# Iodine-Mediated Electrochemical C(sp<sup>2</sup>)–H Amination: Switchable Synthesis of Indolines and Indoles

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**ABSTRACT:** A metal-free electrochemical intramolecular  $C(sp^2)$ -H amination using iodine as a mediator was developed. This method enables a switchable synthesis of indoline and indole derivatives, respectively, from easily available 2-vinyl anilines.

I ndolines and indoles are prevalent structures in bioactive intermediates, natural products, and medicines.<sup>1,2</sup> The synthesis of indolines and indoles remains a huge interest in the field of organic chemistry. Direct  $C(sp^2)$ -H amination shows a powerful and practical strategy for the synthesis of indolines and indoles.<sup>3</sup> The general methods involve metal catalysis (Scheme 1A).<sup>4,5</sup> To meet the requirement of the particular purity in biological and medicinal chemistry, significant contributions are based on metal-free oxidation reactions.

#### Scheme 1. Synthesis of Indolines and Indoles



Recently, the metal-free amination or diamination of 2-vinyl aniline has attracted chemists' attention. A series of hyper-valent iodine-mediated intramolecular amination reactions were reported.<sup>6</sup> For instance, both Johnston's efficient synthesis of indolines and Muniz's rapid preparation of indoles are intramolecular aminations with hypervalent iodine(III) as

the oxidant (Scheme 1B). NIS-mediated amination reactions for the synthesis of indolines and indoles were also reported.<sup>7</sup> Other methods for the synthesis of indoles via  $C(sp^2)$ -H amination include sulfonium ion catalysis,<sup>8</sup> selenium catalysis with *N*-fluorobenzenesulfonimide (NFSI) oxidation,<sup>9</sup> 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) mediation,<sup>10</sup> and 3,5-dichlorobenzoic acid catalysis in the presence of dioxygen.<sup>11</sup> Among these amination reactions, the metals and stoichiometric oxidants are usually necessary to conduct the reaction. Therefore, it is highly desirable to develop a more efficient metal-free oxidation system.

Organic electrochemistry, employing an electron as the reagent, has been discovered to be an efficient and environmental friendly tool in organic synthesis.<sup>12</sup> Recently, some elegant methods for the synthesis of indolines and indoles were reported in this field.<sup>13</sup> For instance, the Vincent group reported a directed electro-oxidative dearomatization of indoles to synthesize indolines.<sup>14</sup> Zeng and coworkers developed the electrochemically catalyzed aminooxygenation of styrenes for the synthesis of indolines.<sup>15</sup> The Xu group developed various methods to synthesize nitrogen-containing heterocyclic compounds via an anodic oxidation.<sup>16</sup> The Lei group developed electrochemical methods for the construction of a  $C(sp^2)$ –N bond or a  $C(sp^3)$ –N bond.<sup>17</sup> Despite this outstanding research, the selective synthesis of indolines and

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indoles in one reaction system still remains challenging. Our group has been focusing on iodine-mediated chemical and electrochemical research for a long time.<sup>18</sup> Herein we report a switchable synthesis of indolines and indoles from readily available 2-vinyl anilines in the presence of Me<sub>4</sub>NI under electrochemical conditions.

Initially, we chose 2-vinyl aniline 1a as the model substrate (Table 1). The reaction was performed in an undivided cell at



	NH 1a Ts	Pt-P I = 10 r electrolyte ( PhNH <sub>2</sub> (1. solven	t mA 1.0 equiv) 0 equiv) t, RT 3aa	Ph
		AE		
entry	electrolyte	(1.0 equiv)	solvent	yield (%)
1	KI		CH <sub>3</sub> CN	26
2	$NH_4I$		CH <sub>3</sub> CN	trace
3	"Bu <sub>4</sub> NI		CH <sub>3</sub> CN	59
4	<sup>n</sup> Bu <sub>4</sub> NBr		CH <sub>3</sub> CN	trace
5	Et <sub>4</sub> NI		CH <sub>3</sub> CN	57
6	Me <sub>4</sub> NI		CH <sub>3</sub> CN	82
7	NaI		CH <sub>3</sub> CN	66
8	Me <sub>4</sub> NI		CH <sub>3</sub> CN/DMF (5.5/0.5)	72
9	Me <sub>4</sub> NI		CH <sub>3</sub> CN/DMSO (5.5/0.5)	76
10 <sup>c</sup>	Me <sub>4</sub> NI		$CH_3CN/H_2O(5.5/0.5)$	83
11	Me <sub>4</sub> NI		$CH_{3}CN/H_{2}O(5/1)$	91
12	Me <sub>4</sub> NI		CH <sub>3</sub> CN/H <sub>2</sub> O (4.5/1.5)	80
13	$Me_4NI(0.2)$	$NH_4BF_4$	$CH_{3}CN/H_{2}O(5/1)$	92
14	$Me_4NI(0.2)$	$^{n}Bu_{4}NBF_{4}$	$CH_{3}CN/H_{2}O(5/1)$	65
15	$Me_4NI(0.2)$	NH <sub>4</sub> PF <sub>6</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (5/1)	94
16	$Me_4NI(0.2)$	NH <sub>4</sub> ClO <sub>4</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (5/1)	84
17 <sup>d</sup>		NH <sub>4</sub> PF <sub>6</sub>	$CH_{3}CN/H_{2}O(5/1)$	n.d.
18 <sup>e</sup>	$Me_4NI(0.2)$	NH <sub>4</sub> PF <sub>6</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (5/1)	n.d.
19 <sup>f</sup>	$Me_4NI(0.2)$	NH <sub>4</sub> PF <sub>6</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (5/1)	96
20 <sup>g</sup>	$Me_4NI(0.2)$	NH <sub>4</sub> PF <sub>6</sub>	$CH_{3}CN/H_{2}O(5/1)$	89

<sup>*a*</sup>Reaction conditions: **1a** (0.3 mmol), electrolyte (1.0 equiv), PhNH<sub>2</sub> (1.0 equiv), and solvent (6 mL); the electrolysis was conducted in an undivided cell at room temperature, Pt–Pt ( $1.5 \times 1.5 \times 0.3 \text{ cm}^3$ ), air, I = 10 mA; AE = auxiliary electrolyte, n.d. = no detection. <sup>*b*</sup>Isolated yields after column chromatography. <sup>*c*</sup>Entry 10: 5.5 mL of CH<sub>3</sub>CN and 0.5 mL of H<sub>2</sub>O, entry 12: 4.5 mL of CH<sub>3</sub>CN and 1.5 mL of H<sub>2</sub>O, and entries 13–20: Me<sub>4</sub>NI (0.2 equiv), AE (1.0 equiv). <sup>*d*</sup>No Me<sub>4</sub>NI. <sup>*e*</sup>Without electricity. <sup>*f*</sup>I = 5 mA. <sup>*g*</sup>I = 15 mA.

a constant current of 10 mA in the presence of KI in CH<sub>3</sub>CN at room temperature. After 3 h, the desired product indoline was obtained with 26% isolated yield (entry 1, Table 1). Then, we investigated different electrolytes, as shown in entries 1-7of Table 1. Of them, Me<sub>4</sub>NI exhibited the best result in comparison with iodide and bromide electrolytes (entries 1-7). The results are perhaps relevant to the solubility, conductivity, and redox potential of the corresponding halogenated electrolytes (Table S3). Considering the poor solubility and conductivity of Me<sub>4</sub>NI in CH<sub>3</sub>CN, other solvents were added to the reaction (entries 8-10). H<sub>2</sub>O was found to be the best choice (entry 10). Delightfully, CH<sub>3</sub>CN/H<sub>2</sub>O (5/1) gave the best result with 91% isolated yield (entry 11). The reaction also conducted well when the stoichiometric Me<sub>4</sub>NI was decreased to a catalytic amount in the presence of an auxiliary electrolyte. Afterward, various

auxiliary electrolytes, such as  $NH_4PF_6$ ,  $NH_4BF_4$ ,  $NH_4ClO_4$ , and  $"Bu_4NBF_4$  were examined in the reaction. It was found that  $NH_4PF_6$  gave the best result (entry 15). The control experiments demonstrated that both  $Me_4NI$  and the electricity were essential for the transformation (entries 17 and 18). Finally, the electric current was examined, and 5 mA showed the best result with the highest yield of 96% (entry 19 vs entries 15 and 20). The optimal conditions were determined, as shown in entry 19.

Having established the optimal electrolytic protocols, the scope of the amines was investigated under standard conditions (Scheme 2). Various amines were employed in





<sup>a</sup>Reaction conditions: 1a (0.3 mmol), Me<sub>4</sub>NI (0.06 mmol), NH<sub>4</sub>PF<sub>6</sub> (0.3 mmol), amine (0.3 mmol), CH<sub>3</sub>CN/H<sub>2</sub>O (5 mL/1 mL); the electrolysis was conducted in an undivided cell at 25 °C for 5 to 6 h. The isolated yields after column chromatography are shown.

the reaction to afford the desired products in good to excellent yields. As for the anilines, both electron-withdrawing groups and electron-donating groups at the para position of anilines were well tolerated (3ab-an). The electronic properties of substituted anilines had some influence on the yields. In general, the electron-deficient anilines gave inferior results compared with electron-rich anilines (3aj-am vs 3af-ai). 1-Naphthylamine also performed well to give the desired product in 80% yield (3ao). Moreover, the secondary anilines also proceed smoothly in 80 and 88% yields, respectively (3ap, 3aq). The aliphatic amines, such as cyclohexylamine and piperidine, also conducted well in excellent and moderate yields (3as and 3at). Notably, benzylamine was also successfully employed in the reaction to afford the target product in 80% yield (3ar).

Subsequently, the scope of 2-vinyl anilines was explored (Scheme 3). A wide range of 2-vinyl anilines underwent the reaction efficiently to afford the corresponding indolines in moderate to excellent yields. It was found that the electronic effect had a great influence on the reaction. Moderate electron density within a certain range gave high yields. The stronger the electron-withdrawing group, the lower the yield (3bh-bl); the stronger the electron-donating group, the lower the yield (3bm-bp). The 4-halogen-2-vinyl anilines showed little difference in yields with a variety of halogens (3ba, 3bb, and





<sup>a</sup>Reaction conditions: 1 (0.3 mmol), Me<sub>4</sub>NI (0.06 mmol), NH<sub>4</sub>PF<sub>6</sub> (0.3 mmol), PhNH<sub>2</sub> (0.3 mmol), CH<sub>3</sub>CN/H<sub>2</sub>O (5 mL/1 mL); the electrolysis was conducted in an undivided cell at 25 °C for 5 to 6 h. The isolated yields after column chromatography are shown.

**3bd**). However, the electronic and steric effects of the substituent on the different positions of 2-vinyl anilines had a significant influence on the yields (**3bc-bf**). For instance, 3-bromo-2-vinyl aniline gave a low yield compared with 4-bromo-2-vinyl aniline and 5-bromo-2-vinyl aniline, whereas 6-bromo-2-vinyl aniline hardly performed the reaction and failed to give the desired product. The disubstituted terminal alkene also completed the reaction well (**3bw**).

On the contrary, it was found that different additives could change the distribution of the products (Table 2). We can control the product distribution by the addition of different additives (entry 4 and entries 6-9). For instance, the addition

Table 2	. 0	ptimization	of	Reaction	Conditions <sup>4</sup>
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	NH 1a Ts	Pt-Pt I= 5 mA electrolyte additive CH <sub>3</sub> CN/H <sub>2</sub> O (5/1),	→ 〔〕 T 4a	N Ts
entry	electrolyte	additive	$T(^{\circ}C)$	yield (%) <sup>b</sup>
1	Me <sub>4</sub> NI	KSCN	25	43
2	Me <sub>4</sub> NI	KSCN	40	70
3	Me <sub>4</sub> NI	KSCN	70	83
4	Me <sub>4</sub> NI	KSCN	80	92
5	Me <sub>4</sub> NI	KSCN	90	90
6	Me <sub>4</sub> NI	NH <sub>4</sub> SCN	80	trace
7	Me <sub>4</sub> NI	NaSCN	80	78
8 <sup>c</sup>	Me <sub>4</sub> NI	KSCN	80	n.d.
9	Me <sub>4</sub> NI	KOTf	80	n.d.
10	KI	KSCN	80	77

"Reaction conditions: 1a (0.3 mmol), electrolyte (1.0 equiv), additive (1.0 equiv) and solvent (CH<sub>3</sub>CN/H<sub>2</sub>O = 5 mL/1 mL); the electrolysis was conducted in an undivided cell for 6 h, Pt–Pt (1.5  $\times$  1.5  $\times$  0.3 cm<sup>3</sup>), air, *I* = 10 mA, n.d. = no detection. <sup>b</sup>Isolated yields after column chromatography. <sup>c</sup>Without electricity.

of potassium thiocyanate (KSCN) promoted the formation of indole product (entry 1). Then, we conducted the reaction at different temperature (entries 1-5). It was found that at 80 °C, the indole yield could be efficiently enhanced (entry 4). Me<sub>4</sub>NI showed a better result as both an electrolyte and a mediator compared with KI (entries 4 and 10). The optimal conditions are listed in entry 4.

Then, we explored the scope of the reaction substrates for the synthesis of indoles (Scheme 4). A series of 5-substituted

## Scheme 4. Synthesis of Indoles<sup>a</sup>



<sup>*a*</sup>Reaction conditions: 1 (0.3 mmol), Me<sub>4</sub>NI (0.3 mmol), KSCN (0.3 mmol), CH<sub>3</sub>CN/H<sub>2</sub>O (5 mL/1 mL); the electrolysis was conducted in an undivided cell at 80 °C for 2 to 10 h. The isolated yields after column chromatography are shown.

indoles with various substituents, such as halogens (4b-h), trifluoromethyl (4i), cyano (4j), carbonyl (4l, 4m), and alkyl (4n-p), were obtained under the electrochemical conditions. Other substituents like phenyl, methoxyl, and nitryl (4r, 4q), and 4k, were also found to be compatible with the electrolytic conditions. The different bromo positions of 2-vinyl aniline were also investigated under the electrolytic conditions. It was found that 4-, 5-, and 6-bromoindole products were obtained (4d-f), whereas 7-bromoindole failed to be obtained, perhaps due to the electronic and steric effect (4g). 4,5-Disubstituted substrates also performed well to afford the desired products under the reaction conditions (4h and 4s). Gratifyingly, the reaction had a broad substrate scope. The reaction provided an innovative and efficient electrochemical method for the rapid synthesis of indoles.

To prove the practicability and expansibility of the method, gram-scale experiments were performed under standard conditions. The desired products **3aa** and **4a** were obtained smoothly in 87 and 90% yields, respectively (Scheme 5).

Scheme 5. Gram-Scale Experiments



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To get insight into the reaction mechanism, control experiments were performed (Scheme 6). First, the reaction



was conducted with chemical oxidant  $I_2$ , giving 20% yield and 76% starting material recovery (Scheme 6a). When the radical inhibitor 2,2,6,6-tetramethylpiperidinooxy (TEMPO) or butylated hydroxytoluene (BHT) was added to the reaction mixture, the corresponding product **3aa** could be obtained in 90 and 86% isolated yield, respectively (Scheme 6b). These results implied that the reaction may not go through a radical process. The radical clock experiment was also conducted under the standard conditions, and the ring-reserved product was obtained (Scheme 6c). The experimental results indicated that the reaction proceed through an ionic process.

On the basis of the previously described experimental results and literature reports,<sup>19</sup> a plausible mechanism was proposed (Scheme 7). Iodide is oxidized to molecular iodine. The iodine reacts with substrate 1a to afford the intermediate 5a; then, the following nucleophilic addition leads to the formation of 5c and further deprotonation gives 5d, followed by the nucleophilic attack of PhNH<sub>2</sub> to form indoline 3aa. In the presence of potassium thiocyanate, the iodide 5d can be substituted by thiocyanate to give 5e. Then, the  $\alpha$ -proton can

Scheme 7. Plausible Mechanism



be caught by the hydroxyl anion, followed by elimination to give indole 4a. Simultaneously,  $H_2O$  is reduced to hydrogen and hydroxyl anion at the cathode.

In conclusion, we developed a method for the switchable synthesis of indolines and indoles by virtue of anodic oxidation under metal-free conditions. This electrochemical intramolecular  $C(sp^2)$ —H amination reaction can avoid the use of a metal catalyst and a stoichiometric oxidant. The reaction can be carried out smoothly under mild conditions, which provides a rapid and efficient method for preparing functionalized indolines and indoles.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01821.

<sup>1</sup>H/<sup>13</sup>C NMR data and spectra of all products and HRMS data of unknown products (PDF)

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#### Notes

The authors declare no competing financial interest.

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