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Benzazole Electrosynthesis

Electrochemical Synthesis of Benzazoles from Alcohols and *o*-Substituted Anilines with a Catalytic Amount of Co^{II} Salt

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Abstract: An electrochemical synthesis of benzazoles directly from alcohols and *o*-substituted anilines has been developed. The reaction conditions have been optimized by varying the composition of the electrolyte and the metal salt used as catalyst. The cyclization proceeds smoothly with a catalytic amount of a cobalt salt under air at room temperature to afford 2-substituted benzimidazoles, benzothiazoles, and benzoxazoles in good to excellent yields with a wide substrate scope.

Introduction

Benzazoles (benzimidazoles, benzothiazoles, and benzoxazoles) and their derivatives are important targets among heterocyclic compounds. Such substructures are widely encountered in pharmaceutical and agrochemical agents.[1] Classical methods for the preparation of benzazoles include metal-catalyzed intramolecular cyclization of *o*-haloanilides or their analogues[2] and the condensation of *o*-substituted anilines with either carboxylic acids, acyl esters, chlorides, amides, nitriles, and such like[3] or aromatic aldehydes.[4] Since alcohols are abundantly available,[5] the development of efficient reactions whereby alcohols are converted into useful classes of compounds is an attractive goal.[6] Direct oxidative cyclization to form benzazoles from alcohols and *o*-thio/hydroxy/aminoanilines is thus especially attractive. However, alcohol-to-heterocycle reactions require high selectivity to achieve dehydrogenation of the C–H and N–H bonds in one pot. Recently, progress has been made by employing alcohols directly to react with *o*-thio/hydroxy/aminoanilines to afford benzazoles.[7]

Electrochemistry has been found to be a powerful method for the synthesis of organic compounds and electrosynthetic processes constitute green chemistry, wherein the electric current takes the place of a stoichiometric amount of a redox agent.[8] Recently, Zeng and co-workers reported an indirect electrochemical synthesis of 2-substituted benzoxazoles from pre-formed Schiff-bases using sodium iodide as a mediator.[9] As part of our ongoing activities in exploring electrochemical reactions,[10] we report here the first example of the direct electrochemical synthesis of benzazoles from alcohols and *o*-substituted anilines in the presence of a catalytic amount of a cobalt salt under air at room temperature.

Results and Discussion

To start our investigation, benzyl alcohol **1a** (0.5 mmol), 1,2-phenylenediamine **2a** (0.75 mmol), and CF_3COOH (1.0 mmol) were added to a one-compartment cell containing an electrolyte of 0.1 M $LiClO_4$ in CH_3CN (5 mL) and Pt foils (1.0 × 1.5 cm^2) as electrodes, and electrolysis was carried out at constant current (20 mA) at room temperature. Benzimidazole **3a** was obtained in 28 % yield after the reaction mixture had been stirred for 150 min (Table 1, entry 1). In this reaction, 1,2-diphenylbenzimidazole was obtained as a by-product. Transition metal salts, specifically $NiSO_4 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, and Co(acac)$_2$, showed promising activities in promoting this reaction (Table 1, entries 2–6). Among them, $CoSO_4 \cdot 7H_2O$ proved to be the best transition metal salt additive, and the desired product was obtained in 86 % yield without any detectable 1,2-diphenylbenzimidazole formation. When the reaction was carried out in anhydrous CH_3CN using anhydrous $CoSO_4$, only a 79 % yield of **3a** was obtained (Table 1, entry 7). It was interesting to observe that by adding a small amount of water, the yield increased to 93 % (Table 1, entry 9). It was also noteworthy that when the Pt foil electrodes were replaced by graphite rods, the product yield was 85 % (Table 1, entry 10). This implied that the Pt electrode did not serve as a catalyst or promoter for this reaction (Table 1, entries 9 and 10). Increasing or decreasing the current both led to a decrease in the product yield (Table 1, entries 11 and 12). A nitrogen atmosphere also led to a lower chemical yield (Table 1, entry 13). No reaction occurred when the reaction mixture was stirred for 150 min without applying a potential difference (entry 14). Among the solvents examined, CH_3CN was found to be the most suitable for this reaction (Table 1, entries 9, 15–17).

Having established the optimal reaction conditions (Table 1, entry 9), we proceeded to examine the reactions of various

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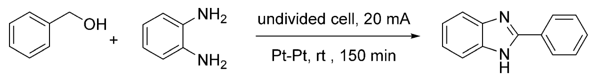
Table 1. Optimization of the reaction conditions for the electrochemical synthesis of benzimidazoles.[a]



1a **2a** **3a**

Entry	Solvent	Catalyst	Yield **3a**[b] [%]
1	CH_3CN	–	28
2	CH_3CN	$NiSO_4·6H_2O$	62
3	CH_3CN	$FeSO_4·7H_2O$	71
4	CH_3CN	$CoSO_4·7H_2O$	86
5	CH_3CN	$CoCl_2·6H_2O$	84
6	CH_3CN	$Co(acac)_2$	66
7	CH_3CN (anhydrous)	$CoSO_4$	79
8	CH_3CN/H_2O (96:4)	$CoSO_4·7H_2O$	83
9	CH_3CN/H_2O (98:2)	$CoSO_4·7H_2O$	93
10[c]	CH_3CN/H_2O (98:2)	$CoSO_4·7H_2O$	85
11[d]	CH_3CN/H_2O (98:2)	$CoSO_4·7H_2O$	88
12[e]	CH_3CN/H_2O (98:2)	$CoSO_4·7H_2O$	75
13[f]	CH_3CN/H_2O (98:2)	$CoSO_4·7H_2O$	72
14[g]	CH_3CN/H_2O (98:2)	$CoSO_4·7H_2O$	N.R.
15	THF/H_2O (98:2)	$CoSO_4·7H_2O$	68
16	DMF/H_2O (98:2)	$CoSO_4·7H_2O$	82
17	$DMSO/H_2O$ (98:2)	$CoSO_4·7H_2O$	74

[a] Unless otherwise noted, a mixture of **1a** (0.5 mmol), **2a** (0.75 mmol), CF_3COOH (1.0 mmol), and metal salt (20 mol%) in solvent (5.0 mL) with 0.1 M $LiClO_4$ was electrolyzed with a pair of Pt foils (1.0×1.5 cm^2) at constant current (20 mA) in an undivided cell at r.t., 150 min, air. N.R.: no reaction. [b] The yield of the product was determined by ^1H NMR spectroscopy. [c] Graphite rod electrodes (diameter: 0.5 cm, height: 1.78 cm). [d] The current was 30 mA. [e] The current was 10 mA. [f] N_2 was used instead of air. [g] No electrolysis.

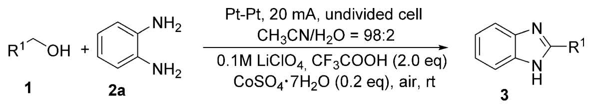
aryl alcohol substrates. As presented in Table 2, the reaction proceeded smoothly with a series of primary alcohol substrates to afford moderate to excellent yields of the corresponding 1,2-benzimidazoles (**3a**–**n**).

It was noteworthy that halogen and nitro groups were tolerated under the electrochemical conditions. Electron-donating (Me, OMe; **3b**–**d**) and electron-withdrawing groups (F, Cl, Br; **3e**–**h**) on the aryl ring had minimal effects on the yield. Only the strongly electron-withdrawing NO_2 group (**3i**,**j**) led to a slight decrease in yield. An alcohol bearing a naphthyl group (**3k**) also participated in this reaction with high reactivity to afford the desired product in 83% yield. Heterobenzylic alcohols also proved to be good substrates for this process, giving good yields of benzazoles under similar conditions (**3l**–**n**). It was also noteworthy that aliphatic alcohols (*n*-butanol and *n*-heptanol) were compatible with the reaction, and the desired products were obtained in yields of 37% and 38%, respectively (**3x**,**y**).

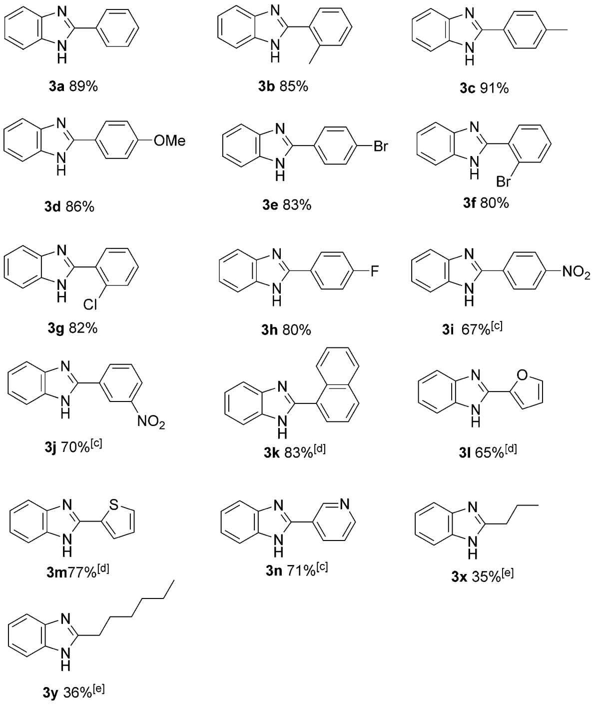
To further examine the scope of this reaction, various substituted 1,2-diaminoarenes were employed. As shown in Table 3, several electron-rich and electron-deficient *o*-diaminobenzenes **2** proved to be good reaction partners with benzyl alcohol **1a**, and the corresponding benzimidazoles (**3o**–**w**) were obtained in good to excellent yields. Similarly, this reaction showed satisfactory tolerance of halogen and nitro groups.

Having successfully achieved the electrochemical synthesis of benzimidazole derivatives, we expanded the reaction

Table 2. Substrate scope of alcohols for electrochemical synthesis of benzimidazole derivatives.[a,b]



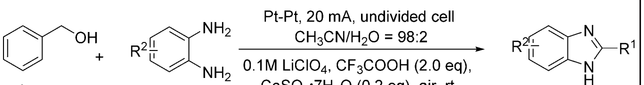
1 **2a** **3**



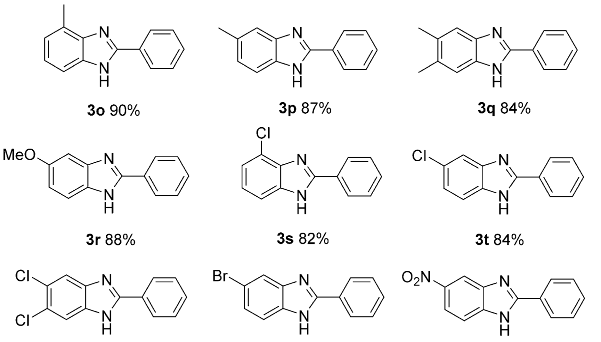
3a 89%
3b 85%
3c 91%
3d 86%
3e 83%
3f 80%
3g 82%
3h 80%
3i 67%[c]
3j 70%[c]
3k 83%[d]
3l 65%[d]
3m77%[d]
3n 71%[c]
3x 35%[e]
3y 36%[e]

[a] Unless otherwise noted, **1** (0.5 mmol), **2a** (0.75 mmol), $CoSO_4·7H_2O$ (20 mol%), CF_3COOH (1.0 mmol), 0.1 M $LiClO_4$, CH_3CN/H_2O (98:2; 5.0 mL), a pair of Pt foils (1.0×1.5 cm^2), constant current (20 mA), undivided cell, r.t., air, 150 min. [b] Isolated yield. [c] 50 °C, t=6 h. [d] 45 °C, t=6 h. [e] Constant current (5 mA), t=12 h.

Table 3. Substrate scope of *o*-aminoanilines for electrochemical synthesis of benzimidazole derivatives.[a,b]



1a **2** **3**

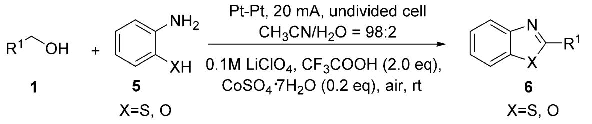


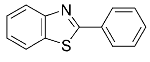
3o 90%
3p 87%
3q 84%
3r 88%
3s 82%
3t 84%
3u 82%
3v 80%
3w 75%[c]

[a] Unless otherwise noted, **1a** (0.5 mmol), **2** (0.75 mmol), $CoSO_4·7H_2O$ (20 mol%), CF_3COOH (1.0 mmol), 0.1 M $LiClO_4$, CH_3CN/H_2O (98:2; 5.0 mL), a pair of Pt foils (1.0×1.5 cm^2), constant current (20 mA), undivided cell, r.t., air, 150 min. [b] Isolated yield. [c] 45 °C, t=6 h.

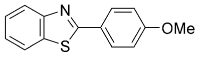
system to the synthesis of benzothiazoles and benzoxazoles, which are also found in numerous pharmaceutical agents. By reacting *o*-aminothiophenol with various aryl alcohols, benzothiazoles were produced in moderate to excellent yields (Table 4, **6a–g**). Furthermore, *n*-butanol also reacted with *o*-aminothiophenol to give the corresponding product in a moderate yield of 40% (Table 4, **6i**). 2-Phenyl-benzoxazole could also be obtained in 40% yield from *o*-aminophenol (Table 4, **6h**).[11b]

Table 4. Electrochemical synthesis of benzothiazole and benzoxazole derivatives.[a,b]

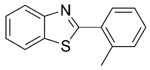




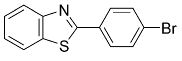
6a 86%



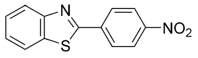
6b 83%



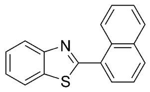
6c 88%



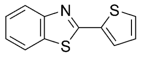
6d 80%



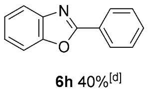
6e 70%[c]



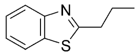
6f 78%



6g 81%



6h 40%[d]



6i 38%[e]

[a] Unless otherwise noted, **1** (0.5 mmol), **5** (0.75 mmol), $CoSO_4·7H_2O$ (20% mol), CF_3COOH (1.0 mmol), 0.1 M $LiClO_4$, CH_3CN/H_2O (98:2; 5.0 mL), a pair of Pt foils (1.0×1.5 cm^2), constant current (20 mA), undivided cell, r.t., air, 150 min. [b] Isolated yield. [c] 50 °C, t=6 h. [d] Constant current (10 mA), 50 °C, t=6 h. [e] Constant current (5 mA), t=12 h.

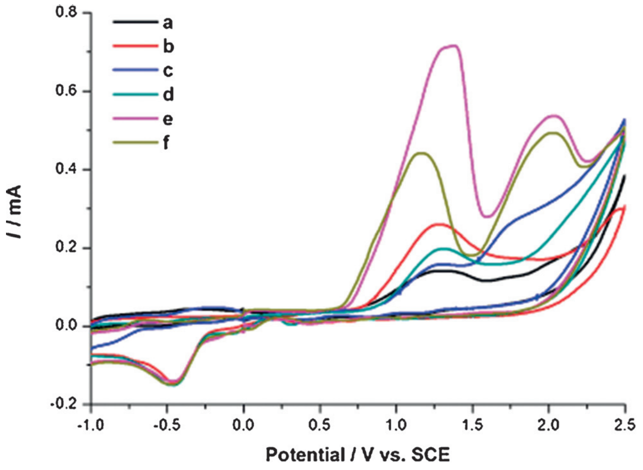
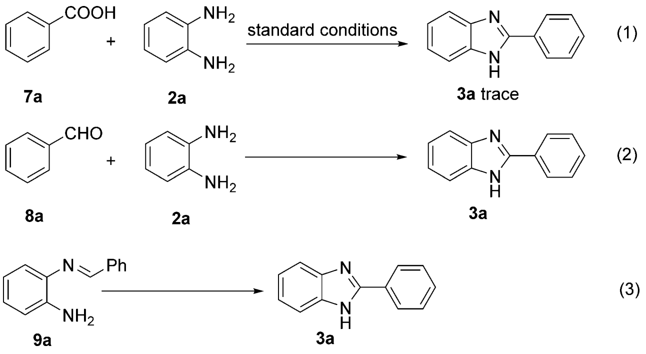


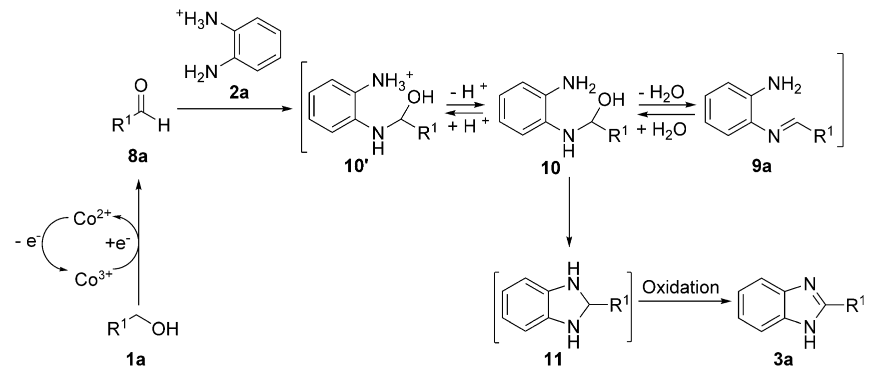
Figure 1. Cyclic voltammograms of the relevant compounds in CH_3CN/H_2O (98:2), using a Pt disk as working electrode, a Pt wire as counter electrode, and a saturated calomel electrode (SCE) as a reference electrode, at a scan rate of 100 mV s^{-1}: (a) 0.1 M $LiClO_4$; (b) 0.1 M $LiClO_4$, CF_3COOH (20 mmol L^{-1}); (c) 0.1 M $LiClO_4$, benzyl alcohol (20 mmol L^{-1}); (d) 0.1 M $LiClO_4$, CF_3COOH (20 mmol L^{-1}), benzyl alcohol (20 mmol L^{-1}); (e) 0.1 M $LiClO_4$, $CoSO_4·7H_2O$ (2 mmol L^{-1}), CF_3COOH (20 mmol L^{-1}), benzyl alcohol (20 mmol L^{-1}); (f) 0.1 M $LiClO_4$, $CoSO_4·7H_2O$ (2 mmol L^{-1}), CF_3COOH (20 mmol L^{-1}).

Cyclic voltammograms (CV) were then studied (see the SI). It is convenient that the oxidation process of benzyl alcohol can be elucidated by CV analysis. As shown in Figure 1,[11] the electrochemical response of benzyl alcohol in an electrolyte of 0.1 M $LiClO_4$ in CH_3CN/H_2O (98:2) exhibited its oxidation peak at E_p=1.78 V vs SCE (curve c). However, when CF_3COOH was added to the reaction mixture, the oxidation peak of benzyl alcohol disappeared (curve d). Furthermore, in the presence of $CoSO_4·7H_2O$, benzyl alcohol, and CF_3COOH, the oxidation peak of Co^{II} (E_p=2.04 V vs SCE) was observed, but the oxidation peak of benzyl alcohol was not detected (curve e).[11a] The above CV results indicated that the acidic reaction conditions inhibited the anodic oxidation of benzyl alcohol to form benzaldehyde. This was also indicated by previous work.[12] We propose that, under our acidic reaction conditions, Co^{III} generated on the anode reacts chemically with benzyl alcohol to give benzaldehyde.[13] In CV studies in the absence of CF_3COOH, the oxidation peak of 1,2-phenylenediamine was observed at E_p=0.45 V vs SCE (SI, Figure S1 k), whereas in the presence of CF_3COOH, it was observed at E_p=0.86 V vs SCE (SI, Figure S1 e). This implies that in our reaction system the acid could have protonated the 1,2-phenylenediamine, making it more difficult to oxidize.[16]

To gain more insight into the reaction mechanism, several other control experiments were carried out (Scheme 1). When a mixture of benzoic acid **7a** and *o*-diaminobenzene **2a** was subjected to the standard conditions, a trace of benzimidazole **3a** was detected [Eq. (1)]. When benzaldehyde **8a** was added dropwise to the reaction system under the standard conditions, benzimidazole **3a** was produced in 76% yield [Eq. (2), a]. Furthermore, the product **3a** was obtained in 78% yield when imine **9a** was used as starting material under the standard conditions [Eq. (3), a]. These results suggested that benzaldehyde **8a** and imine **9a** might be intermediates in this reaction. Next, the effects of oxygen and Co^{II} were studied, and it was found that reactions under a nitrogen atmosphere or in the



Scheme 1. Control experiments. For reaction (2): **8a** was added dropwise to the reaction system a) at standard condition, **3a**=76%; b) at standard conditions but without $CoSO_4·7H_2O$, **3a**=34%. For reaction (3): a) at standard conditions, **3a**=78%; b) using anhydrous solvent and reagents, N_2, **3a**=20%; c) at standard conditions but without $CoSO_4·7H_2O$, **3a**=45%; d) using anhydrous solvent and reagents, O_2 (balloon), **3a**=70%.



Scheme 2. A possible mechanism for the benzazole synthesis.

absence of cobalt(II) sulfate gave much lower yields. This confirmed that molecular oxygen and Co^{II} played crucial roles in this transformation (entry 13 in Table 1; [Eq. (2)], b; [Eq. (3)], b,c). Moreover, it was observed that water enhanced this transformation (entries 7 and 9 in Table 1; [Eq. (3)], a,d).[14]

On the basis of our control experiments, the cyclic voltammograms, and salient literature,[12–15] a possible mechanism for this reaction is proposed, as depicted in Scheme 2. Benzyl alcohol **1a** is oxidized to benzaldehyde **8a** by Co^{III} generated on the anode. Benzaldehyde **8a** quickly condenses with protonated diamine **2a** to give the intermediate **11** through cyclization of intermediate **10**. Subsequently, rapid oxidative dehydrogenation of benzazoline **11** generates the target compound benzimidazole **3a** by the combined effects of Co^{III}, anodic oxidation, and O_2.

Conclusion

In conclusion, an electrochemical strategy for the synthesis of benzazoles directly from benzylic alcohols and *o*-substituted anilines in the presence of a catalytic amount of a cobalt salt has been developed. This method is atom-economic and is carried out in a one-compartment cell at room temperature under air. It is enhanced by water, and gives 2-substituted benzimidazoles, benzothiazoles, and benzoxazoles in good to excellent yields with a wide range of functional groups. Further extension of this electrochemical protocol to the synthesis of other heterocycles is underway.

Experimental Section

Synthesis of 2-phenylbenzimidazole (3a)

An electrolyte of 0.1 M $LiClO_4$ in CH_3CN/H_2O (98:2; 5.0 mL) was added to a round-bottomed flask. Benzyl alcohol (52 μL, 0.5 mmol, 1.0 equiv), 1,2-phenylenediamine (81.1 mg, 0.75 mmol, 1.5 equiv), $CoSO_4{\cdot}7H_2O$ (28.1 mg, 0.1 mmol, 20 mol%), and CF_3COOH (74 μL, 1.0 mmol, 2.0 equiv) were then added. The resulting solution was electrolyzed with a pair of Pt foils ($1.0\times1.5\ cm^2$) as electrodes at constant current (20 mA) at room temperature for 150 min ($3.73\ F\,mol^{-1}$). Thereafter, the reaction mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. The concentrated residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford the pure product **3a**.

Acknowledgements

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Keywords: alcohols · benzazoles · cobalt · electrochemistry · *o*-substituted anilines

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