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# Domino N-/C- or N-/N-/C-arylation of imidazoles to yield polyaryl imidazolium salts via atom-economical use of diaryliodonium salts

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Herein, we disclose Cu-mediated domino di-/triarylation reaction of imidazoles to efficiently access polyaryl imidazolium salts in a single step via using two aryls as well as anion of a diaryliodonium salt. The diarylation shows high atom economy and excellent selectivity with unsymmetrical iodonium salts.

Diaryliodonium salts, as old brand compounds discovered in 1894,<sup>[1]</sup> have blossomed into one of the most efficient arylating reagents owing to the advantages of high reactivity and easy preparation.<sup>[2]</sup> However, poor atom economy is their common drawback since at least one equivalent of aryliodide residual is generated as "waste". In recent years, a new pattern, namely atom-economical use of both aryl groups of the diaryliodonium salt, has emerged.<sup>[3]</sup> In most of the atomeconomical cases cyclic diaryliodonium salts are utilized, which undergo an intramolecular reaction in the second process.<sup>[4]</sup> The intramolecular aryl migration of acyclic iodonium salts have been reported by Shafir<sup>[5]</sup> and Wang<sup>[6]</sup>. The concept about atom-economical application of alkynyl iodine(III) derivatives<sup>[7]</sup> and ArI(OAc)<sub>2</sub><sup>[8]</sup> have also been demonstrated.

Comparatively, the acyclic diaryliodonium salts undergoing a tandem intermolecular arylation is more challenging and the examples are relatively rare. Dual arylation at the same site of S<sup>[9]</sup> and N<sup>[10]</sup> have been reported to synthesize diaryl sulfides and triarylamines, respectively. The first example of bondforming at two different positions was tandem C-/Narylation reaction of indoles reported by Greaney (Fig. 1a)<sup>[11]</sup>. Subsequently, Greaney performed a domino N-/C-arylation reaction of pyrazoles via generation of a directing group in situ (Fig. 1b).<sup>[12]</sup> Muñiz described a domino borylation/Suzuki-Miyaura reaction of diaryliodonium salts to form biaryl skeletons (Fig. 1c).<sup>[13]</sup> In these domino reactions two differential conditions are necessary and both iodine atom and anion are abandoned. Li and co-workers reported a cyclization of 2-formylbenzonitrile and aryl-mesityl iodonium salts with utilization of the iodine atom, while the atom economy was dramatically lowered due to two equivalents of iodonium salts were wasted.<sup>[14]</sup> Since in most cases the mass of anions, such as OTf<sup>-</sup>, OTs<sup>-</sup> and PF<sub>6</sub><sup>-</sup>, generally abandoned in previous reports are weightier than iodine atom, the overall atom economy (AE) is not that high.<sup>[15]</sup> To our knowledge, atomeconomical use of the anion as well as the two aryls of a diaryliodonium salt to form ionic compounds has not been reported yet.





Fig. 1 Atom-economical use of diaryliodonium salts for different bond formation in one pot.

In order to enhance the AE by utilizing the two aryls and anion, we turned our attention to polyaryl azolium salts, which are important organic optoelectronic materials,<sup>[16]</sup> anion exchange materials<sup>[17]</sup> and *abnormal* N-heterocyclic carbenes (*a*NHCs) precursors.<sup>[18]</sup> While the synthesis of polyaryl imidazoliums,

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especially pentaaryl imidazoliums, needed tedious procedure or noble metal catalyst.<sup>[19]</sup> Imidazoles could be quaternized by diaryliodonium salts leaving the aryl iodides as "waste",<sup>[20]</sup> while the C2-H of imidazolium salts could be arylated by aryl iodides.<sup>[21]</sup> Hence, a question is formed in our mind: if the aryl iodide residuals, generated in the *N*-quaternization, could be captured to initiate the following *C*-arylation to form polyaryl imidazolium salts (Fig. 1d). Herein, we report the domino *N*-/*C*-arylation of *N*-substituted imidazoles with high atom economy and selectivity in an identical condition, leaving an iodine atom as the only "waste". Furthermore, a novel *N*-/*N*-/*C*-arylation reaction of imidazoles to form pentaaryl imidazoliums in a single step is revealed for the first time.

Table 1 Optimization of the diarylation reaction conditions <sup>a</sup>			
Ph <sup>-N</sup> N 1a	+ BF₄ + Ph <sup>-/</sup> Ph 2a 20 h	/─_\ BF₄ I ↓ <sup>+</sup> N <sub>&gt;</sub> Ph + Ph <sup>-</sup> 3a	→ BF <sub>4</sub> → N → <sup>+</sup> N → Ph Ph 4a
Entry	Metal/base (equiv)	Time (h)	Yield (%) <sup>b</sup> <b>3a:4a</b>
1 <sup><i>c</i></sup>	Cu(OAc) <sub>2</sub> (0.1); NaOAc (1)	4; 20	42:29
<b>2</b> <sup><i>c</i></sup>	Cu <sub>2</sub> O (0.1); NaOAc (1)	4; 20	40:37
3 <sup>c</sup>	Cu <sub>2</sub> O (0.1); K <sub>2</sub> CO <sub>3</sub> (1)	4; 20	0:46
4 <sup><i>c</i></sup>	Cu <sub>2</sub> O (0.1); K <sub>3</sub> PO <sub>4</sub> (1)	4; 20	0:74
5	Cu <sub>2</sub> O (0.1), NaOAc (1)	20	trace:15
6	Cu <sub>2</sub> O (0.1), K <sub>2</sub> CO <sub>3</sub> (1)	20	0:0
7	Cu <sub>2</sub> O (1)	20	0:78
8	Cu(OAc) <sub>2</sub> (1)	20	45:10
9	CuSO <sub>4</sub> (1)	20	20: 23
10	CuCl (1)	20	trace:30
11	Cu <sub>2</sub> O (0.05)	20	96:0
12 <sup><i>d</i></sup>	Cu <sub>2</sub> O (1)	20	0:86
13 <sup>e</sup>	Cu <sub>2</sub> O (1)	20	0:80

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), copper salt (x equiv) and base (y equiv) were stirred in DMF (1 mL). <sup>*b*</sup> Isolated yields. <sup>*c*</sup> The copper catalyst was added in *step 1* (4 hours) and the base was added in *step 2* (20 hours). <sup>*d*</sup> **2a** (0.2 mmol, 1 equiv). <sup>*e*</sup> Ph<sub>2</sub>IOTf was used instead of Ph<sub>2</sub>IBF<sub>4</sub>.

Initially a two-step operation was tried by choosing N-phenyl imidazole 1a and diphenyliodonium tetrafluoroborate 2a as the standard substrates. The reaction was catalyzed by a copper salt for 4 hours in step 1 before a base was added for another 20 hours in step 2 (Table 1, entries 1-4). K<sub>3</sub>PO<sub>4</sub> was most efficient and gave dual arylating product 4a in 74% yield (entry 4). However, the reaction was inefficient when the catalyst and the base were added at the same time (entries 5 and 6). These results implied the base was ineffective in step 1. Pleasingly using one equivalent of basic Cu<sub>2</sub>O instead of the base could give 4a as the sole product in a good yield of 78% (entry 7). While the diarylation was frustrated when cutting down the dose of Cu<sub>2</sub>O or reducing the reaction time (see ESI<sup>+</sup>). Also the acidic copper salts (entries 8-10) and other metal salts (such as [Pd] and [Ag], see ESI+) were confirmed undesirable. A reversed result was observed when cutting down the usage of Cu<sub>2</sub>O to 5 mol%, in which 3a was solely generated in 96% yield (entry 11). Pleasingly reducing the dose of 2a to 1 equivalent could isolate 4a

in the highest yield of 86% with a high AE of 65% (entry 12). Treatment of Ph<sub>2</sub>IOTf with **1a** could also afford **4a3OTf** in Cashigh yield of 80% (AE= 61%), indicating that the weightier anions were compatible well in this reaction (entry 13).



**Scheme 1** Selectivity of aryl transfer of unsymmetrical iodonium salts in *N*-quaternization. The groups in bold transfer first.

Before exploring the scope of the diarylation, the selectivity of aryl transfer with unsymmetrical iodonium salts in the *N*-quaternization was tested by using 5 mol% Cu<sub>2</sub>O as the catalyst (Scheme 1). Treatment of **1a** with [*o*-MePh-I-Ph]BF<sub>4</sub> **2g** or [Ph-I-uracil]OTf **2i** could afford **3a** or **3a-OTf** in 90% and 72% yields, respectively, and the regio-isomeric **3b** and **3c** were not detected. This result implied that less sterically hindered phenyl group transferred first contrarying to Greaney's case.<sup>[12]</sup> Then we extended the examples to vinyliodonium salt [(*E*)-styryI-I-Ph]OTf **2k**. As expected, the styryl component transferred with complete selectivity to exclusively deliver **3d** in 85% yield.



Scheme 2 Scope of imidazoles. Reaction conditions: 1 (0.2 mmol), 2a (0.2 mmol) and  $Cu_2O$  (1 equiv) were stirred in DMF (1 mL) for 20 h, isolated yields.

With the results in hand, the scope of imidazoles was examined first (Scheme 2). Both electron-rich and electron-deficient functional groups, such as methyl, methoxy, dimethylamino, cyano and halogen, on the phenyl ring of (benz)imidazoles were well Published on 21 August 2019. Downloaded on 8/21/2019 11:04:15 PM

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tolerated and gave the corresponding triarylated (benz)imidazolium salts in good to high yields (**4b-f** and **4h-m**) with high AE values up to 66% (see ESI<sup>+</sup>). The bulky 1-naphthyl imidazole and benzimidazole were both performed smoothly (**4g** and **4n**). Notably, *N*-thienyl benzimidazole also could react with **2a** effectively and afford **4o** in a good yield of 66%. The *N*-alkyl imidazole, such as *N*-ethyl benzimidazole and *N*-methyl imidazole, performed more efficient and gave **4p** and **4q** in excellent yields of 90% and 94%, respectively.

Then the scope of iodonium salts was examined with (hetero)aryl substituted imidazoles under the optimized reaction conditions and the results are summarized in Scheme 3. Various symmetrical iodonium salts containing both electron-rich and electron-deficient groups were compatible well and gave corresponding products 5a-h in good yields. As expected, unsymmetrical iodonium salts could also diarylate 1a smoothly, where less sterically hindered aryls transferred first with complete selectivity in the first arylation and then the 2-iodotoluene generated in situ was captured in the second arylation (5i-k). Among them 5k was isolated in the lowest yield because that mono N-arylated compound 3e was isolated as a by-product (see ESI<sup>+</sup>). The imidazolium **5I** containing a styryl group could be generated in a good yield of 71%. In each case no regioisomers were observed, it revealed excellent selectivity of this N-/C-diarylation reaction. Generally, the comprehensive factors of reasonable substrate ratio (1:1), high yields and anion utilization make the diarylation exhibit high atom economy.



 $\label{eq:scheme 3} \begin{array}{l} \mbox{Scheme 3} & \mbox{Scope of diaryliodonium salts. Reaction conditions: $1$ (0.2 mmol), $2$ (0.2 mmol) and Cu_2O (1 equiv) were stirred in DMF (1 mL) for 20 h, isolated yields. \end{array}$ 

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Scheme 4 Scope of triarylation. Reaction conditions: 6 (0.2 mmol), 2 (0.4 mmol) and  $Cu_2O$  (1.1 equiv) were stirred in DMF (1.5 mL) for 20 h, Isolated yields. <sup>*a*</sup> Yield of diarylation using an *N*-aryl triazole/imidazole as substrate. <sup>*b*</sup> 100 °C. <sup>*c*</sup> Yield of 8f-OTs.

As we know, the N-H arylation of azoles with diaryliodonium salts has been well established,<sup>[22]</sup> we would like to see if it could happen in our condition. Thus a novel domino triarylation (Narylation/N-quaternization/C-arylation) could be realized from simple azoles and diaryliodonium salts in one pot. As shown in Scheme 4, various azoles could be triarylated smoothly by two equivalents of diaryliodonium salts and gave corresponding polyaryl azolium salts in moderate to high yields. For examples, compounds 7a-d could be obtained from simple azoles in satisfactory yields via this triarylation.<sup>[23]</sup> Pleasingly pentaaryl imidazolium salts 8a-f were efficiently obtained in high yields from commercially available 4,5diaryl imidazoles and corresponding iodonium salts. It is worth noting that compounds 8b-e were achieved for the first time and they cannot be afforded by Ghonim's and Liu's methods.<sup>[19]</sup> The reaction of 6a and Ph<sub>2</sub>IOTs delivered salt 8f-OTs in 49% yield with OTs as the counteranion. Using 1,4,5-triphenyl imidazole 1s and 2a to undergo a diarylation gave 8a in an approximate yield to that of triarylation, indicating that this triarylation was very efficient. Besides, phenanthrene-fused triarylimidazolium 9 belonging to polyaryl imidazolium as well as polycyclic imidazolium salt was reached in 50% yield for the first time. The triarylation also show good selectivity in the reaction of 6a, 2a-OTf and [Ph-I-mesityl]OTf (2I), giving 3a-OTf and 4a-OTf in 20% and 67% yields, respectively, without mesityl transferred products observed (see ESI+).

Based on the above findings (catalytic amount of Cu<sub>2</sub>O for *N*quaternization and equivalent amount of Cu<sub>2</sub>O for *C*-arylation) and previous reports,<sup>[20-22,24,25]</sup> a possible mechanism is proposed (see ESI<sup>+</sup>). Initially, diaryliodonium salt adds oxidatively to the Cu<sup>1</sup> species generate Ar–I and a Ar–Cu<sup>III</sup> species, which react with imidazoles to give *N*-aryl imidazoles **2**.<sup>[22]</sup> **2** reacts with Ar–Cu<sup>III</sup> species could afford imidazolium **3**.<sup>[20,24]</sup> Then an NHC–Cu<sup>1</sup> complex **I** is formed between **3** and Cu<sub>2</sub>O. The oxidative addition of **I** with Ar–I gives an NHC–Cu<sup>III</sup> complex **II**, which undergoes reductive elimination to give the final product.<sup>[21,25]</sup>

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In conclusion, Cu<sub>2</sub>O-mediated domino *N*-quaternization/*C*arylation of *N*-aryl/alkyl imidazoles in a single operation has been developed for the first time, where all the two aryls and anion except the iodine atom of an acyclic diaryliodonium salt are used. This diarylation features high efficiency, good functional tolerance, ease operation, excellent selectivity and high atom economy. The unprecedented *N*-arylation/*N*quaternization/*C*-arylation reaction between imidazoles and diaryliodonium salts is achieved as a short and efficient method to construct polyarylated imidazolium salts. This work supplies new utilization mode of diaryliodonium salts to inspire the synthetic chemistry of ionic compounds. Investigation on these polyarylated imidazolium salts as novel organic photoelectric materials are in progress in our laboratory.

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## **Conflicts of interest**

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There are no conflicts to declare.

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