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# Manganese-Catalyzed Electrochemical Tandem Azidation– Coarctate Reaction: Easy Access to 2-Azo-benzonitriles

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One-pot cascade synthesis

eco-benian byproducts

External chemical oxidant free with

electrochemically driven azidation of 2*H*-indazole followed by coarctate fragmentation is developed to synthesize the 2-azobenzonitrile motif. This manganese-catalyzed transformation is external-chemical-oxidant-free and operates at ambient temperature under air. This methodology exhibits good functional group tolerance, affording a broad range of substrate scopes of up to 89% isolated yield. Diverse derivatization of the 2-azo-benzonitrile product resulted in other valuable scaffolds.

oarctate reactions belong to a specific class of concerted reactions that comprise a reactive center (coarctate atom) at which simultaneously, two bonds are cleaved and two bonds are formed in a single step.<sup>1</sup> These versatile reactions exhibit broad applications for the construction of important carbo- and heterocyclic motifs via ring-closing pathways. Conversely, ring-opening strategies provide access to several highly conjugated systems that are otherwise synthetically more challenging.<sup>3</sup> For example, a conjugated ene-ene-yne scaffold D can easily be prepared through a coarctate reaction by the fragmentation of a five-membered heteroarene by involving a reactive carbene/nitrene intermediate C (Scheme 1a).<sup>1c,4</sup> However, the generation of the appropriately functionalized active heteroarene B is not straightforward and typically requires multiple steps that reduce the overall efficiency of this strategy. To circumvent this issue, we envisioned a single-step oxidative C-H functionalization<sup>5</sup> of the easily available fivemembered heterocycle A to deliver the required active derivative B, which upon a subsequent fragmentationcoarctate reaction will produce the conjugated ene-ene-yne scaffold D in a one-pot cascade pathway.

Azo-benzonitriles, consist of two valuable functional groups and have multiple applications in natural products, agrochemicals, pharmaceuticals, polymers, dyes, and photoresponsive switches.<sup>6</sup> The syntheses of azoarenes involve the coupling of aromatic nucleophiles with diazonium salts, the oxidative coupling of aniline derivatives, the reduction of nitroaromatics, and so on.<sup>7</sup> Traditionally, aryl nitriles are prepared by using a copper-catalyzed Sandmeyer and Rosenmund–von Braun reaction or by other transition metalcatalyzed cyanations of aryl halides.<sup>8</sup> However, these approaches generally require harsh reaction conditions and use extremely toxic reagents like cyanides. Thus it is highly desirable to establish economic and green protocols for the synthesis of both azoarenes and benzonitriles. Scheme 1. One-Pot Cascade Strategy to Afford Conjugated Ene-Ene-Yne Skeleton

Practical and scalable protocol

synthetic applications

Broad substrate scope and various



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On the basis of the aforementioned mechanistic rationale (Scheme 1a), we realized that the 2-azo-benzonitrile (ene-eneyne) scaffold 3 can easily be accessed from the corresponding azido indazole derivative 2 via a denitrogenative ring fragmentation-coarctate reaction (Scheme 1b). Traditional methods for the azidation consistently require a stoichiometric amount of oxidants, including peroxydisulfates, hypervalent iodines, or high-valent metals, a high temperature, and a prolonged reaction time.<sup>9</sup> In addition, azidotrimethylsilane (TMSN<sub>3</sub>) is the most commonly used azide source, which is toxic, volatile, and relatively expensive. As a part of our ongoing research program on the development of reaction methodologies based on redox processes,<sup>10</sup> we envisioned a direct electrochemical azidation of the indazole derivatives to produce 2 by using inexpensive sodium azide. This economical and environmentally benign approach is a new addition to the available methods for the functionalization of indazoles<sup>11</sup> and also bypasses the multistep synthesis of azido derivatives involving harsh oxidants and toxic reagents.

Recently, organo-electrochemistry has realized a renaissance for redox-mediated transformations,<sup>12</sup> which has opened a new platform in organic synthesis from an environment-friendly and economic perspective. The use of electricity concedes the avoidance of stoichiometric redox reagents and also restricts the use of toxic reagents and the generation of unwanted byproducts.<sup>13</sup> In 2017, Lin first established an electrochemical approach for the diazidation of alkenes from sodium azide.<sup>14</sup> Herein we report the successful implementation of the electrogenerated azide radical in the C3–H azidation of various 2*H*-indazoles and a follow-up fragmentation to access the conjugated 2-azo-benzonitrile derivatives. Advantageously, this undivided cell electrolysis proceeds under externalchemical-oxidant-free condition at room temperature and under air, which supports its sustainability.

Our investigation was initiated by using 2-(p-tolyl)-2*H*-indazole (1a) and sodium azide as the model substrates in an undivided cell equipped with a graphite anode and a platinum cathode (Table 1). When the electrolysis was regulated at a constant current of 10 mA in MeCN/AcOH solvent mixture and LiClO<sub>4</sub> as the electrolyte in the presence of MnBr<sub>2</sub> (5 mol %) catalyst, the desired 2-azo-benzonitrile product **3a** was

Tabl	e 1.	O	otimization	of	the	Reaction	Conditions	5 <sup>4</sup>
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	MnBr <sub>2</sub> (5 mol%) NaN <sub>3</sub> (3 equiv) LiClO <sub>4</sub> (0.1 M) MeCN/TFA (20:1) 1a C(+)/Pt(-), 10 mA, rt 2.5 h, undivided cell	CN N <sup>SN</sup> 3a Me
entry	deviation from the standard condition	yield (%) <sup>b</sup>
1	MeCN/AcOH (12:1) as the solvent	66
2	none	81 $(78)^c$
3	$MeCN/H_2O$ (12:1) as the solvent	20
4	MeCN as the solvent	10
5	5 mA for 5 h	70
6	16 mA for 1.5 h	72
7	without catalyst	40
8	$Mn(OAc)_2$ instead of $MnBr_2$	58
9	without current	0

<sup>*a*</sup>Reaction conditions: 1a (0.2 mmol), NaN<sub>3</sub> (0.6 mmol), MnBr<sub>2</sub> (5 mol %), LiClO<sub>4</sub> (0.1 M) in MeCN/TFA (20:1, 6 mL), C anode, Pt cathode, undivided cell, constant current = 10 mA, at rt under air for 2.5 h. <sup>*b*</sup>NMR yield. <sup>*c*</sup>Isolated yield.

formed in 66% yield. Further optimization revealed that the MeCN/TFA mixture furnished better results, and **3a** was obtained in 81% <sup>1</sup>H NMR yield and in 78% isolated yield. Presumably, trifluoroacetic acid (TFA) facilitates the solubility of the reagents and also enhances the cathodic proton reduction.

Significantly lower yields of **3a** were obtained in the MeCN/ $H_2O$  (entry 3) mixture and also in the dry MeCN (entry 4). Either raising the current flow to 16 mA or lowering it to 5 mA also resulted in a decreased reaction yield (entries 5 and 6). In the absence of the manganese catalyst, a 40% yield of **3a** was detected, most likely through the direct anodic oxidation of azide (entry 7), but only 5 mol % MnBr<sub>2</sub> assists in efficiently reinforcing the oxidation of azide and improves the yield. However, another manganese salt displayed lower efficiency (entry 8). As expected, no desired product was obtained without running the current (entry 9).

To disclose the utility of the developed method, the substrate scope with various N-2-substituted 2H-indazoles was surveyed (Table 2). In the beginning, the effects of different N-2-substituted 2H-indazoles were explored. 2-Aryl-2H-indazoles bearing electron-donating ortho-, meta-, and para-substituted alkyl  $(-Me, -^{n}Bu, -^{t}Bu)$  and alkoxy (-OMe)groups in the phenyl ring efficiently provided the corresponding products in good yields (3a-3h). The reaction with halogen substituents such as para-F, para-Cl, and meta-Cl in the phenyl ring occurred smoothly for this transformation, furnishing moderate to good yields of the expected products (3i-3k). In addition, electron-deficient arene- (-CN- and -COMe-substituted) and heteroarene-bearing 2H-indazoles were found to be compatible with this reaction protocol to give the corresponding azo-ene-yne products (31-30). Naphthylsubstituted indazole derivative gave rise to the desired product 3p in 72% yield. Moreover, aliphatic-substituted 2H-indazole at the N-2 position responded well in this system to provide a good yield (3q-3r).

Next, we evaluated differently substituted arene moieties in 2*H*-indazoles to justify the general applicability of the developed method (Table 3). The electron-rich, 5,6-dimethoxy-substituted 2*H*-indazole conversantly delivered the expected rearrangement products in very good yields (**3s**, **3t**). Single-crystal X-ray analysis of **3s** was determined to support the structure. Different 5-halo-substituted (-F, -Cl) arenes were well tolerated and afforded the product in excellent yields (**3u-3y**). The gram-scale reaction of **3u** proceeded to give 72% yield, which supports the scalability and applicability of this protocol.

To manifest the colossal applicability of the current protocol, one of the 2-azo-benzonitrile compounds (3u) was synthetically converted to different valuable derivatives (Scheme 2). Selective Grignard addition to the azo functionality was performed at a lower temperature without affecting the nitrile group to form 4u in good yield. When the temperature was increased and an excess amount of Grignard reagent was used, addition to both azo and nitrile functionalities was observed to deliver the substituted ketone 5u in excellent yield. In both cases, the alkyl group regioselectivity was added to the more electron-deficient N atom, which was confirmed by a nuclear Overhauser effect (NOE) experiment. (See the SI for details.) Nucleophilic aromatic substitution of the fluorine atom delivered **6u** without reacting with the other functionalities. Finally, a selective reduction of the azo group through transfer hydrogenation in

Table 2. Substrate Scope Using Various Two-Substituted Indazoles $^{a,b}$ 



<sup>*a*</sup>Reaction conditions: 1 (0.2 mmol), NaN<sub>3</sub> (0.6 mmol), MnBr<sub>2</sub> (5 mol %), LiClO<sub>4</sub> (0.1 M) in MeCN/TFA (20:1, 6 mL), C anode, Pt cathode, undivided cell, constant current = 10 mA, at rt under air for 2.5 h. <sup>*b*</sup>Isolated yield.

*situ* produced the corresponding hydrazine derivative, which upon coarctate cyclization reconstructed the indazole ring to form 7u in good yield.

To comprehend the mechanism of the cascade process, we performed several studies (Figure 1 and Scheme 3). First, cyclic voltammetric (CV) experiments of indazole 1a and sodium azide were carried out as model substrates. Oxidation peaks were noticed at 1.50 and 1.03 V vs Ag/AgCl for 1a and NaN<sub>3</sub> respectively. MnBr<sub>2</sub> alone exhibits a quasi-reversible oxidation peak at 0.75 and 0.86 V due to the oxidation of Mn(II) and the free bromide counteranion, respectively (see the SI); however, in the presence of NaN<sub>3</sub>, an oxidation peak appeared at 0.43 V. This potential suggests that an oxidation wave of azide-bound Mn(II) due to the anionic ligand stabilized the Mn(III) oxidation state. An ultraviolet-visible (UV-vis) spectroscopy experiment also supported the oxidation of the Mn(II)-N<sub>3</sub> complex to Mn(III)-N<sub>3</sub> through electrolysis of the azide and Mn(II) mixer and showed a characteristic peak at 465 nm due to the ligand-to-metal

# Table 3. Substrate Scope Using Various Arene-Substituted Indazoles $^{a,b}$



<sup>*a*</sup>Reaction conditions: 1 (0.2 mmol), NaN<sub>3</sub> (0.6 mmol), MnBr<sub>2</sub> (5 mol %), LiClO<sub>4</sub> (0.1 M) in MeCN/TFA (12:1, 6 mL), C anode, Pt cathode, undivided cell, constant current = 10 mA, at rt under air for 2.5 h. <sup>*b*</sup>Isolated yield.

Scheme 2. Various Derivatizations of the 2-Azo-benzonitrile Compound



charge-transfer transition. In a separate experiment, the rate of formation of the azo-benzonitrile product **3a** during electrolysis was monitored using UV–vis spectroscopy by following the absorbance at 435 nm ( $\lambda_{max}$  of **3a**) at different time intervals. An increase in the absorbance indicates the steady formation of **3a** with the constant current flow (10 mA).

The reaction was completely shut down by the addition of TEMPO, suggesting a radical nature of the reaction (Scheme 3a). Furthermore, the azide radical was captured using styrene 8, and two radical addition products 9 and 10 were formed along with azo-benzonitrile product 3a (Scheme 3a). To identify the precursor of the intermediate for the coarctate reaction, azido indazole 11 was synthesized following a reported method.<sup>4b</sup> Electrolysis under the standard reaction



Figure 1. (A) Cyclic voltammogram of 1a and NaN<sub>3</sub>. (B) Cyclic voltammogram of NaN<sub>3</sub> + MnBr<sub>2</sub>. (C) UV spectra of Mn(II) $-N_3$  species. (D) Kinetic plot for the formation of 3a.



conditions (Scheme 3b) produced the expected product 3a in high yield (86%) within a very short reaction time (20 min).

To get additional insight into the reaction mechanism, we performed a series of experiments at constant potential with and without the involvement of the manganese catalyst (Scheme 3c). The formation of product 3a (34%) was observed at the lower potential (0.8 V) only in the presence of manganese catalyst. This indicates the generation of the azide radical only through the assistance of the manganese catalyst and not by direct oxidation at the anode. However, the direct oxidation of the azide anion becomes operational at a higher potential (1.20 V) than the corresponding oxidation peak (1.03 V), and 3a was formed even without using the manganese catalyst. Notably, using the manganese catalyst in

a constant potential experiment at 1.20 V, which is much lower than the oxidation peak of 2*H*-indazole (1.50 V for 1a), provided a significant amount of product 3a (59%). This result disfavors the possibility of the direct electrochemical oxidation of 2*H*-indazole during the product formation.

On the basis of CV and UV experimental data, several control experiments, and literature reports, a plausible mechanism of the cascade reaction is depicted in Scheme 4.

Scheme 4. Plausible Mechanistic Pathway



At the onset, ligand exchange with sodium azide generates the  $Mn(II)-N_3$  complex A. Under electrochemical conditions, single-electron oxidation of A at the anode produces Mn(III)-N<sub>3</sub> species **B**. Electrogenerated **B** facilitates the formation of an azide radical and assists the reaction at a comparatively low applied potential. As observed in the control experiments (Scheme 3c), an additional pathway for the direct oxidation of the azide anion on the anode surface to form the azide radical becomes feasible at the higher electrode potential. Thereafter, selective azide radical addition at the C3 position of indazole<sup>10b,11b</sup> provided C. Subsequently, one-electron oxidation and deprotonative aromatization form the azido indazole E. Under the electrochemical conditions, the kinetically labile E (as observed for 11 in Scheme 3b) undergoes denitrogenative coarctated reaction, most likely via the nitrene intermediate F, to afford the azo-benzonitrile product 3. Unlike the previously reported fragmentations, which require a high temperature,<sup>1c</sup> this reaction occurs at ambient temperature. Thus the possibility of an electric-field-induced rearrangement reaction cannot be ruled out.<sup>15</sup> Finally, proton reduction on the platinum cathode surface generates dihydrogen and maintains the charge balance in the overall electrochemical process.

In conclusion, we have developed a green method for the azide radical generation by employing an earth-abundant manganese catalyst and the cheapest azide source. This electro-

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oxidative azidation of indazoles is followed by a coarctate fragmentation to deliver the azo-benzonitrile moiety under air and at room temperature. A series of azo-benzonitrile derivatives containing diverse functional groups have been synthesized in high yields. The gram-scale electrolysis revealed the practical synthetic potential of this methodology, which is otherwise challenging using the combination of traditional chemical oxidants and azide sources due to uncontrolled reactions and the risk of explosion. Mechanistic details suggest a precedented radical pathway. More synthetic applications of this electrochemically generated azide radical in other cascade processes are currently ongoing in our laboratory.

# ASSOCIATED CONTENT

### **9** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00169.

Experimental procedures and spectral data for all new compounds (PDF)

### **Accession Codes**

CCDC 2019834 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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# Notes

The authors declare no competing financial interest.

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