

Electrochemical Cross-Coupling of $C(sp^2)$ —H with Aryldiazonium Salts via a Paired Electrolysis: an Alternative to Visible Light Photoredox-Based Approach

Yang-ye Jiang,^a Gui-yuan Dou,^a Luo-sha Zhang,^a Kun Xu,^a R. Daniel Little,^b and Cheng-chu Zeng^{a,*}

- ^a Beijing Key Laboratory of Environmental and Viral Oncology, College of Life Science & Bioengineering, Beijing University of Technology, Beijing 100124, People's Republic of China E-mail: zengcc@bjut.edu.cn
- ^b Department of Chemistry & Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106–9510, USA

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Abstract: Photoredox-based C–H bond functionalization constitutes one of the most powerful and atomeconomical approaches to organic syntheses. During this type of reaction, single electron transfer takes place between the photocatalyst (**PC**) and redox- active substrates. Electrosynthesis also involves electron transfer between substrates and electrodes. In this paper, we focus upon electrochemical cross-coupling of $C(sp^2)$ –H with aryldiazonium salts and have developed an efficient electrochemical approach to the Minisci-type arylation reaction. The constant current paired electrosynthesis proceeds in a simple undivided cell without external supporting electrolyte, features a wide range of substrates and is easy to scale-up. These results demonstrate that photoredox-based cross-coupling of $C(sp^2)$ –H with aryldiazonium salts can also proceed successfully under paired electrolysis conditions, thereby contributing to understanding of the parallels between photosynthesis and electrosynthesis.

Keywords: paired electrolysis; photoredox-based reactions; cross-coupling; quinoxalin-2(1*H*)-ones; aryldiazonium salts

Introduction

The functionalization of C–H bonds has attracted increasing attention in organic chemistry, medicinal chemistry and material sciences due to their atom economy and cost efficiency characteristics. Moreover, this approach is particularly important in the late-stage functionalization of molecules of medicinal interest.^[1] Although metal-catalyzed methodology has been well developed for the C–H bonds functionalization, stoi-chiometric amounts of oxidant are frequently required to regenerate the active catalyst.^[2]

Photoredox-based visible light initiated reactions, catalyzed either by a transition metal complex,^[3] or by organic dyes^[4] have emerged as a powerful alternative strategy. Mechanically, a photoexcited state, **PC***, is produced when the **PC** is irradiated using visible light (see Figure 1a). In turn, **PC*** behaves as a strong oxidant or reductant toward the substrate, **Sub**. Using oxidative quenching as an example, the **PC*** undergoes

a single electron transfer (SET) with the substrate to give its cation radical, PC^+ . Simultaneously, the substrate is reduced to the corresponding anion radical, Sub^- . Thereafter, a series of conversions (e.g., bond cleavage, protonation or coupling) converts Sub^- to an intermediate, Int1. When the redox potential of PC^+ is higher than that of Int1, a second SET may take



Figure 1. Comparison of photoredox-based process and paired electrolysis.

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place to afford the product and regenerate the **PC** (Figure 1a). Overall, this type of reaction only consumes light energy (photons). Nevertheless, the photocatalyst-based sequence is photocatalyst-dependent and its success depends upon the compatibilities of the potentials of the substrate with **PC** (here, $E(PC^+/PC^+)$ compared with E (Sub⁻/Sub), and $E(PC^+/PC)$ vs E (Int2/Int1)).

Organic electrochemistry has emerged as an efficient, green and environmentally friendly method, by which to achieve the C-H bond functionalization.^[5] Given the inherent parallels that both electrosynthesis and photoredox chemistry utilize electrons as reagents to activate the substrate molecule, many organic transformation have been translated from photoredoxcatalysed methodology to electrochemical processes and vice versa.^[6] This concept is illustrated in Figure 1b. The electrochemical reduction of a Sub generates the corresponding Sub-, which converts to an intermediate, Int1. If the electrochemical reaction is carried out in an undivided cell, the Int1 may be oxidized at the surface of the anode to form a second intermediate, Int2, which then goes on to produce the product. In this electrochemical process, only electricity energy is consumed. One main advantage of the electrochemistry strategy is that the potential of the electrodes (anode and cathode) can be controlled by the operator, rather than depending upon the potentials accessible to the photocatalyst; the electrodes function as the PC. In addition, workup, separation and isolation is required to recycle PC, whereas the electrode can simply be removed from solution.

Arylation reactions are widely used in organic synthesis to construct arylated compounds.^[7] Photocatalyzed arylation of $C(sp^2)$ -H bonds has emerged as a promising and useful strategy. It has been reported that, by employing Ru,^[8] and Ir^[9]-based transition metal photocatalysts, or an organic dye such as eosin Y^[10] under visible light irradiation, aryl diazonium salts undergo a series of transformations with (hetero) arenes or alkenes to give arylated products (Figure 2a). Based on these understanding, we envisioned that the photocatalyzed arylation of $C(sp^2)$ –H bonds might also proceed electrochemically. This communication describes our efforts and demonstrates for the first time that electrochemical paired electrolysis is an alternative to the visible light photoredox-based oxidation quenching approach (Figure 2b).



Figure 2. Arylation of $C(sp^2)$ –H bonds.

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Results and Discussion

We chose quinoxalin-2(1H)-one (1 a) and phenyldiazonium salt 2 a as the model substrates to demonstrate our concepts. Initially, the reaction was carried out under photochemical conditions using eosin Y as photocatalyst. As expected, the desired coupling product 3 aa was isolated in a 65% yield (Table 1,

Table 1. Optimization of the reaction condition	ns. ^[a]
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\bigcirc	H N + 1a	N ₂ BF ₄ 2a	C felt(+)-Ni(-) <u>CCE</u> , 4 mA/cm ² Et ₄ NBF ₄ (1.5 equiv.) DMSO, 25 °C	H N Jaa
entry	deviation f	rom standaı	d conditions	yield (%) ^[b]
1	eosin Y, D	MSO, blue	LEDs, N ₂	65 ^[c]
2	none		on DMA on anlyon	84 17 44 ^[d]
3	CH_3CN, M	IEOH, DMF	of DMA as solven	$11 1/-44^{[d]}$
4	MeOH:DMSO (5:1), MeOH:DMF (5:1) or MeOH:DMSO (5:1) as solvent			or $23-3/1-1$
5	no electricity			0 ^[e]
6	2 mA	2		82 ^[e]
7	6 mA			76 ^[e]
8	No externa	al electrolyte	2	76

^[a] Reaction conditions: **1a** (0.2 mmol) and **2a** (0.4 mmol) in DMSO (3 mL), undivided cell, 25 °C, current of 4 mA, graphite felt and Ni plate cathode (working area: 1 cm²) and constant current electrolysis (CCE) for 2.5 h, 1.88 F/mol.

^[b] Yield determined by HPLC.

^[c] Isolated yield.

^[d] n-Bu₄NClO₄ (1.5 equiv.) was used as electrolyte.

^[e] Et₄NBF₄ (1.5 equiv.) was used as electrolyte.

entry 1). With this result in mind, we chose to explore the transformation electrochemically. Notably, without current, the desired product was not detected (Table 1, entry 5). It was observed that the best results could be obtained by conducting a constant current electrolysis at 4 mA/cm^2 in an undivided cell equipped with a graphite felt anode and a nickel plate cathode without supporting electrolyte. Under these conditions, the desired product 3 aa was obtained in an 84% yield (Table 1, entry 2). Although the 2.0 equiv. phenyldiazonium salt was used, the biphenyl was not detected. Use of other solvents such as CH₃CN, MeOH, DMF and DMA provided 17%-44% yields of 3 aa (Table 1, entry 3). The use of mixed solvent systems did not improve the reaction efficiency (Table 1, entry 4). The electrochemical arylation proved insensitive to the choice of electrolyte, although the use of Et₄NBF₄ provided a slightly improved yield (72% vs 64%-71%; see SI Table S2 for details). It was observed that the anode and cathode materials play an important role (see SI Table S3 for details). In addition,



an almost identical yield (82%) of **3aa** was obtained when the current was reduced from 4 to 2 mA/cm^2 (Table 1, entry 6), but the reaction time increased to 5 h. Moreover, increasing the current to 6 mA/cm^2 resulted in lower yield of **3aa** (Table 1, entry 7). To our delight, the electrochemical reaction also worked well without Et₄NBF₄ as the external supporting electrolyte and a comparable yield of **3aa** was obtained (Table 1, entry 8), which highlights the advantages of this chemistry as a "green and sustainable" process.

Having the optimal reaction conditions in hand, we turned to investigate the generality of the protocol. As shown in Table 2, initially, when *N*-substituted quinox-

 Table 2. Substrate scope of heterocycles.^[a,b]



^[a] Reaction conditions: 1 (0.2 mmol) and 2a (0.4 mmol) in DMSO (3 mL), undivided cell, 25 °C, current of 4 mA, graphite felt and Ni plate cathode (working area: 1 cm²) and electrolysis for 2–4 h, 1.5–3.0 F/mol.

^[b] Isolated yield.

alinones were allowed to react with 2a under the standard conditions, the corresponding arylated products were afforded in moderate to good yields. For example, N-methyl and N-allyl quinoxalinones gave the corresponding products 3ba and 3ca in 61% and 45% yields, respectively. Notably, in the case of 1c, the arylation reaction occurred selectively on the heterocyclic ring, instead of the allylic subunit. Nbenzyl substituted quinoxalinones, bearing an electrondonating group (R=4-CH₃, 4-OCH₃, 4-t-Bu, 3,5-di- CH_3) or a halogen atom (R = F, Cl, Br) also worked well and gave the corresponding products 3 da-3 la in 49%-70% yields. For the N-acetyl substituted quinoxalinone 1 m ($R^2 = CH_2CO_2Et$), the arylated adduct 3 ma was obtained in a 54% yield. In the case of N-amidyl substituted quinoxalinone 1n, the adduct 3na, whose framework is common to antitumor and antimicrobial agents, was obtained in a 39% yield under the standard electrochemical conditions. Next, quinoxalinones with substituents on the aryl ring were investigated under the standard condition. When the substituents on the aryl ring corresponded to electron-donating group, 6,7di-CH₃, or halogen, 6-Cl, 6,7-di-Cl and 6,7-di-F, the corresponding products **30a–3ra** were obtained in moderate to good yields (68%–83%). Notably, when pyrazin-2-ol was used as the substrate, product **3sa**, a natural product and antibacterial agent of TN82, was obtained in a 76% yield. When benzo[g]quinoxalin-2 (1*H*)-one was electrolyzed under the standard conditions, the corresponding product **3ta** was isolated in a 49% yield. Besides, electron-deficient heterocycle quinoxaline, **1u**, also proceeded well to give the desired **3ua** in a 56% yield.

To further explore the practicality of the electrochemical arylation reaction, reactions of quinoxalin-2 (1H)-one **1a** with a variety of aryldiazonium salts **2** were investigated and the results are presented in Table 3. The electrochemical reactions exhibited an

 Table 3. Substrate Scope of Aryldiazonium Couplings.^[a,b]



^[a] Reaction conditions: 1a (0.2 mmol) and 2 (0.4 mmol) in DMSO (3 mL), undivided cell, 25 °C, current of 4 mA, graphite felt and Ni plate cathode (working area: 1 cm²) and electrolysis for 2–4 h, 1.5–3.0 F/mol.
 ^[b] Isolated visited

^[b] Isolated yield.

excellent tolerance for both electron-donating and electron-withdrawing groups on the aryl ring. For instance, with 4-CH₃ and 4-OCH₃ on the aryl diazonium salts, the desired products **3 ab** and **3 ac** were obtained in 64% and 67% yields, respectively. In addition, halogen atom (4-F, 4-Cl and 4-Br) substituted aryl diazoniums can also work well and the corresponding products **3 ad–3 af** were obtained in moderate yields (54%–57%). However, when the strong electron-withdrawing nitro group was appended to C4 of the aryl ring, the product **3 ag** was not detected and the starting material **1 a** was recovered. In contrast, when

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electron-withdrawing groups, 4-CF₃, 4-CN and 4-SO₂CH₃ were substituted on the aryl ring, the desired products **3ah–3aj** were obtained in 32%–62% yields. In addition, when the substituents were 2-CH₃ and 3-CH₃, the aryl diazonium salts also worked satisfactorily and gave the corresponding products 3 ak and **3 al** in 46% and 20% yields. What's more, the product **3 am** was obtained in a 41% yield when the α naphthalene diazonium salt was used as the source of aryl radical. Notably, the products **3 an** and **3 ao** were not detected when the 2-Br or 2-I-substituted phenyldiazonium salts were employed, due to the possible reduction reaction of aryl bromides or aryl iodides in the electrochemical condition.^[11,12] In addition, the heterocyclic aromatic diazonium salt 2p could also give the corresponding product 3 ap in 54% yield. However, when the heterocyclic aryl diazonium salt, **2q**, was used as the aryl radical precursor, the desired product **3 aq** was not detected and the starting material

was recovered. The practicality of the protocol was demonstrated by using the aqueous solution and a scale-up reaction (see SI Table S4 for details). As shown in Scheme 1,



Scheme 1. Gram-Scale Experiment.

when 20 mmol of 1s (1.92 g) was treated with 40 mmol of aryl diazonium salt 2a by using a circulation pump in conjunction with an undivided cell that was equipped with graphite as anode and cathode, the product 3sa was obtained in 53% yield (1.82 g (10.6 mmol), see the SI Figures S5–S7 for the details), the gram scale reaction time is similar to the small scale, suggesting that the electrochemical protocol might be useful for small scale industrial settings.

To examine the reaction mechanism, a series of control experiments were first performed. As shown in Scheme 2, when the mixture of 1a and 2a was electrolyzed in the presence of 2.0 equiv. of TEMPO under the standard reaction conditions, only a trace of the desired product 3aa along with a radical trapping product 4 was detected by GC-MS (run 1). The results implicate that a radical process involves a phenyl radical. In addition, it was observed that 3aa was not detected when the electrolysis was carried out in the anodic compartment of a divided cell under the standard reaction conditions (run 2), whereas, 53% yield of 3aa was obtained in the cathodic compartment (run 3). Moreover, nearly the same yield of 3aa was obtained when the process was conducted under a

2: run vield of 3aa conditions 1 standard conditions, 1.5 F/mol, 2.0 equiv. TEMPO Trace 2 standard conditions, 1.5 F/mol, divided cell in anodic compartment 0% standard condition, 1.5 F/mol, divided cell in cathodic compartment 53% standard condition, 1.5 F/mol, divided cell in cathodic compartment 4 50% under N_2 standard condition, electrolyze for 0.5 h (0.38 F/mol), then stirring for 3 h without current, divided cell in cathodic compartment 36% 6 standard condition, electrolyze for 0.5 h (0.38 F/mol) then stirring for 54% 3 h without curren

Scheme 2. Control experiments.

nitrogen atmosphere (run 4). These results clearly show that cathodic reduction leads to the formation of the aryl radical. It is noteworthy that **3 aa** could be isolated in a 36% yield in a divided cell (run 5) and improved to a 54% yield in an undivided cell (run 6) when only catalytic amount of charge was applied. This information indicates that a radical chain reaction pathway may also be involved, in addition to the anodic oxidation.

Cyclic voltammograms (CV) of diazonium salt 2hin the absence and presence of 1a were also recorded in an effort to provide additional mechanistic insights. As shown in Figure 3, diazonium salt 2h exhibited an irreversible reduction wave at -0.85 V vs Ag/AgNO₃ (0.1 M in CH₃CN), corresponding to the reduction of 2h to form the phenyl diazo radical, **5**. In the presence of 1a, the reduction current of 2h decreased from 33 μ A to 19 μ A. The result discloses that, in addition to the heterogenerous electron transfer of 2h with the cathode, an intermediate stemmed from 1a may under-



Figure 3. Cyclic voltammograms of 2h and related compound in 0.1 M *n*-Bu₄NBF₄/DMSO using platinum disk as the working electrode, Pt wire, and Ag/AgNO₃ (0.1 M in CH₃CN) as the counter and reference electrode, respectively, at a scan rate of 0.1 V s⁻¹: Background (black line), 5 mM of 1a (red line), 5 mM of 2h (blue line) and 5 mM of 2h in the presence of 15 mM of 1a (green line).

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Scheme 3. Proposed mechanism for the electrochemical arylation of 1 a with aryldiazonium salts.

go homogeneous electron transfer with **2 h** in solution, thereby decrease the concentration of **2 h**.

Based on the control experiments, CV analysis and literature reports,^[13] two pathways for the electrochemical arylation of $C(sp^2)$ -H with aryldiazonium salts are suggested and illustrated in Scheme 3. Thus, the aryl diazonium salts are initially reduced at the surface of the cathode to generate corresponding phenyl diazo radicals 5. Following loss of molecular N_2 , the resulting aryl radical 6 adds to guinoxalin-2 (1H)-one 1a generating radical intermediate 7. Subsequently, intermediate 7 is oxidized at the anode to afford the corresponding product 3 (pathway 1). In addition to the paired electrolysis pathway, intermediate 7 also undergoes homogeneous electron transfer in solution with the aryldiazonium salts followed by loss of a proton to give the product 3, along with the generation of 5 (pathway 2). Since the radical chain reaction also induce the formation of phenyl diazo radicals 5, only catalytic amount of charge is required.

Conclusion

In summary, we have developed an efficient electrochemical approach to the arylation of $C(sp^2)$ –H. The paired electrosynthesis proceeds in a simple undivided cell without external supporting electrolyte, features a wide range of substrates and is easy to scale-up. The achievement of the electrochemical cross-coupling of $C(sp^2)$ –H with aryldiazonium salts has disclosed that some of photoredox-based reactions may also proceed successfully under paired electrolysis conditions. This result further demonstrates the parallels of photosynthesis and electrosynthesis.

Experimental Section

General Procedure for the Synthesis of 3-arylsubstituted Quinoxalinones

An undivided cell was equipped with a graphite felt anode $(1.0 \times 4 \text{ cm}^2)$ and a Ni plate cathode $(1.0 \times 4 \text{ cm}^2)$ and connected to a direct (DC) regulated power supply. To the cell was added quinoxalinone (1, 0.2 mmol), aryl diazonium salt (2, 0.4 mmol) and 3.0 mL of DMSO. The mixture was electrolyzed using constant current conditions (~4 mA cm⁻²) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the quinoxalinone, 1.5–3.0 F/mol), the reaction mixture was extracted with DCM for 4 times. And the organic solvent was washed by water for 5–8 times, dried over Na₂SO₄, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired pure product.

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FULL PAPER

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Y.-y. Jiang, G.-y. Dou, L.-s. Zhang, K. Xu, R. D. Little, C.-c. Zeng*

