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Catalyst-Free Electrosynthesis of Benzimidazolones through Intramolecular Oxidative C-N Coupling

Jiang-Sheng Li,[a]* Pan-Pan Yang,[a] Xin-Yun Xie,[a] Si Jiang,[a] Li Tao,[b] Zhi-Wei Li,[a] Cui-Hong Lu[a] and Wei-Dong Liu[c]

[a] Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, School of Chemistry and Food Engineering, Changsha University of Science & Technology, Changsha, 410114, China
Fax: (+86)-73185258733; Phone: (+86)-73185258733; e-mail: jsli@csust.edu.cn
[b] State Grid Hunan Electric Power Company Limited Research Institute, Changsha, 410004, China
[c] National Engineering Research Center for Agrochemicals, Hunan Research Institute of Chemical Industry, Changsha 410007, China.

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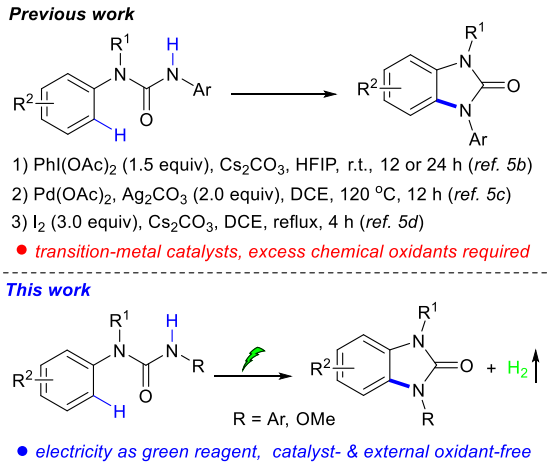
Abstract: The electrochemical synthesis of *N*, *N*'-disubstituted benzimidazolones from ureas through an intramolecular anodic dehydrogenative N-H/C-H coupling has been developed. The reaction undergoes under the undivided electrolysis conditions and obviates the need for any catalysts and chemical oxidants.

Keywords: Electrosynthesis; Dehydrogenative coupling; C-N formation; Benzimidazolones; Ureas

Benzimidazolones are widely found as privileged structures in numerous natural alkaloids,[1] bioactive molecules,[2] and dye pigments.[3] To date, a diverse array of efficient approaches have been documented for ready access to such scaffolds.[4] Among them, the intramolecular oxidative aryl C-H amidation of ureas, prefabricated or generated *in situ* by the addition of aniline to isocyanates, is one of the most fascinating protocols in terms of high atom-economy.[5] In 2015, Fu's group reported a metal-free oxidative C-H amidation annulation of ureas mediated by $PhI(OAc)_2$ along with Cs_2CO_3 to access benzimidazolone derivatives.[5b] Later on, Youn and Kim disclosed a one-pot sequential addition and oxidative cyclization from anilines and isocyanates promoted by $Pd(OAc)_2$ as a catalyst and Ag_2CO_3 as a terminal oxidant.[5c] In 2018, Chang and his collaborators utilized the combination of iodine and Cs_2CO_3 to enable this transformation under the reflux of 1,2-dichloroethane.[5d] Nevertheless, these methods still suffer from some drawbacks such as the requirement of noble-metal catalysts, and the need for a large excess of chemical oxidants (e.g. $PhI(OAc)_2$, Ag_2CO_3, I_2) and bases (e.g. Cs_2CO_3). Thus, it remains desirable to develop an eco-friendly and efficient strategy to achieve the assembly of benzimidazolone scaffolds.

Electrochemical synthesis constitutes a convenient, efficient, and sustainable avenue for the creation of new chemical bonds.[6] In 2018, Zeng and his co-authors reviewed the use of electrochemical techniques in the establishment of heterocyclic structures through intra- and intermolecular annulation processes reported from 2000 to then.[6f] This compilation substantiates that the organic electro-oxidative synthesis in the anode of an undivided cell has been developed into an appealing tool for the synthesis of potentially bioactive heterocyclic compounds.[7] It is noted that anodic oxidation enables a direct functionalization of N-H bonds through the formation of *N*-centered radicals under constant current electrolysis,[8] and obviates the requirement of difficult-to-prepare N-X bonds (X = halo, aryloxyl) and the production of undesired byproducts. To our knowledge, the utilization of amides, amidines, carbamates, and ureas as the *N*-centered radical precursors to realize the construction of nitrogen-containing heterocycles, for example, pyrazolones,[8b] pyrrolidinones,[8c] oxazolones,[8d] imidazolones,[8d] fused azoles,[8e-h] indoles,[8i] and lactams,[8j] has been demonstrated. Very recently, Xu's group presented an electrochemical dehydrogenative cascade cyclization for the efficient synthesis of highly substituted benzimidazolones from an acyclic precursor, urea-tethered 1,5-enyne.[9] However, benzimidazolones have not yet been achieved from simple aryl ureas by means of this sustainable strategy so far.

In our continuous efforts towards the construction of heterocycle skeletons,[10] we herein report an electrochemical synthesis of benzimidazolones from trisubstituted ureas through an anodic oxidative C-N

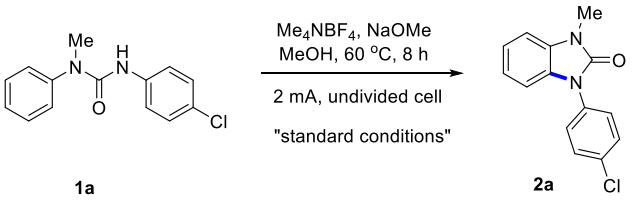


Scheme 1 Access to benzimidazolones via intramolecular N-H/C-H coupling.

coupling, which is devoid of transition-metal reagents and chemical oxidants (Scheme 1).

Initially, we chose the urea **1a** as the precursor for this investigation on electrochemical intramolecular cyclization conditions, so as to obtain our desired potentially bioactive benzimidazolone nucleus. Electrolysis was conducted in a three-necked flask as an undivided cell equipped with a Reticulated Vitreous Carbon (RVC) plate as the anode and a Pt plate as the cathode. Precursor **1a** underwent an electrochemical oxidative annulation in the presence of NaOMe (1 equiv) as a base in dry MeOH at 60 °C for 8h, wherein the current was kept constant at 2 mA, and Me_4NBF_4 (1 equiv) was used as the electrolyte. To our delight, product **2a** was achieved in 66% yield under these conditions (Table 1, entry 2). Other electrolytes were tested, which are composed of different cations (Me_4N^+, Et_4N^+, and *n*-Bu_4N^+) and counterions (BF_4^-, PF_6^-). It was found that **2a** was obtained in slightly lower yields (Table 1, entry 2 & 3). Thus, the use of Me_4NBF_4 was of the best choice for this electrochemical reaction. Decreasing the amount of Me_4NBF_4 to 0.2 equivalent, or even to zero, delivered the yield of 60%, 40%, respectively (Table 1, entries 4 & 5). Then, other solvent systems were considered, such as MeOH and its mixtures, MeCN, HFIP, and *i*-PrOH without further treatment. Surprisingly, the use of undried MeOH afforded the highest reaction efficiency (Table 1, entry 1 vs 6, 7). Reducing the dose of base or changing the base kinds led to a remarkable decline in the yield (Table 1, entries 8 & 9). Besides, changing the current density, the electrolysis temperature, or the reaction atmosphere exerted awful impacts on the electrolysis (Table 1, entries 10-12). The use of other electrode materials instead gave negative results (Table 1, entry 13).

Table 1 Optimization of the electrolysis conditions [a]



Entry	Deviation from standard conditions	Yield [%][b]
1	none	87
2[c]	with M_4NBF_4 (M = Me, Et, *n*-Bu)	66, 50, 59
3[c]	with M_4NPF_6 (M = Me, Et, *n*-Bu)	53, 57, 53
4[c]	use of Me_4NBF_4 (20 mol%)	60
5[c]	no electrolyte	40
6	with MeCN, HFIP, ^{i}PrOH	10, 45, 30
7	with MeOH:THF (1:1) or MeOH:H_2O (5:1)	45, 38
8	use of NaOMe (20 mol%), or no base	35, 34
9	with Na_2CO_3 or Cs_2CO_3	67, 20
10	1 mA, 3 mA, 4 mA, 5 mA	50, 65, 58, 57
11	at 30 °C	43
12	under air	48
13	Pt (+)|Pt (-), or C (+)|C (-)	trace, 25

[a]Reaction conditions: undivided cell, RVC anode (100 PPI, 1.2 cm × 1 cm × 1 cm), Pt cathode, constant current = 2 mA, **1a** (0.1 mmol), base (1.0 equiv), electrolyte (1.0 equiv), solvent (6 mL), 60 °C, under Ar for 8 h. [b] Yields are for isolated products. [c]Dry solvent. HFIP = hexafluoroisopropanol.

Having established the standard electrolysis conditions, the cyclization precursor scope was explored. Firstly, keeping the –Ar part of urea **1** as 4-chlorophenyl, secondary amine fragments were taken into account for the reaction compatibility, and the results are depicted in Table 2. Overall, all the ureas **1a-o** tested proceeded smoothly to provide their corresponding products **2a-o** in moderate to good yields. The substituents R^1 of the secondary amines could be an alkyl (–Me, –Et, and –*n*-Pr) or aryl group (–Ph), giving rise to the corresponding annulated products in the range of 78%–87% yield (**2a-2d**). A diverse array of R^2 substituents on the aromatic ring of precursors **1** were also compatible with this electrolysis (**2e-2m**), which include methyl, methoxy, phenyl, formyl, ester, halo, and trifluoromethyl. Noteworthy, a formyl group was found to be inert without undergoing electro-oxidation (**2h**). Furthermore, the electron properties of the substituents R^2, either electron-rich or electron-poor, imposed extremely limited impacts on the cyclization efficacy (**2f** vs **2i**). When urea **1n** derived from *N*-methyl 2-naphthylamine was used instead in the electrolysis, product **2n** was obtained in good yield and high regioselectivity. In addition, the urea containing an *N*-methyl-pyridyl-2-amine moiety was identified to be an effective substrate, thus generating its pyrido-fused imidazolone **2o** in 77% yield.

Next, we turned our attention to investigating the effect of the primary amine moiety in precursors **1** on the electrolysis reaction (Table 3). Under our standard electrolysis conditions, the primary aniline fragments were first taken into account. The ureas **1** bearing an electron-donating (–Me) or electron-withdrawing group (–Cl, $–CF_3$) underwent a smooth electrolysis, thereby generating their corresponding products **2** in

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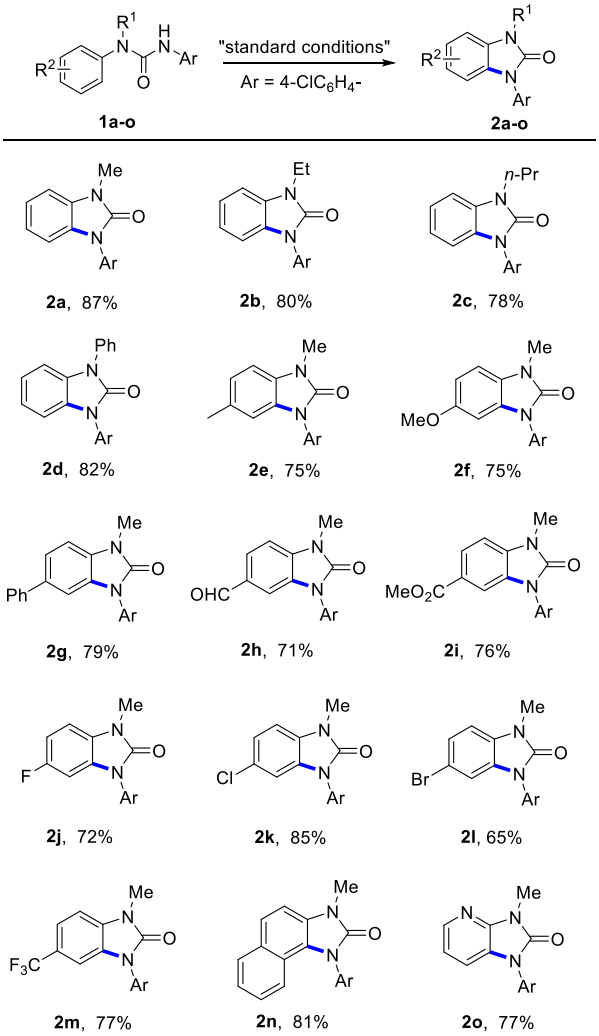
Table 2. Scope with respect to secondary amine fragments of ureas.[a]

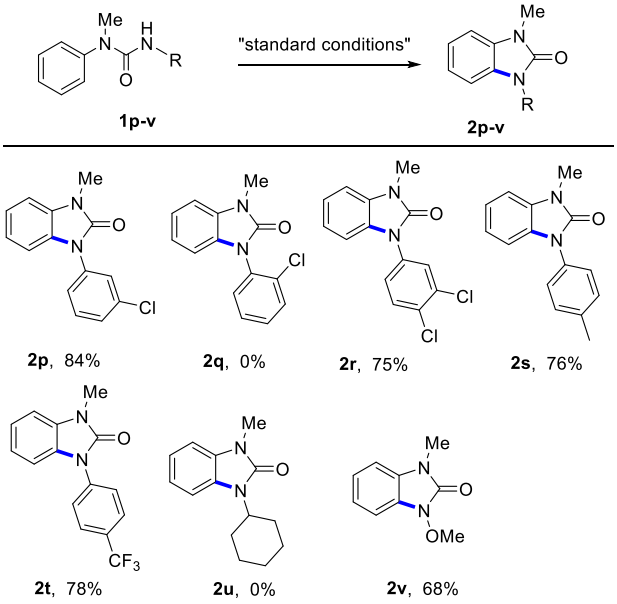


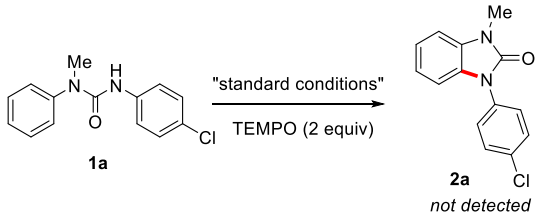
[a]Standard conditions: undivided cell, RVC anode, Pt cathode, constant current = 2 mA, **1** (0.1 mmol), NaOMe (1.0 equiv), Me_4NBF_4 (1.0 equiv), undried MeOH (6 mL), 60 °C, under Ar for 8 h. Isolated yields are given.

moderate to good yields. However, the introduction of the -Cl group to the *ortho*-position caused the failure of the electrolysis (**2q**), suggesting that the substituent steric hindrance might govern this oxidation process. The replacement of the Cl group in **1a** with a strong electron-pulling CF_3 resulted in a slight decay of the yield (**2t**, 78%).

This electrosynthetic method was then extended to ureas with a primary aliphatic amine, a challenging substrate for the previously reported oxidative cyclizations.[5b-d] Unfortunately, negative results for the substrate with a *c*-hexyl (**1u**) were observed under our standard conditions, and re-screening electrochemical conditions, including various bases and Lewis acids, failed to improve the reaction (please see ESI, Section 3). Nontheles, *N*-methoxy urea **1v** was found to be an effective precursor in the transformation, thereby delivering *N*-methoxy-*N*-methyl benzimidazolone (**2v**) in 68% yield.

Table 3 Scope with respect to primary amine fragments of ureas.





Scheme 2 Radical-trapping experiment.

To shed light on this electrolysis mechanism, a radical-trapping experiment was conducted under the standard electrolysis conditions (Scheme 2). It turned out that no product **2a** was detected in the presence of TEMPO (2 equiv), which probably indicates that a radical process was involved in this electrochemical oxidation.[11] Moreover, the fact that the addition of NaOMe as a base could facilitate the electrolysis, implied that a deprotonation step occurs to generate an anion during the cyclization process, which can then be readily oxidized through the single-electron transfer on the anodic surface.

Furthermore, we carried out the cyclic voltammetry (CV) experiments to figure out the role of the base added in the electrolysis. As depicted in Figure 1, no obvious oxidation peaks were observed for substrate **1a** (green) and NaOMe (red), respectively, in the range of 0-0.9 V vs Ag/AgCl, whereas a mixture of **1a** with NaOMe displayed a strong oxidation signal at E_p = 0.72 V, which is ascribed to the anodic oxidation of a nitrogen anion to its nitrogen radical. Evidently, as is in accordance with the results in Table 1 (entry 1 vs 8), the addition of NaOMe promotes the electrolysis by deprotonation of ureas.

Based on previous work[8] and the aforementioned observations, a plausible electrolysis mechanism for this dehydrogenative annulation of ureas is proposed

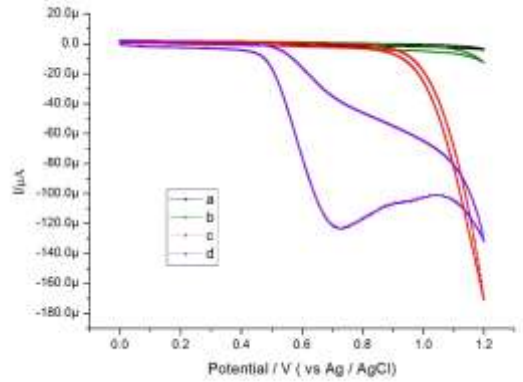
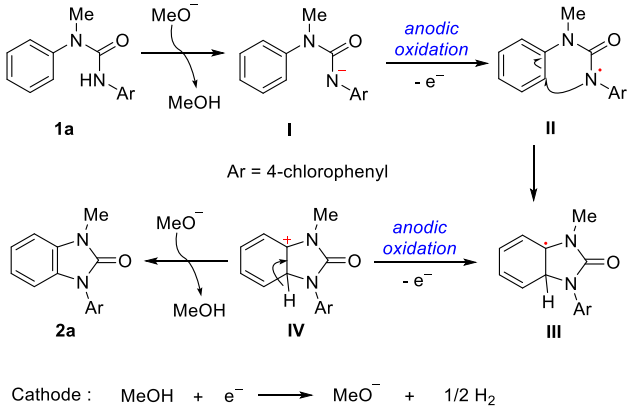


Figure 1. Cyclic voltammograms recorded in *n*-Me_4NBF_4/MeOH (0.1 M): (a) blank, (b) **1a** (0.006 M), (c) NaOMe (0.015M), (d) **1a** (0.006 M) + NaOMe (0.015 M).



Scheme 3. Proposed mechanism.

(Scheme 3). In the first step, urea **1a** is deprotonated by NaOMe to generate its nitrogen anion **I**. Then, the anion **I** is oxidized to its nitrogen radical **II** in the anode, which subsequently undergoes an intramolecular radical addition to derive a cyclized radical species **III**. Further anodic oxidation and subsequent deprotonation furnish benzimidazolone **2a**.

In summary, we have disclosed a catalyst-free electrochemical intramolecular dehydrogenative N-H/C-H annulation reaction of functionalized ureas at constant current in an undivided cell. This electrolysis protocol allows for the synthesis of *N*,*N*'-disubstituted benzimidazolones promoted only by a base, with no need for transition-metal catalysts and/or excess chemical oxidants. Thus, it provides a green and powerful alternative to present approaches to benzimidazolones. Such catalyst-free electrosynthetic methods are currently being investigated for the construction of other heterocycles in our laboratory.

Experimental Section

Typical Procedure for the Electrosynthesis of the Cyclization Products.

A 10 mL three-necked round-bottom flask was charged with a urea **1** (0.1 mmol), Me_4NBF_4 (0.1 mmol), and NaOMe (0.1 mmol). The flask was equipped with a condenser, a RVC plate (100 PPI) anode (1.2 cm × 1 cm × 1 cm) and a platinum plate (1 cm × 1 cm) cathode and then flushed with argon. MeOH (6 mL) was added with a syringe. The constant current (2 mA) electrolysis was carried out at 60 °C (oil bath temperature) until complete consumption of **1**. The reaction mixture was cooled to room temperature, followed by addition of water (10 mL) and ethyl acetate (10 mL). The phases were separated and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic solution was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **2**.

Acknowledgements

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[11] Under our standard galvanostatic conditions, TEMPO was probably oxidized to a TEMPO cation prior to the substrate. However, the simultaneous oxidation of the substrate could not be ruled out. Moreover, the *in situ* generated TEMPO cation didn't enable the reaction as as it did in TEMPO-mediated electrochemical transformations. Therefore, we hypothesized that, in the presence of TEMPO (2 equiv.), radical II, which was generated electrochemically or by a TEMPO cation, could couple with the unoxidized TEMPO to prohibit the formation of the products. For an example of the radical-trapping experiment in the case of $E_{TEMPO} < E_{substrate}$: a) D. He, J. Yao, B. Ma, J. Wei, G. Hao, X. Tuo, S. Guo, Z. Fu, H. Cai, *Green Chem.* 2020, 22, 1559-1564. For examples of TEMPO-mediated electrosynthesis: b) F. Xu, L. Zhu, S. Zhu, X. Yan, H. C. Xu, *Chem. Eur. J.* **2014**, *20*, 12740-12744; c) H. B. Zhao, P. Xu, J. Song, H. C. Xu, *Angew. Chem. Int. Ed.* **2018**, *57*, 15153-15156; d)X. Y. Qian, S. Q. Li, J. Song, H. C. Xu, *ACS Catal*. **2017**, *7*,2730-2734.

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