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Electrochemical Synthesis of Carbodiimides via Metal/Oxidant-Free Oxidative Cross-Coupling of Amines and Isocyanides

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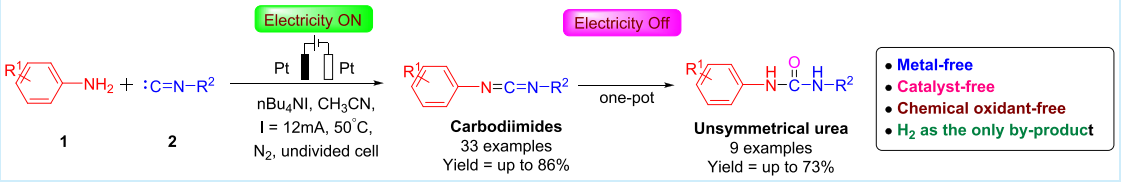

ABSTRACT: This work discloses an electrochemical oxidative cross-coupling of amines with aryl and aliphatic isocyanides. In an undivided cell, the reaction proceeds without involving any transition-metal catalyst, oxidant, or toxic reagents providing carbodiimides in good yields, thereby circumventing stoichiometric chemical oxidants, with H_2 as the only byproduct. Moreover, carbodiimides were in situ converted into unsymmetrical ureas in moderate to good yields using an electricity ON−OFF strategy.

Carbodiimides are important structural motifs in organic chemistry and have been used in all areas, from academia to industry.[1] These compounds have been extensively exploited for many years as the excellent coupling reagent for the peptide synthesis[2] as well as intermediates or precursors for heterocycles.[3,4] Among them, *N*,*N*′-diisopropylcarbodiimide (DIC) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) are the reagents most commonly used. Additionally, it has drawn attention because of its ubiquitous applications in agricultural,[5a] medicinal,[5b] and polymer chemistry,[5c] where new desired heterocycles can be synthesized through judicious choice of the reaction conditions and coupling partners. These intrinsic qualities of carbodiimides, along with the avalanche of research on their use in the synthesis of druglike molecules, make them a privileged group for synthetic chemists. Thus, extensive research efforts have been devoted to the development of methods that provide access to functionalized carbodiimides. The most common method of preparing carbodiimides are dehydration of ureas,[6] and dehydrosulfurization of thioureas using mercuric oxide[7a,b] methanesulfonyl chloride,[7c] sulfur dioxide, thionyl chloride,[7d] and phosgene.[7e] However, either these methods involve toxic and hazards reagents or produce large amount of waste. Alternatively, isocyanide emerged as a diversified coupling partner of amines or azides for the carbodiimide synthesis with relatively high atom economy.[8] More recently, the group of Wang and Ji developed an elegant approach for the synthesis of carbodiimides catalyzed by I_2 using a direct cross-coupling reaction of isocyanides with amines under metal-free conditions using cumene hydroperoxide as the oxidant.[9f] Despite major progress in the field, the use of transition-metal catalysts (e.g., Pd, Au, etc.)[9a−d] or oxidants[9e] is unavoidable, which ultimately restricts their practical use. Therefore, a general and straightforward carbodiimide synthesis under mild conditions is still highly desirable.

In recent years, electrosynthesis has been emerged as a welcome development in chemistry because it has been considered as an environmentally benign alternative for various organic transformations.[10] In noncatalytic electro-organic synthesis, reactive intermediates generated by anodic oxidation and/or cathodic reduction, is a promising green approach to produce final products by involving sequence of chemical transformations.[11−13] Consequently, transformation of amines into other useful motifs is of great significance because of its widespread availability. Simultaneously isocyanides have been exploited extensively for the several important heterocycle syntheses.[14] However, isocyanide−amide coupling by electrochemical dehydrogenative reaction is not well established. Herein, we report the first electrochemical synthesis of carbodiimides in an undivided cell under remarkably mild reaction conditions (Scheme 1b). These reactions avoid metal catalyst and potentially minimize the amounts of requisite reagents and chemical waste.

At the outset of our studies, we explored the coupling of amine (**1a**) and isocyanide (**2a**) under different reaction parameters. After considerable experimentation, an optimal

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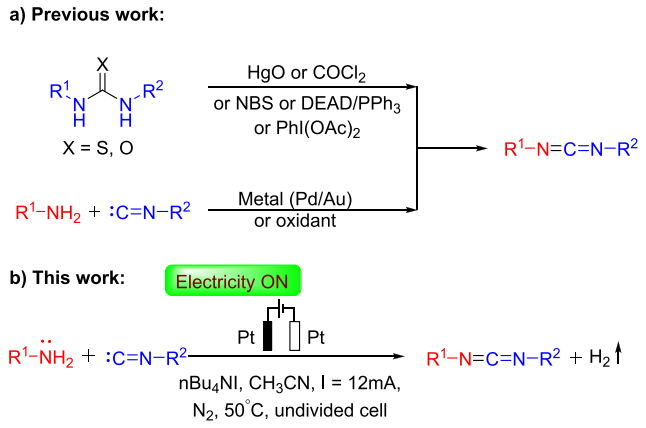
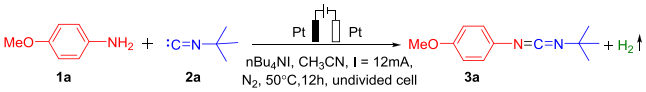
Scheme 1. Some Previous Conventional Reports and Present Electrochemical Approach for the Synthesis of Carbodiimides



yield of product **3a** was obtained in 82% yield under constant current (12 mA) for 12 h in the presence of nBu_4NI and CH_3CN as the solvent (Table 1, entry 1), while platinum anode and platinum cathode electrodes were found to be beneficial. On the contrary, the yield was slightly diminished by using DMA as the solvent choice (entry 2). Among a variety of supporting electrolytes, NH_4I and nBu_4NBF_4 demonstrated poor efficiency compared to nBu_4NI (17, 8% yield, entries 3 and 4). In order to test the electrode effect, platinum plates/RVC and RVC/RVC were applied for and furnished compound **3a** in 76 and 37% yields respectively (entries 5 and 6). Moreover, changing the operating current (20 or 6 mA) was proved to be less efficient as well (26 and 43%, entries 7 and 8). When the reaction was carried out at room temperature, **3a** was obtained in 18% yield only (entry 9). No desired product was obtained without electricity (entry 10).

Table 1. Optimization study: Effects of Reaction Parameters.[a]



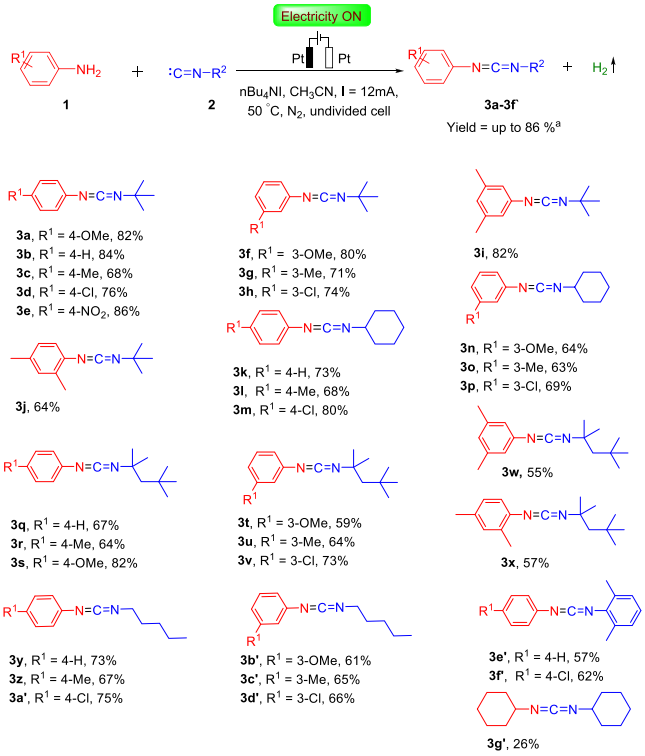
entry	variation from standard conditions[a]	yield[b] (%)
1	none	82
2	DMA (10 mL) instead of CH_3CN	62
3	NH_4I instead of nBu_4NI	17
4	nBu_4NBF_4 instead of nBu_4NI	8
5	RVC(+)|Pt(−) instead of Pt(+)|Pt(−)	76
6	RVC(+)|RVC(−) instead of Pt(+)|Pt(−)	37
7	20 mA instead of 12 mA, 12 h	26
8	6 mA instead of 12 mA, 12 h	43
9	rt instead of 50 °C	18
10	no electricity, N_2	NR
11	8 h instead of 12 h	61
12	20 h instead of 12 h	77
13	nBu_4NI (1 equiv)	46
14[c]	I_2	0

[a]Reaction conditions: All reactions were performed with platinum anode, platinum cathode, constant current = 12 mA, **1a** (0.25 mmol), **2a** (0.50 mmol), nBu_4NI (1 mmol), CH_3CN (6 mL), 50 °C, 12 h, undivided cell. [b]Isolated yield. [c]I_2 (1 equiv) was used as reagent at 50 °C. NR = no result, DMA = dimethyl acetamide.

Extending the reaction time did not alter the reaction yield much but reducing the reaction time to 8h reduced the yield of **3a** (Table 1, entries 11 and 12). Further investigation showed that, reaction proceeded with low yields when 1 mmol nBu_4NI was used, this is possibly due to the dual role of nBu4NI, where it was used as both electrolyte and reagent in the reaction (Table 1, entry 13). No desired product was isolated when I_2 was used at 50 °C as stochiometric reagent for the synthesis of **3a** (Table 1, entry 11).[9f]

With the optimized conditions in hand (Table 1, entry 1), many efforts have been utilized to explore the applicability of this transformation (Table 2). Initially, we investigated the developed protocol using various substituted amines with *tert*-butyl isocyanide for the synthesis of carbodiimides **3a−j** (Table 2). Anilines bearing electron-donating groups (EDG) as well as electron-withdrawing groups (EWG) were well tolerated in this transformation (**3a−j**) and furnished the desired carbodiimides in good yields (up to 86%). Electron-donating groups such as methoxy and methyl afforded the corresponding products in 68 to 84% yields (**3a**, **3c**, **3f**, **3g**, and **3i**). Halide substituents such as Cl afford the desired products in good yields (**3d** and **3h**). It is to be noted that EWGs such as *p*-NO_2 bearing aniline furnished the carbodiimide **3e** in excellent yield (yield = 86%), whereas 2,4-dimethyl-substituted aniline furnished the desired carbodiimide **3j** in 64% yield. Further, the scope of isocyanides was investigated (Table 2, **3k−f′**), although no specific electronic effect on the reaction yield was observed when aliphatic isocyanides were subjected to the reaction. Secondary aliphatic isocyanides, i.e., cyclohexyl isocyanide gave the desired products **3k−p** in good yields (up to 80%) with *meta* and *para* EWG as well as EDG-substituted anilines. It is worth noting that tertiary aliphatic isocyanides

Table 2. Substrate Scope[a]



[a]Isolated yield.

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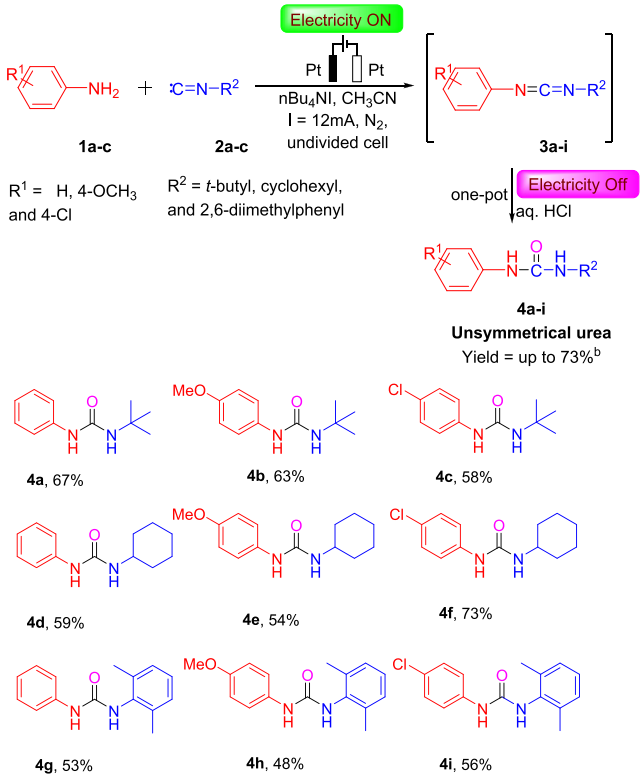
also led to the corresponding products **3q−x** in good yields (up to 82%) except with disubstituted anilines, which furnished the moderate yields of desired carbodiimides **3w** (55%) and **3x** (57%). It is to be also noted that the primary aliphatic isocyanides gave the desired carbodiimides **3y−d′** in 61−75% yields with substituted anilines. It is noteworthy that aromatic isocyanide 2,6-dimethylphenylisocyanide furnished the desired carbodiimides **3e′**,**f** in 57−62% yields. In addition, we were also interested in the coupling of aliphatic amine and isocyanide to enhance the scope of the reaction for the synthesis of coupling agent DCC (**3g′**). However, the yield of compound **3g′** was found to be relatively poor and isolated in 26% yield.

To further demonstrate the utility of our above reactions, and in order to evaluate the versatility of this novel electrochemical system, we applied the carbodiimides to unsymmetrical urea transformation in a one-pot reaction employing an electricity ON−OFF approach (Table 3). After

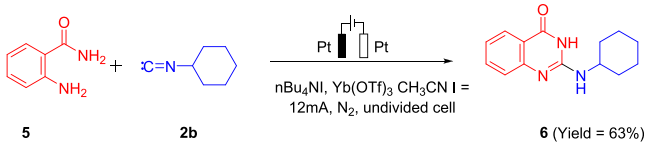
Table 3. One-Pot Unsymmetrical Synthesis of Urea 4a−i via In Situ Generated Carbodiimides[a,b]



[a]Reaction conditions: All reactions were performed with Pt anode (25 mm × 15 mm × 3 mm), Pt cathode (25 mm × 15 mm × 3 mm), constant current = 12 mA, **1a−c** (0.5 mmol), **2a−c** (1.0 mmol), nBu_4NI (2 mmol), CH_3CN (6 mL), 50 °C, 12 h, undivided cell followed by addition of 5 mL of 0.1 M HCl at 80 °C for 6 h. [b]Isolated yield.

the completion of the amine and isocyanide coupling reaction in the electricity ON condition, subsequent conversion of this carbodiimide to the final unsymmetrical ureas **4a−i** was achieved in the electricity OFF condition using aq HCl. As can be seen in Table 3, most aliphatic as well as aromatic isocyanides underwent smooth transformation to afford the corresponding unsymmetrical urea **4a−i** in moderate to good yields (up to 73%). Tertiary as well as secondary aliphatic isocyanides furnished the unsymmetrical urea **4a−f** in moderate to good yields (54−73%) utilizing the intermediate carbodiimide to final unsymmetrical urea **4a−f** in an electricity OFF condition. Secondary isocyanide, i.e., cyclohexyl isocyanide with 4-chloroanilines furnished the good yield (73%) of unsymmetrical urea **4f**, whereas 4-methoxyaniline furnished the moderate yield (54%) of **4e**. Aromatic isocyanides also afforded the unsymmetrical aromatic urea **4g−i** in moderate yields (48−56%) in one pot following the same ON−OFF electrochemical reaction conditions. Additionally, 2-amino quinazolinone derivative **6** was also synthesized by the reaction of anthranilamide **5** and cyclohexyl isocyanide using a modified procedure, where 10 mol % $Yb(OTf)_3$ was used as an additional catalyst in addition to the standard reaction condition (Scheme 2). The desired compound **6** was isolated in 63% isolated yield.

Scheme 2. One-Pot Synthesis of Substituted Aminoquinazolinone 6



In addition, cyclic voltammetry (CV) experiments were performed to investigate the redox potential of the substrates (Figure 1) and were in accordance with previous reports.[15]

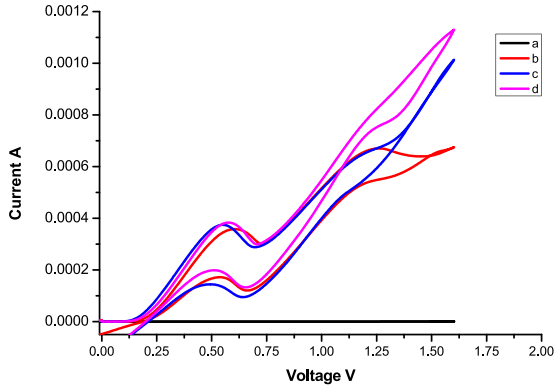


Figure 1. Cyclic voltammograms of reactants and the mixture in 0.05 M nBu_4NI/CH_3CN using a glassy carbon-disk working electrode Pt disk as counter electrode; Ag/AgCl as reference electrode, at 0.1 V/s scan rate: (a) only CH_3CN (without nBu_4NI), (b) nBu_4NI (0.05M), (c) **2a** (0.01 M) + nBu_4NI (0.05M), (d) **1a** (0.01 M) + **2a** (0.01 M) + nBu_4NI (0.05M).

Curve a (in the absence of $^nBu_4NI$) showed no oxidation peak (0.0−1.6 V vs Ag/AgCl). The CV of nBu_4NI had two oxidation peaks at 0.60 and 1.21 V (curve b), which correspond to the oxidation of I^- to I_3^- and I_3^- to I_2, respectively. Interestingly, we found that the CV of **2a** (in the presence of nBu_4NI) presented only one oxidation peak at 0.54 V, and of oxidation peak I_3^- to I_2 disappeared, possibly due to the formation of carbonimidic diiodide intermediate in curve c (Figure 1). The CV of the mixture of **1a**, **2a**, and nBu_4NI demonstrated an apparent oxidation peak at 0.58 V (curve d), due to the possible chemical interaction between the three compounds. As far as aniline is concern, in trace d, there is no obvious peak for aniline was observed because aniline showed

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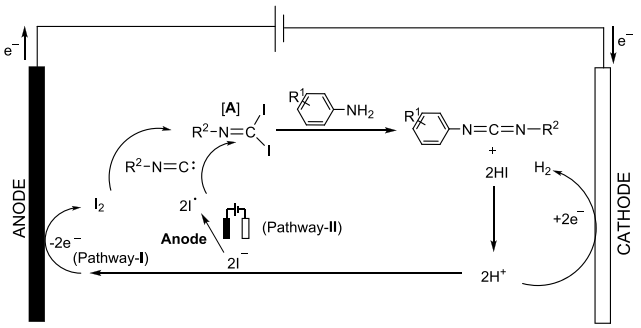
oxidation peak only at very high scan rate and high concentration of aniline.[16]

On the basis of our mechanistic studies, the proposed mechanism of electrochemical oxidative coupling of amines and isocyanides is depicted in Scheme 3. The reaction might

Scheme 3. Plausible Mechanism



be initiated by the I_2 generation by the nBu_4NI oxidation at anode in pathway I. Generated I_2 was reacted with isocyanide for the generation of carbonimidic diiodide intermediate **A**.[9e,17] Subsequently intermediate **A** was coupled with amines provided required carbodiimide and HI. Second, nBu_4NI oxidation at anode generated iodide radicals which was subsequently trapped by isocyanides to generate carbonimidic diiodide intermediate **A** in pathway II followed by the coupling with amines provided carbodiimides. Finally, H_2 gas emerged by the reduction of HI at cathode, and I_2 was regenerated at anode.

In conclusion, we have developed a novel and practical electrochemical oxidative cross-coupling reaction of amines with isocyanides using readily accessible amines via C−N bond formation, affording carbodiimides under metal-free and oxidant-free conditions. This oxidative cross-coupling using a general, reliable, and straightforward methodology delivers a variety of substituted carbodiimides in good to excellent yields (up to 86%). Furthermore, the utility of this approach was successfully extended to the synthesis of diverse unsymmetrical ureas in moderate to good yields (up to 73%) in a one-pot reaction using an electricity ON−OFF approach. Thus, this work not only represents a metal-free strategy for cross-coupling of isocyanides with amines for carbodiimide synthesis but also provides an efficient approach to unsymmetrical functionalized urea synthesis under mild conditions. Further synthetic applications including multigram-scale synthesis are currently ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00510.

Experimental details and spectral data of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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