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# C–N Bond Couplings of Azoles and Imides with Tropylium and Xanthene Cations Generated by Electrochemical Oxidation

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Dedicated to Professor Antonio M. Echavarren on the occasion of his 64th birthday

**Abstract:** An approach for electrochemistry-enabled intermolecular oxidative C–N coupling reactions of azoles and imides with 1,3,5-cycloheptatriene and xanthenes is disclosed. The reaction proceeds via the anodic oxidation of 1,3,5-cycloheptatriene or xanthenes to generate the tropylium ion or xanthene cations, followed by a nucleophilic attack of azoles and imides to form C–N bond.

#### Introduction

Cross dehydrogenative couplings (CDC) of C–H/N–H are one of the most efficient C–N bond formation reactions in organic chemistry,<sup>[1]</sup> avoiding the prefunctionalization of substrates. Electrochemical oxidation<sup>[2]</sup> has been introduced as an elegant alternative to external chemical oxidants used in the formation of C–N bonds.<sup>[3]</sup> Mechanistically, these anodic C–N bond constructions occur by the generation of a nitrogen-centered radical, which is subsequently trapped by a carbon-based substrate to form a C–N bond. These reactions perform well when using intramolecular trapping strategies, normally employing unsaturated C–C bonds, thus delivering five or six-membered nitrogen-containing heterocycles (Scheme 1a).<sup>[4]</sup> In contrast, carbocation intermediates are seldom involved in C–N bond formation reaction in electrochemical transformations.<sup>[3h,3]</sup>

Usually, carbocations generated at the anode are very reactive species, referred to as 'hot carbocations'.<sup>[6]</sup> They easily undergo reactions with mildly nucleophilic solvents (e.g., CH<sub>3</sub>CN, MeOH, etc.), rearrangement, or elimination to form alkenes. Accordingly, in order to facilitate the formation of C–N bonds, the carbocation intermediates should be well stabilized and long-lived.<sup>[6]</sup> For example, α-heteroatoms, such as N, O and S, are generally required to stabilize the carbocations generated by electrochemical oxidation (Scheme 1b).<sup>[2I]</sup> Therefore, the strategy of forming C–N bond from carbocation intermediates generated by electrochemical oxidation is still under development. Herein, we report an intermolecular oxidative C–N coupling reactions of azoles and imides with 1,3,5-cycloheptatriene<sup>[7]</sup> and xanthenes by

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Supporting information for this article can be found under:

electrochemical oxidation,<sup>[8-10]</sup> that proceed via tropylium and xanthene cations as key intermediates (Scheme 1c).

a) Electrochemical oxidative C-N bond formations initiated via N-centered radical



b) Electrochemical oxidative C-N bond formations initiated via C-centered carbocation





Scheme 1. Cross-dehydrogenative couplings of C-H/N-H bond by electrochemical oxidation.

We decided to choose 1,3,5-cycloheptatriene/xanthene and azoles/imides to exemplify the feasibility of this new strategy due to their natural merits: 1) by either chemical or electrochemical methods, 1,3,5-cycloheptatriene is known to be easily oxidized into cycloheptatrienyl cation,<sup>[11]</sup> tropylium, which is aromatic, stable and can react with many nucleophiles to form a covalent bond; 2) xanthenes are important motifs and are reported to be oxidized under electrochemical conditions to form stabilized diarylcarbenium ions;<sup>[10]</sup> 3) azoles and imides are important moties in organic chemistry<sup>[12,13]</sup> and normally serve as good nucleophiles.

#### **Results and Discussion**

Guided by this hypothesis, we investigated the model reaction of 1,3,5-cycloheptatriene with phthalimide. As shown in Table 1, with tetra-*n*butylammonium tetrafluoroborate as supporting electrolyte, acetonitrile as solvent, graphite (+) / nickel (–) as electrodes, the desired product (**3a**) was obtained in 30% yield (entry 1). Tetra-*n*butylammonium perchlorate was found to be the most effective supporting electrolyte (entry 4). When Pt (+) / Pt (–) were used as electrodes, the yield decreased to 30% (entry 5). With HOAc,

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NaOAc or ferrocene as additives, the yield was not improved (entries 6-8). We found the duration of electrolysis is a critical factor (entry 9, 10). At 1.7 hours, 89% yield was observed, while after 1.9 hours, the yield dropped to 40%. This is attributed to the further oxidation of the product, a derivative of cycloheptatriene, after depletion of starting 1,3,5-cycloheptatriene. In addition, all these reactions were conducted under air, and no obvious difference in yield was observed under a nitrogen atmosphere.

Table 1. Optimization of reaction conditions for	generating 3a.
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O N	<b>.</b> .	C(+)   Ni(-), supporting electro	lyte		
0 1a	2a	MeCN, 23°C, und 7 mA, undivided	er air cell	o 3a	
Entry <sup>[a]</sup>	Supporting electrolyte	Additive	Time (h)	Yield (%) <sup>[b]</sup>	
1	<sup>n</sup> Bu₄NBF₄	-	1 h (1.3 F/mol)	30	
2	₽Et₄NPF6	-	1 h (1.3 F/mol)	37	
3	₽Bu₄NPF6	-	1 h (1.3 F/mol)	55	
4	<sup>n</sup> Bu <sub>4</sub> NClO <sub>4</sub>	-	1 h (1.3 F/mol)	70	
5 <sup>[c]</sup>	<sup>n</sup> Bu₄NClO₄	-	1 h (1.3 F/mol)	30	
6	<sup>n</sup> Bu₄NClO₄	HOAc <sup>[d]</sup>	1 h (1.3 F/mol)	31	
7	<sup>n</sup> Bu <sub>4</sub> NClO <sub>4</sub>	NaOAc <sup>[e]</sup>	1 h (1.3 F/mol)	30	
8	<sup>n</sup> Bu <sub>4</sub> NCIO <sub>4</sub>	Ferrocene <sup>[f]</sup>	1 h (1.3 F/mol)	20	
9	<sup>n</sup> Bu <sub>4</sub> NCIO <sub>4</sub>	-	1.7 h (2.2 F/mol)	89	
10	<sup>n</sup> Bu <sub>4</sub> NCIO <sub>4</sub>	-	1.9 h (2.5 F/mol)	40	

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), supporting electrolyte (0.025 M), 8 mL MeCN, 23 °C, under air. [b] Yield determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] Pt (+) / Pt (-) were used as electrodes. [d] 0.4 mmol HOAc. [e] 0.4 mmol NaOAc, MeCN/H<sub>2</sub>O = 8 mL: 1mL. [f] 5 mol%.

With the efficient conditions for obtaining product **3a** established, we explored the substrate scope of this transformation (Scheme 2). Phthalimide, succinimide and maleimide were all found to effectively react with 1,3,5-cycloheptatriene under standard conditions to give the desired C-N coupling products (**3a-3c**), although **3c** was obtained in slightly lower yield probably due to the polymerization of maleimide during electrolysis.<sup>[14]</sup> 4-Bromopyrazole and benzimidazole also worked smoothly to give

**3d** and **3e**, leaving the untouched bromo which can be potentially further functionalized. Similarly, 1,2,4-triazole also coupled well with 1,3,5-cycloheptatriene during electrolysis, providing **3f** in 80% yield. Benzotriazole reacted well under standard conditions, albeit, a N<sup>1</sup> and N<sup>2</sup> (8:1, thermodynamic controlled) mixture of substituted cycloheptatrienes were obtained after purification due to the fast, reversible dissociation of **3g** at room temperature.<sup>[15]</sup>



Scheme 2. Scope of the C-N bond formation of 1,3,5-cycloheptatriene with imides and azoles by electrochemical oxidation. Reaction conditions: 1 (0.3 mmol), 2a (0.6 mmol), "Bu<sub>4</sub>NCIO<sub>4</sub> (0.025 M), 8 mL MeCN, 23 °C, under air, constant current (7 mA), 3 h. Isolated yields after column chromatography were reported. [a] The reaction was performed for 1.5 h.

Xanthene derivatives are an important class of organic compounds and known to be oxidized to form stabilized cations.<sup>[10]</sup> We assumed xanthene derivatives could be applied to react with imides and azoles under electrochemical conditions to further demonstrate our strategy. As expected, the desired C-N coupled products were produced in good to excellent yields. As shown in Scheme 3, not only imides were good N sources (**5a**, **5b**), but also azoles, such as pyrazoles (**5c**, **5d**), 1*H*-indazole (**5e**), benzimidazole (**5f**), triazoles (**5g-5i**) reacted well with xanthene under standard conditions. Furthermore, 9*H*-thioxanthene also worked with imides and azoles to provide **5j-5m** in good yield under slightly modified conditions, in which 1.2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added as a co-solvent to dissolve 9*H*-thioxanthene. Benzyl acridine-10(9*H*)-carboxylate reacted smoothly under standard conditions to give **5n-5p** in good yield.

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Scheme 3. Scope of the C-N bond formation of xanthenes with imides and azoles by electrochemical oxidation. Reaction conditions: 1 (0.3 mmol), 4 (0.45 mmol), "Bu<sub>4</sub>NCIO<sub>4</sub> (0.025 M), 8 mL MeCN, 23 °C, under air, constant current (7 mA), 3 h. Isolated yields after column chromatography were reported. [a] The reaction was performed for 1.5 h. [b] CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) was added as a co-solvent, 9H-thioxanthene (0.9 mmol). [c] Benzyl acridine-10(9H)-carboxylate (0.9 mmol).

In order to learn the oxidation / reduction potentials for the substrates, the cyclic voltammetry (CV) experiments of 1,3,5cycloheptatriene, xanthene, benzotriazole and imides were carried out in acetonitrile shown in Figure 1 (for details, see the SI). For cycloheptatriene, its electrochemical behavior in acetonitrile was investigated by Abraham<sup>[11d]</sup> with the aid of CV, experiments at the rotating ring disk electrode (RRDE) and controlled potential electrolysis. They proposed a mechanism of the electrochemical oxidation proceeds through cycloheptatriene radical cation dimerization: the dimer cations decompose under deprotonation into one equivalent each of the tropylium cation and the starting compound cycloheptatriene. In our CV experiment of cycloheptatriene, an obvious oxidation potential peak was observed at 1.3 V (see Figure 1 and S2). We attribute it to the oxidation of cycloheptatriene in agreement with Abraham's precedent. For xanthene, three obvious oxidation peaks at 1.4 V, 1.7 V and 2.1 V were observed in acetonitrile (see Figure 1 and S3). The Yoshida group has investigated the electrochemical oxidation of diarylmethanes including xanthene.<sup>[10]</sup> They found the carbocations can be trapped in situ by DMSO during the electrochemical process, thus demonstrating the presence of carbocations. Based on these experimental results and the literature support, we believe 1,3,5-cycloheptatriene and xanthene are most likely been oxidized to their respective cations at the anode of our electrochemical reactions.

For benzotriazole (see Figure 1 and S4 ), succinimide (see Figure 1 and S5) and phthalimide (see Figure 1 and S6), several obvious reduction peaks were seen from -1.5 V to -3.3 V, with one exception of a weak oxidation peak of benzotriazole at 1.7 V with its small peak current (only 8% of oxidation peak current of cycloheptatriene). Furthermore, in order to obtain more redox information for the electrochemical reactions, we also conducted the CV experiments of the mixture solutions of cycloheptatriene / xanthene and imines (see Figure S7-11) in acetonitrile. The recorded CV curves were mostly consistent with the combination of their individual spectrums. These results also pointed out that in these mixture solutions, the cycloheptatriene / xanthene will be oxidized during the electrolysis process.



Figure 1. Cyclic voltammograms recorded in 0.025 M Bu<sub>4</sub>NClO<sub>4</sub>-MeCN solution: scan rate: 50 mV s<sup>-1</sup>; starting potential: 0V; glass carbon (3 mm diameter, Working Electrode); platinum plate (Counter Electrode); Ag/AgNO<sub>3</sub> (0.01 M AgNO<sub>3</sub> in MeCN, Reference Electrode)

During the preparation of this manuscript, Li reported an intermolecular anodic oxidative C-N bond formation of xanthenes with azoles in the presence of 20 mol% of MsOH as an effective promoter.<sup>[9b]</sup> Regarding the reaction mechanism, they found that by adding radical trapping agents, either 2,6-di-tert-butyl-4methylphenol (BHT) or hydroquinone, the desired C-N coupling was fully suppressed. Therefore, they proposed the process occurred in the following pathway: alkyl and nitrogen radicals are both generated by anodic oxidation of the xanthene and azole, respectively, which is followed by a radical-radical combination to give the final product. However, the radical-trapping experiments do not unambiguously rule out alternative mechanistic pathways. These results only demonstrated that a radical, serving as a key intermediate, is generated in the reaction process. However, it may not be this radical intermediate that directly precedes the final product.

To obtain more solid experimental information, we designed control experiments using H-type divided cell separated by an

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AMI-7001 membrane (Table 2). The reactions were conducted under the standard conditions, and both the divided anodic chamber and cathodic chamber contained the same solution, including substrates, solvent and supporting electrolyte. If the reactive intermediates are generated at the anode, the final product should be obtained in the anodic chamber and should match the product obtained in an undivided cell. Indeed, in the case of benzotriazole (1g) and xanthene (4a), the desired product 5i was produced in 22% yield in the anodic chamber, although the efficiency of electrolysis is lower than that in the undivided cell. In contrast, 5i was not detected in the cathodic chamber (entry 1, Table 2). Similar results were obtained in the case of 1H-indazole (1j) and xanthene (entry 2, Table 2). These experiments demonstrate that the reaction of azoles with xanthene occur at the anode. Furthermore, when commercially available tropylium tetrafluoroborate (6a) was treated with benzotriazole (1g), the desired product 3g was formed in 92% yield (entry 3, Table 2), which is almost identical with the vield under electrolysis shown in Scheme 2. This is consistent with our mechanistic hypothesis that 1,3,5-cycloheptatriene is oxidized at the anode to tropylium ion, which is then attacked by benzotriazole to form the C-N coupling product.

We also conducted these control experiments using imides reactants combined with 1,3,5-cycloheptatriene or xanthene (Table 3). From the divided cell experiments of phthalimide (1a) and 1,3,5-cycloheptatriene (2a), the desired product 3a was obtained only in trace amount in both chambers (entry 1). In case of succinimide (1b) and xanthene (4a), no product was detected in both chambers. In addition, when phthalimide was treated with tropylium tetrafluoroborate (6a), only 21% yield was obtained, which is much lower than the yield (89% by NMR) under electrolysis. In case of succinimide (1b), the desired product 3b was not detected at all. Moreover, we found that product 3a was obtained in 99% yield by mixing potassium phthalimide and tropylium tetrafluoroborate in MeCN at room temperature. These experimental results show that imides behave differently to azoles in the reactions with 1,3,5-cycloheptatriene and xanthene under electrochemical conditions. Based on the reduction peaks of phthalimide's CV (Figure 1), we think the more nucleophilic anion is likely involved. The phthalimide anion may be generated by either a direct cathodic reduction of phthalimide or deprotonation by a base, which would be produced via cathodic reduction.<sup>[3h,3i,13b,13c,16]</sup> Therefore, both electrodes are involved for the reaction of imides with 1,3,5-cycloheptatriene and xanthene.

Table 2. Comparing experiments of azoles using H-type divided cell.

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[a] Reaction conditions: C(+)/Ni(-), 0.025 M<sup>n</sup>Bu<sub>4</sub>NCIO<sub>4</sub>, MeCN, 23 °C, under air.
[b] Yield determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using 1,4-dimethoxybenzene as an internal standard. [c] Each chamber contained **1g** (0.6 mmol), **4a** (0.9 mmol), 16 mL MeCN, 7mA, 3.4 h. [d] Each chamber contained **1j** (0.6 mmol), **4a** (0.9 mmol), 16 mL MeCN, 7mA, 3.2 h. [e] **1g** (0.2 mmol), **6a** (0.6 mmol), 8 mL MeCN, no electricity, 1 h. [f] Not detected.

 Table 3. Comparing experiments of imides using H-type divided cell.



[a] Reaction conditions: C(+)/Ni(-), 0.025 M "Bu4NCIO4, MeCN, 23 °C, under air.
[b] Yield determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using 1,4-dimethoxybenzene as an internal standard. [c] Each chamber contained **1a** (0.6 mmol), **2a** (1.8 mmol), 24 mL MeCN, 7mA, 3.4 h. [d] Each chamber contained **1b** (0.6 mmol), **4a** (0.9 mmol), 16 mL MeCN, 7mA, 1.2 h. [e] **1a** (0.2 mmol), **6a** (0.6 mmol), 8 mL MeCN, no electricity, 1 h. [f] **1b** (0.2 mmol), **6a** (0.6

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mmol), 8 mL MeCN, no electricity, 1 h. [g] **1a-K** (0.2 mmol), **2a** (0.6 mmol), 8 mL MeCN, 7mA, 1 h. [h] **1a-K** (0.2 mmol), **6a** (0.6 mmol), 8 mL MeCN, no electricity, 1 h. [i] Not detected.

Based on these experimental results and the fact that xanthene / cycloheptatriene or their radicals can be easily oxidized to generate stabilized carbocations,<sup>[8a,10,11d]</sup> we believe the carbocations are the most plausible key intermediates in these C– N bond forming reactions. A similar mechanism has also been proposed in Zeng's work on electrochemical C-N cross-coupling of xanthenes with *N*-alkoxyamides, although the nitrogen anions are produced by a base additive (1.0 equivalent of Na<sub>2</sub>CO<sub>3</sub>).<sup>[9a]</sup> A representative pathway of C-N bond formation of cycloheptatriene and xanthenes with imides and azoles is shown in Scheme 4.



Scheme 4. Proposed mechanism for electrochemical C-N coupling.

#### Conclusions

In summary, we report an electrochemistry-enabled intermolecular oxidative C-N coupling reactions of azoles and imides with 1,3,5-cycloheptatriene and xanthenes. Mechanistic studies demonstrated the tropylium ion and xanthene cations are generated by anodic oxidation and serve as the key intermediates to form the C–N bond. These cationic intermediates are highly electrophilic and are attacked directly by azoles to deliver the C–N coupled products. In the case of imides, due to their low nucleophilicity, cathodic reduction of imides to their anions is proposed to be involved.

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**Keywords:** electrochemistry • carbon-nitrogen bond • anode • oxidation • synthesis

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# COMMUNICATION

Layout 2:

#### Key Topic: Electrochemical Oxidation

## COMMUNICATION



1,3,5-Cycloheptatriene and xanthenes undergo anodic oxidation to generate the tropylium ion and xanthene cations, followed by a nucleophilic attack of azoles and imides to form C–N bonds.

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C–N Bond Couplings of Azoles and Imides with Tropylium and Xanthene Cations Generated by Electrochemical Oxidation