrenium ion intermediate (Scheme 3). Such cationic nitrogen intermediates can be observed in hypervalent iodine mediated amination reactions.^[6–7] A detailed cyclovoltammetric study of anilide moieties had measured two distinct oxidation peaks based on which a diyl mechanism was delineated before.^[12] Here, we speculated that the anodic oxidation of substrate **1a** produces a highly acidic cation radical **A**. Proton abstraction of this cation radical by 1,1,1,3,3,3-hexafluoroisopropan-2-olate generated at cathode results in *N*-acyl radical intermediate **B** formation. It is important to mention that a direct proton abstraction from substrate **1a** is not possible considering the *pK*_a value of the 1,1,1,3,3,3-hexafluoroisopropan-2-olate. This *N*-acyl radical **B** further undergoes a second oxidation at the anode with formation of nitrenium ion **C**. The rearomatization of the intermediate **D** formed by nucleophilic attack of the aryl ring to the nitrenium ion **C** afforded carbazole **2a**. At this point, another reaction possibility is a competitive formation of the side product **6a**. The added base in the reaction reacts with hexafluoroisopropanol to form the salt which helps to eliminate the requirement of an additional supporting electrolyte for electrolysis.^[16] This was confirmed by carrying out the reaction

Table 1. Optimization of reaction conditions.^[a]

Entry	Base (equiv.)	Solvent	Yield ^[b]
1 ^{[c][d]}	–	HFIP	n.d.
2 ^[c]	–	HFIP	trace
3 ^[c]	KOtBu (2)	HFIP	57
4	KOtBu (1)	HFIP	52
5	KOtBu (1)	TFE	n.d.
6	KOtBu (1)	MeCN	n.d.
7	LiOtBu (1)	HFIP	59
8	Et ₃ N (2)	HFIP	56
9	DBU (2)	HFIP	45
10	NaOEt (1)	HFIP	60
11 ^[e]	NaOEt (0.75)	HFIP	63

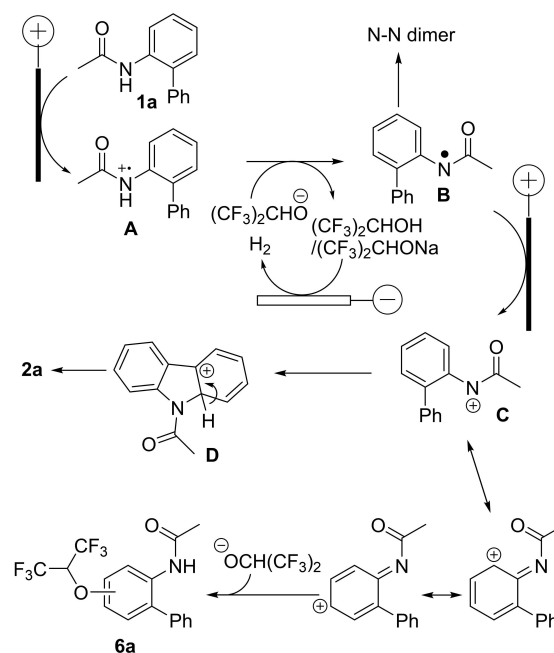
[a] Reaction conditions: constant current electrolysis (5 mA) for 3 h (~3.2 F/mol) using graphite electrodes: **1a** (0.2 mmol), solvent (0.06 M). [b] Isolated yield. [c] *n*-Bu₄NBF₄ (0.2 mmol, 1 equiv.) as supporting electrolyte. [d] Glassy carbon anode and platinum plate cathode. [e] 3 mA current and 2.8 F/mol charge passed in 5 h. n.d. = not detected.



Scheme 2. Substrate scope of intramolecular amination. Reaction conditions: constant current electrolysis ($I = 3 \text{ mA}$) until 2.8 F/mol charge passed (Q) using graphite electrodes for ~5 h: 1 (0.2 mmol), solvent (0.06 M). Isolated yields. [a] Ratio of isolated regioisomers.

using sodium salt of hexafluoroisopropanol to obtain 55% of product **2a** (see Supporting Information for details).

To extend the generality of the reaction, we commenced our studies to the development of an intermolecular variant for this electro-oxidative C–H amination (see Supporting Information for optimization).^[17] Preliminary studies showed that the coupling reaction between *N*-(4-methoxyphenyl) acetamide (**3a**) and 1-methylnaphthalene (**4a**) proceeds smoothly to give product **5a** in excellent yields in presence of potassium *tert*-



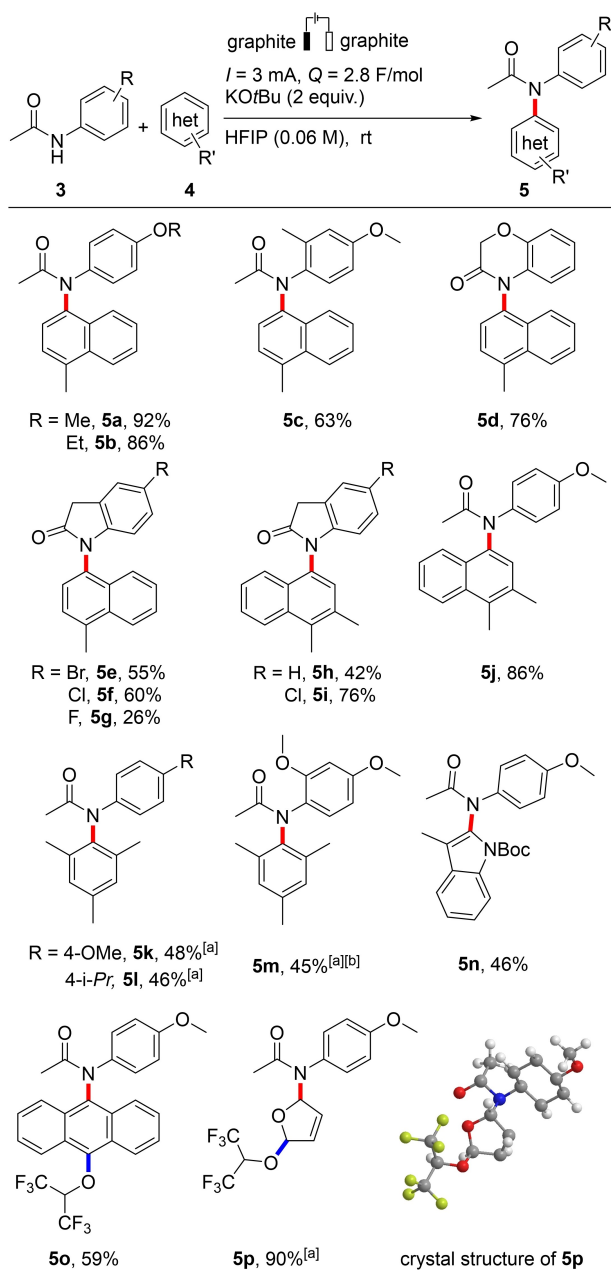
Scheme 3. Plausible mechanism.

butoxide using 1,1,1,3,3,3-hexafluoroisopropanol as solvent. Afterwards, the scope of the intermolecular amination was evaluated (Scheme 4). We were delighted to see that various acetanilides undergo cross coupling reactions with **4a** to give the corresponding products in moderate to excellent yields (**5a–5c**). Additionally, heterocycles such as oxindole derivatives were successfully coupled with 1-methylnaphthalene (**5d–5g**). Other arene and hetero(arene) coupling partners also participated in our electro-oxidative C–N cross coupling reaction to provide the corresponding products (**5h–5n**). Surprisingly, electrolysis of anthracene with **3a** resulted in the formation of product **5o**. An unprecedented dual C–H functionalization by a tandem C–N/C–O bond formation was observed when furan was used as coupling partner. The structure of product was further confirmed by X-ray crystallography (**5p**).

In summary, we have developed the first transition-metal-free direct electrolytic approach for the synthesis of carbazole derivatives using graphite electrodes. The developed method does not require any organoiodine catalysts and is simple. Additionally, we demonstrated the possibility of an *in situ* generation of supporting electrolyte for electrolysis using common inorganic bases in acidic solvents like hexafluoroisopropanol. Moreover, our preliminary results showed promising findings for an intermolecular variant of electrochemical C–H amination.

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Scheme 4. Substrate scope of intermolecular amination. Reaction conditions: constant current electrolysis ($I = 3 \text{ mA}$) until 2.8 F/mol charge (Q) was passed using graphite electrodes for $\sim 5 \text{ h}$: **3** (0.2 mmol), **4** (0.4 mmol, 2 equiv.), potassium *tert*-butoxide (0.4 mmol, 2 equiv.), HFIP (0.06 M, 3 mL). Isolated yields. [a] 5 equiv. of arene was used as coupling partner. [b] 1:1 DCM: HFIP (3 mL).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: amination · carbazole · electrochemistry · heterocycles · nitrenium ion

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