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Electrochemical Synthesis of Carbazoles by Dehydrogenative Coupling Reaction

Anton Kehl,[a] Niclas Schupp,[a] Valentina M. Breising,[a] Dieter Schollmeyer,[a] and Siegfried R. Waldvogel[a] *

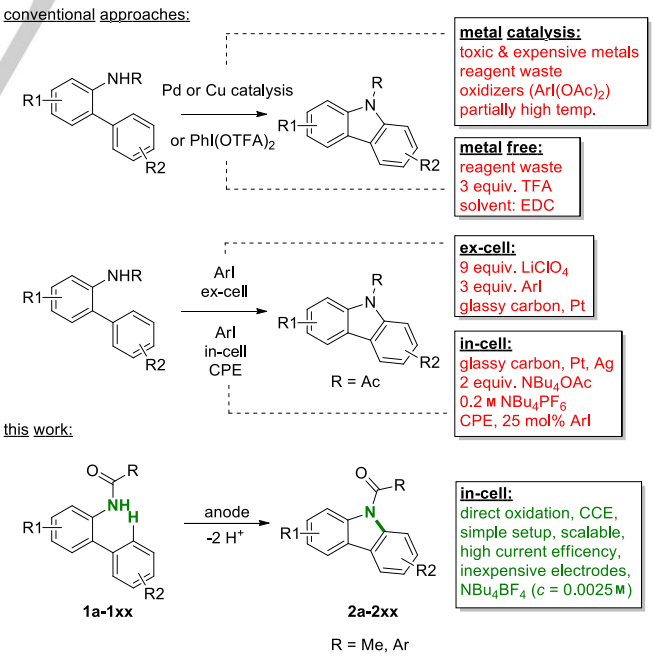
In the memory of Prof. Dr. Kilian Muñiz

Abstract: A constant current protocol, employing undivided cells, a remarkably low supporting electrolyte concentration, inexpensive electrode materials, and a straightforward precursor synthesis enabling a novel access to N-protected carbazoles by anodic N,C bond formation using directly generated amidyl radicals is reported. Scalability of the reaction is demonstrated and an easy deblocking of the benzoyl protecting group is presented.

Carbazole was first isolated and characterized by Graebe and Glaser, which employed a high-boiling coal tar distillate, in 1872.[1] In the same year, Braun and Greiff reported a synthesis using aniline as starting material and intense heating in the course of a distillation process,[2] which was confirmed by Graebe and additionally refined employing diphenylamine as substrate in order to achieve higher yields.[3] The relevance of this compound class can be perceived when its potential use in the pharmaceutical sector[4] due to their anti-Alzheimer,[5] antibacterial,[6] fungicidal,[7] antitubercular,[8] antitumor properties,[9] or in the technical assignment[10] is taken into account.

Since the discovery of carbazole, reams of methods tackling different moieties in order to build up this particular scaffold were reported.[11] One convenient and straightforward access is by a cyclization reaction via a C,N bond formation. Classical strategies utilizing this approach are usually in demand of metal catalysis (Pd,[12] Cu,[13,14] Ir,[15] Rh[16]), oxidizers,[13] pre-functionalization,[17] or strongly elevated temperatures[18] which result in several drawbacks. On the one hand, leastwise stoichiometric amounts of oxidizers, toxic and partially expensive metal complexes, and essential leaving groups evoke reagent waste on an unfavorable scale. On the other hand, harsh conditions can narrow down the operational area, if the preservation of labile functionalities is targeted. Hence, improvements with regards to atom economy and ecology are highly desired.

Electrochemistry, which can be considered as a 'green' alternative,[19] representing a synthetic tool with inherent safety and extraordinary reaction pathways.[20] By solely employing electric current as inexpensive and sustainable reducing or oxidizing agent, amounts of waste are tremendously diminished and thus toxic reagents can be superseded. Two noteworthy approaches in the past decade considered the application of electrochemical means in order to generate a reactive species which facilitated the conversion in an ex-cell protocol. Nishiyama et al. reported the access to a hypervalent iodine species which was generated at constant current conditions (scheme 1).[21] After electrolysis, mostly substrates with electron releasing substituents were added to accomplish the reaction. Francke et al. refined this approach in elegantly combining the reagent and the supporting electrolyte. A few carbazoles were made with the newly designed reagent.[22] Recently, Powers et al. reported an in-cell approach with a broader scope (scheme 1).[23] However, that method relies also on hypervalent iodine species (25 mol% of 4-iodoanisole or substrate-dependent the more sophisticated 2,2'-diiodo-4,4',6,6'-tetramethyl-1,1'-biphenyl) two supporting electrolytes at once and constant potential conditions with a sophisticated three-electrode-setup. The unfortunate inconvenience of those three features evoked by the effort to separate the recyclable reagent and the ex-cell conditions or the constant potential setup are not optimal if a process with scaleup potential is desired.



Scheme 1. Conventional approaches and our electrochemical access to N-protected carbazoles. TFA = trifluoroacetic acid; EDC = 1,2-dichloroethane; CPE = constant potential electrolysis; CCE = constant current electrolysis.

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The electrochemistry of carbazoles and their predominant sensitivity towards side reactions are well-known and impede a progress in this direction.[24] Powers et al. addressed this issue by applying a mediated constant potential protocol. The employment of amidyl radicals as reactive intermediates was well explored in the last two decades and is associated with cyclization reactions[25] including rearrangements,[26] hydroaminations.[27] We reported a resources and user friendly methodology to afford amidyl radicals by direct oxidation in order to construct 5- and/or 6-membered heterocycles by dehydrogenative N,N,[28–30] N,C,[31] or O,C[32] coupling reactions. Herein we describe a new synthetic approach for N-protected carbazoles (scheme 1). With a straightforward synthesis to N-protected aminobiphenyl precursors, common electrode materials and a simple two-electrode arrangement utilizing a constant current protocol, this setup provides a general applicable access to this compound class.

The precursor synthesis was facilitated by treating a 2-aminobiphenyl with benzoyl chloride or acetic anhydride. If more elaborated derivatives are desired, an ordinary Suzuki reaction can be employed which involves 2-bromo- or 2-iodoaniline derivatives and the corresponding arylboronic acids. A subsequent protection of the amino function provides the precursor with this approach in two easy to perform steps (see Supporting Information).

The electrolytic conditions for the direct N,C coupling reaction were scrutinized within screening studies. Most of the applied conditions of the previously reported protocol for the synthesis of *N*-aryl-phenanthredin-6-ones served as indication for further investigation. The optimization was performed in undivided 5 mL Teflon® cells, which provide a time-efficient and straightforward screening approach.[33] 2-(4-Methylbenz)amido-5-chlorobiphenyl (**1a**) served as test substrate, since this particular aniline moiety has proven as a suitable candidate for the imminent electrochemical conditions.[30,31] Tested solvents such as methanol and ethanol resulted in a low conversion and alkoxylated byproducts. Acetonitrile and dimethyl sulfoxide displayed almost no conversion (see Supporting Information for additional data). 2,2,2-Trifluoroethanol yielded only a complex mixture of largely unidentified compounds according to gaschromatographic data. 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) exclusively enables an selective conversion due to its radical stabilizing properties.[34] However, the conversion was still incomplete. Further optimization efforts revealed that tetrabutylammonium tetrafluoroborate (NBu_4BF_4) allowed superior conversion compared to the default supporting electrolyte tetrabutylammonium hexafluorophosphate (NBu_4PF_6). The remarkably low concentration of supporting electrolyte (0.0025 M) enables sufficient conductivity for the electrotransformation. In order to ensure full conversion an addition of 15% of water is recommended. Higher (>20%) or lower (<5%) contents of water are significantly counterproductive. After accomplished electrolysis HFIP is almost entirely recovered by distillation, thus a small fluorine footprint can be retained.[35] As table 1 indicates, we tested a small set of common electrode materials. However, boron-doped diamond (BDD) and isostatic graphite offer a full conversion of the starting material and the highest yields of 73% and 65%, respectively. The amount of applied charge of 2.1 F is slightly higher than the theoretical amount needed of 2.0 F. Glassy carbon on the other hand revealed a rather low conversion and yield of 28%. Application of closely the theoretical amount of charge is necessary to keep over-oxidation products on a low level. Since isostatic graphite is the least expensive material, we decided to stick to it in order to provide a cost-efficient protocol as far as possible. Furthermore, the impact onto the yield of cathode materials were explored. Steel exhibited a performance inferior to the established nickel cathode. As far as platinum and graphite are concerned, a result similar to the nickel electrode was determined. Nevertheless, nickel was chosen for the final protocol. However, an application of this protocol is suitable for pharmaceutically active ingredients, since traces of toxic metals can be avoided by the choice of the electrode material. The last aspect of the optimization (Table 2) was the determination of a suitable current density, which is a key parameter in the organic electrosynthesis. The outcome of this study clearly indicates that best results (65%) are achieved with a current density of 1 mA/cm^2. Higher current densities decrease the conversion of the substrate and yield due to rising degradation reactions. Additionally, we replaced the 4-methylbenzoyl protecting group (**1a**) by the less expensive benzoyl group (**1b**).

Table 1. Influence of electrode materials onto the yield of **2a**.

Entry	anode	cathode	conversion [%][a]	yield [%][b]
1	**graphite[c]**	**nickel**	**>99**	**65**
2	BDD	nickel	>99	73
3	glassy carbon	nickel	41	28
4	graphite[c]	graphite[c]	>99	62
5	graphite[c]	steel[d]	70	42
6	graphite[c]	platinum	>99	68

0.2 mmol substrate **1a**, 0.0025 M NBu_4BF_4 in 4.25 mL/0.75 mL HFIP/H_2O, charge: 2.1 F, undivided cell; current density: 1 mA/cm^2; [a] based on recovered starting material; [b] isolated yield; [c] highly isostatic graphite; [d] stainless steel (VA 1.4571).

Table 2. Influence of current density onto the yield of **2a**.

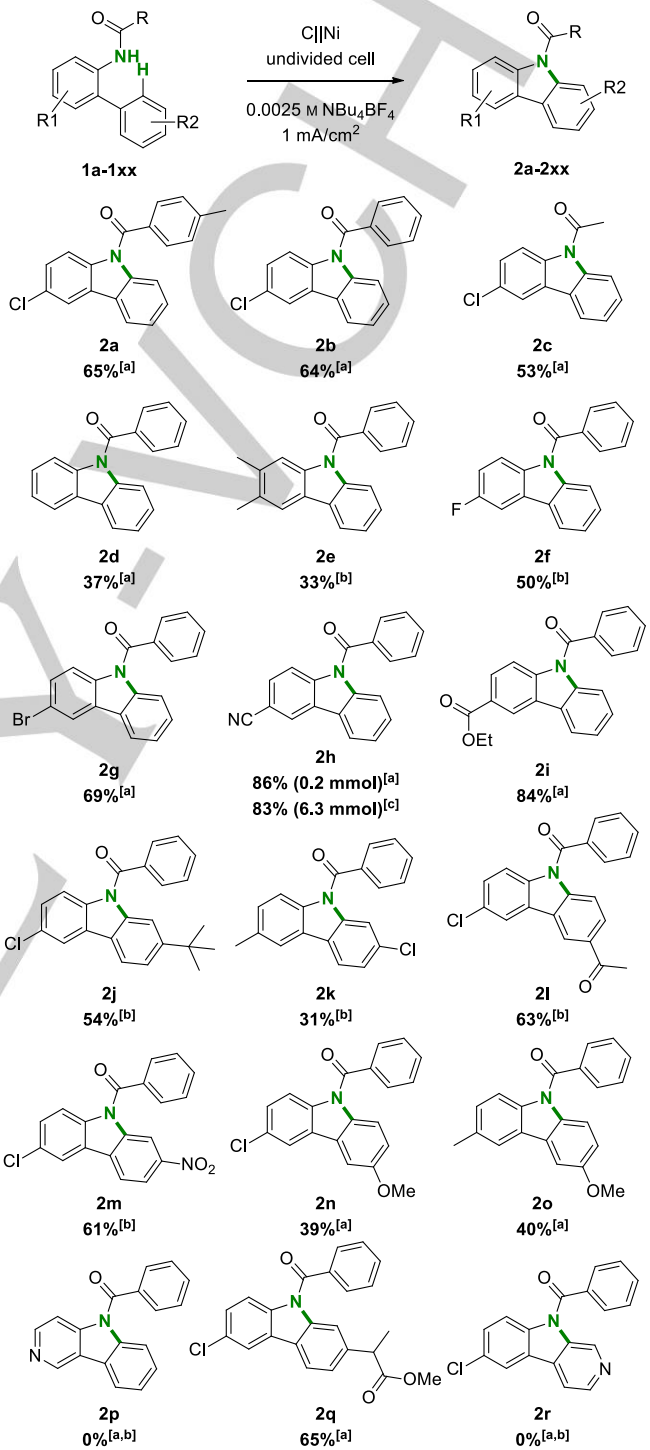
Entry	current density [mA/cm^2]	conversion [%][a]	Yield [%][a]
1	0.5	>99	52
2	**1.0**	**>99**	**65**
3	2.0	85	50
4	3.0	69	42
5	4.0	65	40
6	5.0	62	33

0.2 mmol substrate **1a**, 0.0025 M NBu_4BF_4 in in 4.25 mL/0.75 mL HFIP/H_2O, anode: highly isostatic graphite, cathode: nickel, charge: 2.1 F, undivided Teflon® cell; [a] based on recovered starting material; [b] isolated yield.

Once the optimization was completed, we were able to establish a broad scope of N-protected carbazoles with various and valuable functional groups (Figure 1). The majority of compounds was synthesized in moderate to very good yields. The formation of the N,C coupled product was verified via X-ray structure analysis of **2d** (Supporting Information). Apart from benzoyl protecting groups, 4-methyl-substituted benzoyl- (**2a**) and acetyl groups (**2c**) were demonstrated to point out the versatility of compatible protecting groups for this transformation. In the given case, the benzoyl groups afforded a slightly higher yield compared to the acetyl protected derivative. The impact of the substituted benzoyl group is insignificant (**2a** and **2b**). Both aryl moieties can contain different substitution patterns (e.g. **2j-o**, **2q**) to ensure a broad scope of compounds. Valuable functional groups such as chloro- (**2a-c**, **2j-n, 2q**), bromo- (**2g**), nitro- (**2m**), keto- (**2l**), ester- (**2i**, **2q**), or cyano- (**2h**), which allow subsequent reactions, are tolerated. Derivatives with electron withdrawing substituents such as **2h** and **2i** work excellent under the applied conditions. The highest yield of 86% was achieved by generation of compound **2h**, which contains a valuable cyano functionality. Additionally, this compound was successfully synthesized on gram scale and with the doubled concentration (0.08 M) in order to demonstrate the scalability of this method. The moderate yields of compounds **2d**, **2e**, **2k**, and the N-protected natural product glycozoline (**2o**) can be explained due to the fact that a free *para*-position or benzylic-position of the anilide moiety results in an elevated probability for side reactions.[28–31] Compounds with electron releasing moieties as represented by **2n** and **2o** performed moderately owing to an incomplete conversion of the starting material, which also could be observed in the synthesis of **2d**, **2e**, and **2k**. A further application of additional charge was counterproductive and resulted in lower yields. In terms of over-oxidation of the product during the electrolysis, its occurrence is likely due to a low potential difference or even a lower potential compared to the precursors (cyclic voltammograms in Supporting Information). Thus, employing too much applied charge above the theoretical amount is not always expedient. Generally, the applied charge ranged between 2.1 F and 2.8 F depending on the starting material. In some cases (**2e**, **2f**, **2j-m**) the addition of 15% water was counterproductive and resulted in a very low conversion of the starting material. In those cases, omission of water provided an increased conversion.

As far as the formation of regioisomers in the case of a non-symmetrical substitution pattern of the second aryl moiety is concerned, solely the compounds with the substituent in 6-position were found as **2l**, **2n**, and **2o** indicate. In order to elucidate the application-related nature of our method, we synthesized a protected carprofen (**2q)** in good yields, which can be deblocked easily, as depicted in scheme 2. Hence, this simple approach to Carprofen with a decent efficiency contributes greatly to the existing methods with its sustainable nature.[36]

Mechanistically, transformation most likely proceeds via a radical pathway. The generation of an amidyl radical through a direct oxidation of the starting material at the anode and a subsequent deprotonation. The latter can be accomplished by an in situ generated anion of HFIP. The amidyl radical might be

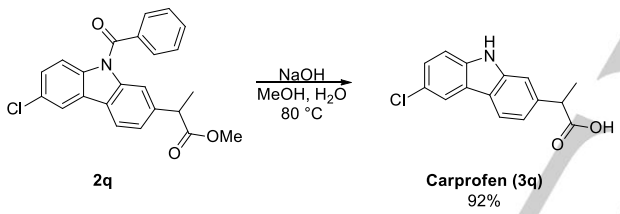


[a] 5 mL Teflon® cell, 0.2 mmol substrate, solvent: HFIP/H_2O(15%)
[b] 5 mL Teflon® cell, 0.2 mmol substrate, solvent: HFIP
[c] 80 mL beaker-type cell, 6.3 mmol substrate, solvent: HFIP/H_2O(15%), applied charge: 2.8 F

stabilized by the π system and solvent HFIP. Cyclization establishes a novel N,C bond with the other moiety of the biphenyl scaffold resulting in a rather stabilized radical species.

Figure 1. Scope of direct electrochemical carbazole synthesis by dehydrogenative N,C cyclization reaction.

A second oxidation step paired with a subsequent rearomatization by extrusion of a proton results in the final product (Supporting Information). We intended to demonstrate that the formation of the amidyl radical is a crucial step in the formation of the carbazoles. Therefore, we implemented a heterocyclic motif in the benzamido moiety (**1p**). Highly electron withdrawing moieties such as pyridine, exhibit a good resistance to oxidation which resulted in a nondetectable conversion and an almost whole starting material recovery (**1p**). Hence, the necessary oxidation potential is not addressed within the applied conditions. Thus, no amidyl radical can be formed (also see cyclic voltammograms in supporting information). The same strategy was utilized to equip the other side of the biphenyl scaffold with a pyridine moiety (**1r**) to see whether the impact on the oxidation of the starting material would match with **1p**. In that case, the oxidation of the starting material is possible, resulting in a complex mixture but no product. This circumstance leads to the conclusion that the oxidation of the amide moiety is crucial for a successful conversion.



Scheme 2. Deblocking of **2q** to obtain Carprofen (**3q**).

With this method a new and sustainable access to N-protected carbazoles in overall good yields by direct oxidation was accomplished. This valuable alternative to the conventional synthetic routes provides the advantage of a very simple in-cell setup, mediator-, metal catalyst-, and organic oxidizer-free conditions as well as inexpensive and long-lasting electrode materials. Furthermore, reagent waste is minimized, minimal supporting electrolyte concentrations are required, and a high current efficiency is provided. Apart from a broad scope, valuable functionalities, which enable subsequent reactions, are accessible. Besides, this protocol features a route to precursors of a natural product (**2o**) and an active pharmaceutical ingredient (**2q**), which can be easily deblocked in high yields (92%). A scale-up of this reaction on a gram scale is possible as demonstrated for **2h**.

Acknowledgements

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Keywords: electrochemistry • N,C coupling • heterocyclic chemistry • green chemistry • carbazoles

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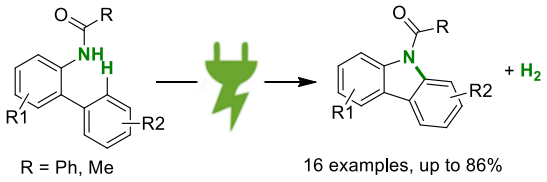

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Electrochemical Synthesis of Carbazoles by Dehydrogenative Coupling Reaction

Direct electrochemical synthesis of N-protected carbazoles in good yields by anodic N,C bond formation. Deblocking of the compounds is demonstrated. Inexpensive electrode materials and a simple, scalable electrolysis setup are employed. Many valuable substituents are tolerated. Access to valuable compounds such as Carprofen is demonstrated.