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Iodobenzene-catalyzed photochemical heteroarylation of alcohols by rupture of inert C–H and C–C bonds

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ABSTRACT

A Minisci-type reaction catalyzed by iodobenzene is disclosed here for the first time. The heteroarylation of unprotected aliphatic alcohols proceeds via alkoxy radical-induced homolytic cleavage of C–H and C–C bonds under photochemical conditions. The use of *m*-CPBA as the oxidant allows the oxidation of iodobenzene to a hypervalent iodine species, driving the catalytic cycle. The method features mild reaction conditions, broad scope of heteroarenes and alcohols, and scaled up preparations. This approach provides a notable supplement to iodobenzene-catalyzed ionic reactions, and opens up a new avenue for its application in radical chemistry.

1. Introduction

The uniquely reactive hypervalent iodine reagents have attracted intense research interest and have frequently been exploited in the laboratory over the past few decades [1–22]. However, some inherent disadvantages, such as their explosive properties, storage difficulties, high expense and poor solubility, have led to concerns about using the reagents. The large amount of aryl iodide discarded as byproduct in the reaction also raises environmental issues, which limit their applications in industry. Iodobenzene is a readily available and inexpensive synthetic feedstock. It has been sometimes employed as an organocatalyst instead of a source of stoichiometric amounts of hypervalent iodine reagents in ionic reactions, which include C–H bond amination [23], biaryl synthesis by C–C bond coupling [24], construction of spiro-heterocyclic compounds via dearomatization of phenols [25], α-acetoxylation/tosyloxylation/fluorination of ketones [26–28], Hoffman rearrangement [29], dibromination and oxidative cleavage of alkenes or alkynes [30,31], and oxidation of alcohols [32,33] (Scheme 1A). In these reactions, iodobenzene is oxidized by strong oxidants, such as *m*-CPBA, to hypervalent iodine, a III or V species, perpetuating the catalytic cycle. Despite these achievements, radical-mediated transformations catalyzed by iodobenzene have been reported only rarely [34–37], presumably because of the functional group incompatibility in the presence of strong oxidants.

Heteroarenes are ubiquitous in natural products and molecules such as pharmaceuticals and organic materials. Construction of structurally diverse heteroarenes is important in organic chemistry [38–42]. Recently, the Minisci reaction has witnessed a rapid growth of synthetic efforts using the reaction, and supplies a robust tool for heteroarene modification by incorporating alkyl groups into nitrogenous heteroarenes [43–51]. Herein, we disclose a conceptually new iodobenzene-catalyzed Minisci reaction operating under photochemical conditions. The interaction of unprotected aliphatic alcohols with hypervalent iodine reagent, generated *in situ* from the oxidation of iodobenzene with.

m-CPBA, is efficient and gives rise to alkoxy radicals, which subsequently engage in 1,5-hydrogen atom transfer (HAT) and β-C-C scission reactions. The radical heteroarylation reaction shows the good compatibility of heteroarenes and alcohols, leading to a variety of functionalized heteroarenes (Scheme 1B).

2. Results and discussion

We began the heteroarylation reaction with commercially available 4-chloroquinoline (**1a**) and *n*-pentanol (**2a**) as model substrates under blue LEDs irradiation (Table 1). Evaluation of the amount of alcohols indicated that excess alcohols were beneficial to improving the conversion (entries 1–3). Other functionalized aryl iodides with either electron-donating or withdrawing substituents did not offer superior catalytic

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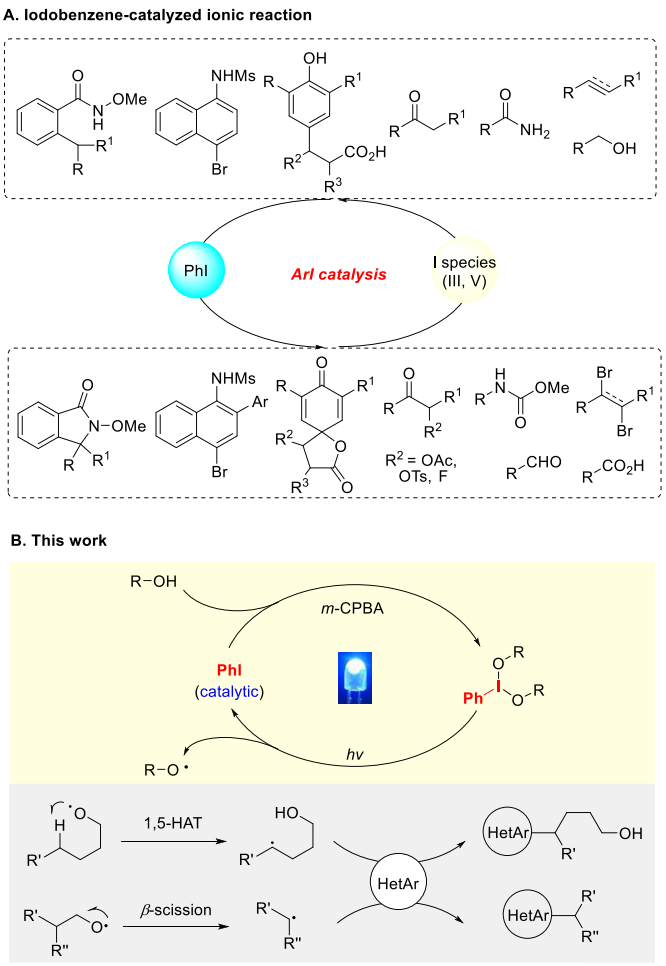


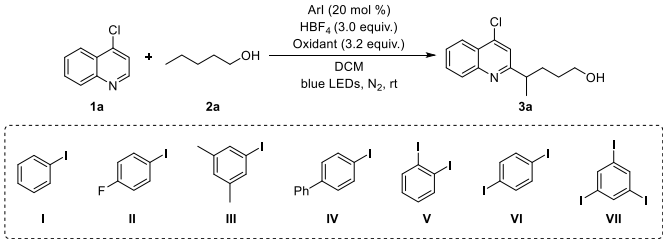
Scheme 1. Iodobenzene-catalyzed reactions.

efficiency than parent iodobenzene (entries 4–6). Benzenes bearing multiple iodides also did not result in better yields (entries 7–9). Replacing *m*-CPBA with other common oxidants, such as Oxone and $K_2S_2O_8$, compromised the reaction outcomes (entries 10 and 11). Varying light source or performing the reaction without light, product **3a** was obtained in low yields (entries 12–14). After a comprehensive survey of reaction conditions (for details, see the SI), the iodobenzene-catalyzed reaction proceeding via 1,5-HAT was found to deliver the best yield of the desired Minisci product (**3a**) in dichloromethane (DCM) using *m*-CPBA as oxidant and HBF_4 as an additive.

With the optimized reaction conditions in hand, the generality of the protocol was assessed (Scheme 2, top). The C2-alkylation of quinoline derivatives bearing a C4-substituent smoothly proceeded via a 1,5-HAT regardless of the electronic characteristics, affording the corresponding products (**3a**-**3e**) in useful yields. The C4 position of quinolines could also be alkylated under the standard conditions, but delivered decreased yields of the products (**3f**-**3i**). Other heterocyclic compounds such as phenanthridine, pyridine and pyrazine containing two nitrogen atoms were converted into the desired products (**3j**-**3l**) respectively. The modification of a pesticide, fenazaquin (**3m**), was also achieved by this method. It was found that electron-rich heteroarenes such as benzothiazole and benzoxazole were not suitable substrates.

The heteroarylation of a set of aliphatic alcohols with 4-chloroquinoline was then examined (Scheme 2, bottom). The reaction of linear primary alcohols occurred regioselectively via 1,5-HAT regardless of the chain length, resulting in δ-heteroarylation (**3n**-**3r**). In the case of **3r**, 1,5-HAT occurred exclusively prior to 1,6-HAT even in the presence of more reactive benzylic C–H bonds. In addition to secondary C–H bonds,

Table 1
Reaction parameters screening.[a]



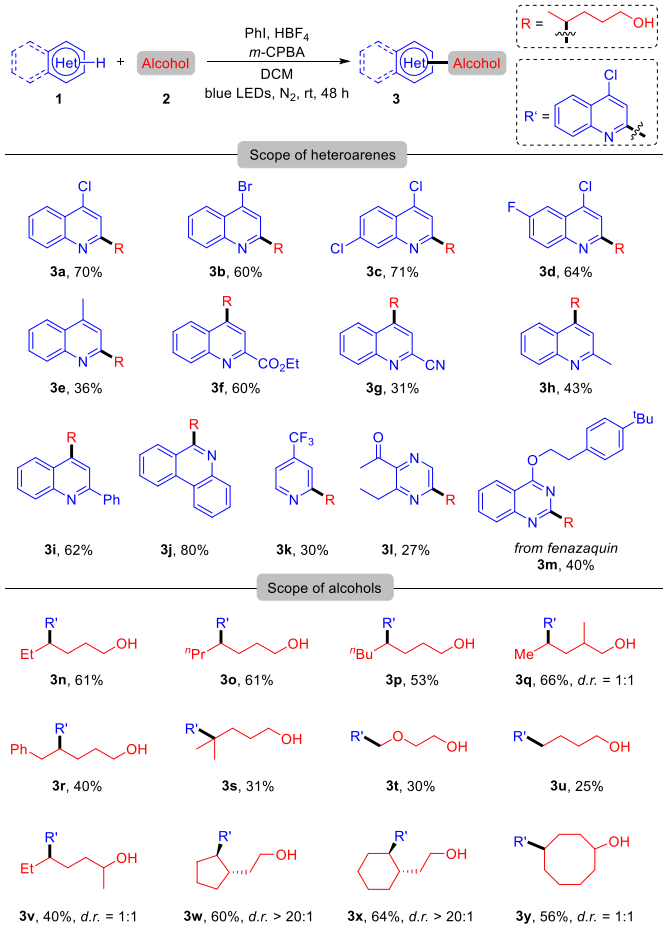
Entry	ArI	Oxidant	Yield[b] (%)
1[c]	**I**	*m*-CPBA	52
2[d]	**I**	*m*-CPBA	61
3	**I**	*m*-CPBA	70
4	**II**	*m*-CPBA	40
5	**III**	*m*-CPBA	63
6	**IV**	*m*-CPBA	60
7	**V**	*m*-CPBA	58
8	**VI**	*m*-CPBA	59
9	**VII**	*m*-CPBA	31
10	**I**	Oxone	<10
11	**I**	$K_2S_2O_8$	<10
12[e]	**I**	*m*-CPBA	51
13[f]	**I**	*m*-CPBA	0
14[g]	**I**	*m*-CPBA	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (3.0 mmol), PhI (20 mol %), HBF_4 (0.6 mmol, 48 wt % in H_2O), and *m*-CPBA (0.64 mmol, added in four portions of 0.16 mmol each in 12 h intervals) in DCM (2.0 mL), irradiated by 2 × 50 W blue LEDs at rt in N_2 for 48 h.
[b] Isolated yield.
[c] **2a** (1.0 mmol).
[d] **2a** (2.0 mmol).
[e] 2 × 30 W blue LEDs.
[f] 30 W green LEDs.
[g] In dark.

tertiary and primary C–H bonds adjacent to an O atom also reacted (**3s** and **3t**); the lower yields can probably be attributed to overoxidation of radical intermediates arising from HAT in the presence of strong oxidants. Notably, the reaction of primary C–H bonds with relatively higher bond dissociation energy (BDE) also proceeded, producing **3u**, albeit in a lower yield. While alkoxy radicals derived from secondary alcohols are prone to trigger β-C-C fragmentation, secondary alcohols are tolerated in this protocol (**3v**). The examples of **3w** and **3x** are noteworthy, as the reactions occurred at a cyclopentyl or cyclohexyl ring, and furnished thermodynamically favored *trans*-products with excellent stereoselectivity (*d.r.* > 20:1). Furthermore, this method supplies an efficient approach to the direct modification of cyclooctanol (**3y**).

Subsequently, the alkylation of heteroarenes through β-C-C scission of alcohols was investigated (Scheme 3, top). Similar to the previous process involving a HAT, isopropylation at C2 or C4 of quinolines using isobutanol as alkyl radical source delivered comparable yields (**5a**-**5h**). Other N-containing heteroarenes such as phenanthridine, quinoxaline and pyrimidine reacted to afford the corresponding Minisci-type adducts (**5i**-**5k**). Remarkably, the antifungal agent, voriconazole (**5l**) could also be alkylated, illustrating the utility of this method in structural elaboration of complex molecular scaffolds.

The performance of a variety of aliphatic alcohols was then evaluated in the formation of alkoxy radicals and subsequent β-C-C scission (Scheme 3, bottom). In addition to isobutanol, other isopropyl radical precursors, such as tertiary alcohols (**4b**-**4d**), also produced the desired product (**5a**) in good yields. Secondary aliphatic alcohols, such as 2-methyl-1-butanol (**4e**), 2-ethyl-1-butanol (**4f**), and an alcohol (**4g**) with benzyl C–H bonds susceptible to radical HAT or oxidation conditions, all are suitable substrates for β-C-C fragmentation and furnished the



Scheme 2. Generality of the reaction via 1,5-HAT. Reaction conditions: **1** (0.2 mmol), **2** (3.0 mmol), PhI (20 mol %), HBF_4 (0.6 mmol, 48 wt % in H_2O), and *m*-CPBA (0.64 mmol, added in four portions of 0.16 mmol each in 12 h intervals) in DCM (2.0 mL), irradiated by 2 × 50 W blue LEDs at rt in N_2 for 48 h. Yields of isolated products are given.

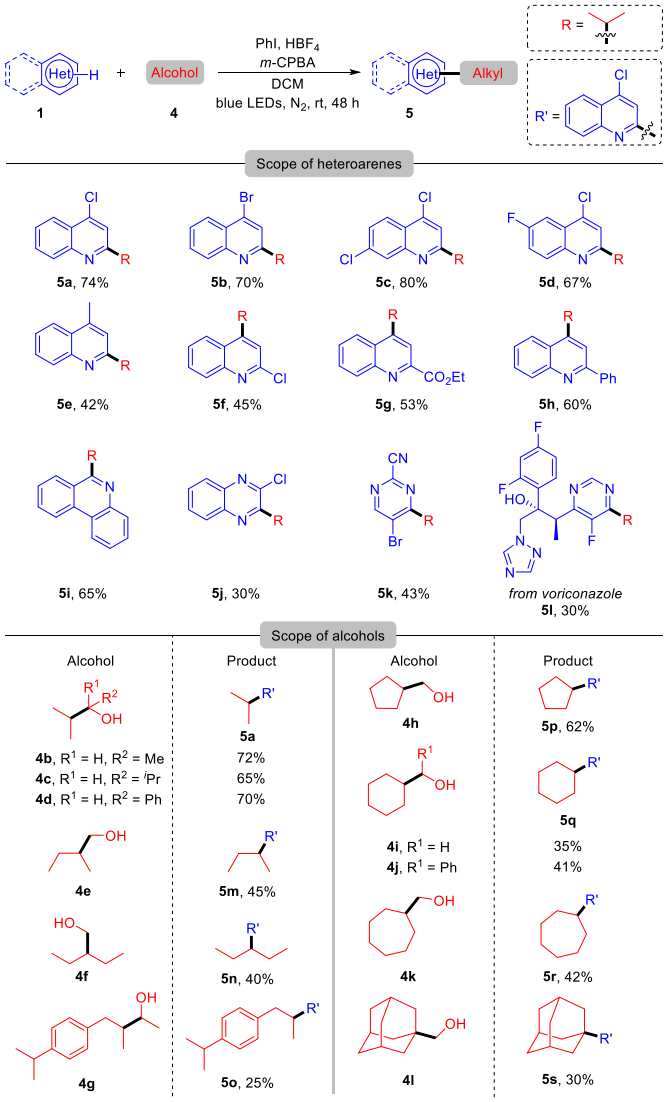
expected products (**5m**-**5o**), respectively. A set of cyclic secondary radicals generated from the corresponding alkanols (**4h**-**4k**) proceeded via *β*-C-C scission with ring opening, and were subsequently trapped by 4-chloroquinoline to give products (**5p**-**5r**). Interestingly, the bulky adamantyl radical derived from 1-adamantanemethanol (**4l**) could readily add to 4-chloroquinoline, leading to product (**5s**).

To demonstrate the practicality of the synthetic method, two types of transformations, proceeding through 1,5-HAT or the *β*-C-C cleavage pathway were carried out under the standard conditions, giving synthetically useful yields (Scheme 4).

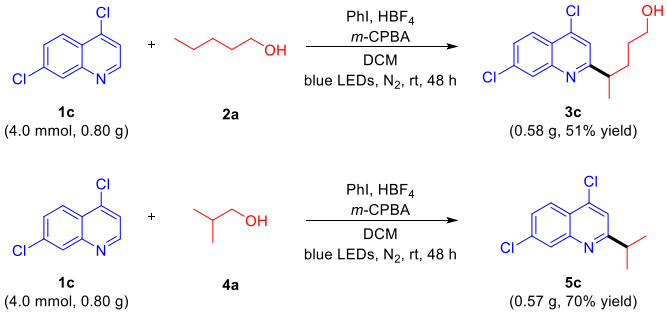
The radical trapping experiment using 1,1-diphenylethylene as radical scavenger was carried out (Scheme 5). The reaction was almost completely inhibited, leading to trace amounts of **3a** and the vinylation adduct detected by HRMS. The result may suggest the involvement of alkoxy radical in the transformation.

The UV-VIS experiments were conducted to probe the formation of photo-absorbing species in the reaction (Scheme 6A). The interaction of PhI, *m*-CPBA, HBF_4, and **2a** generated a new species which displayed weak light absorption above 420 nm region. It suggested the possible energy transfer from blue LED to the new species which triggered the homolysis of I–O bond to generate alkoxy radical [11].

Based on the experimental results and previous reports, proposed mechanistic pathways are shown in Scheme 6B. Initially, the mixture of iodobenzene, *m*-CPBA and HBF_4 generates a hypervalent species (**A**) [31] and *m*-chlorobenzoic acid (*m*-CBA). The formation of $[Ph\text{-}I\text{-}OH]^+$ species could be evidenced by HRMS analysis (see the SI). Interaction between **A**

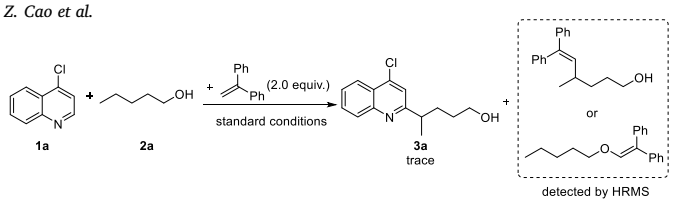


Scheme 3. Generality of the reaction via *β*-C-C scission. Reaction conditions: **1** (0.2 mmol), **4** (3 mmol), PhI (20 mol %), HBF_4 (0.6 mmol, 48 wt % in H_2O), and *m*-CPBA (0.64 mmol, added in four portions of 0.16 mmol each in 12 h intervals) in DCM (2.0 mL), irradiated by 2 × 50 W blue LEDs at rt in N_2 for 48 h. Yields of isolated products are given.

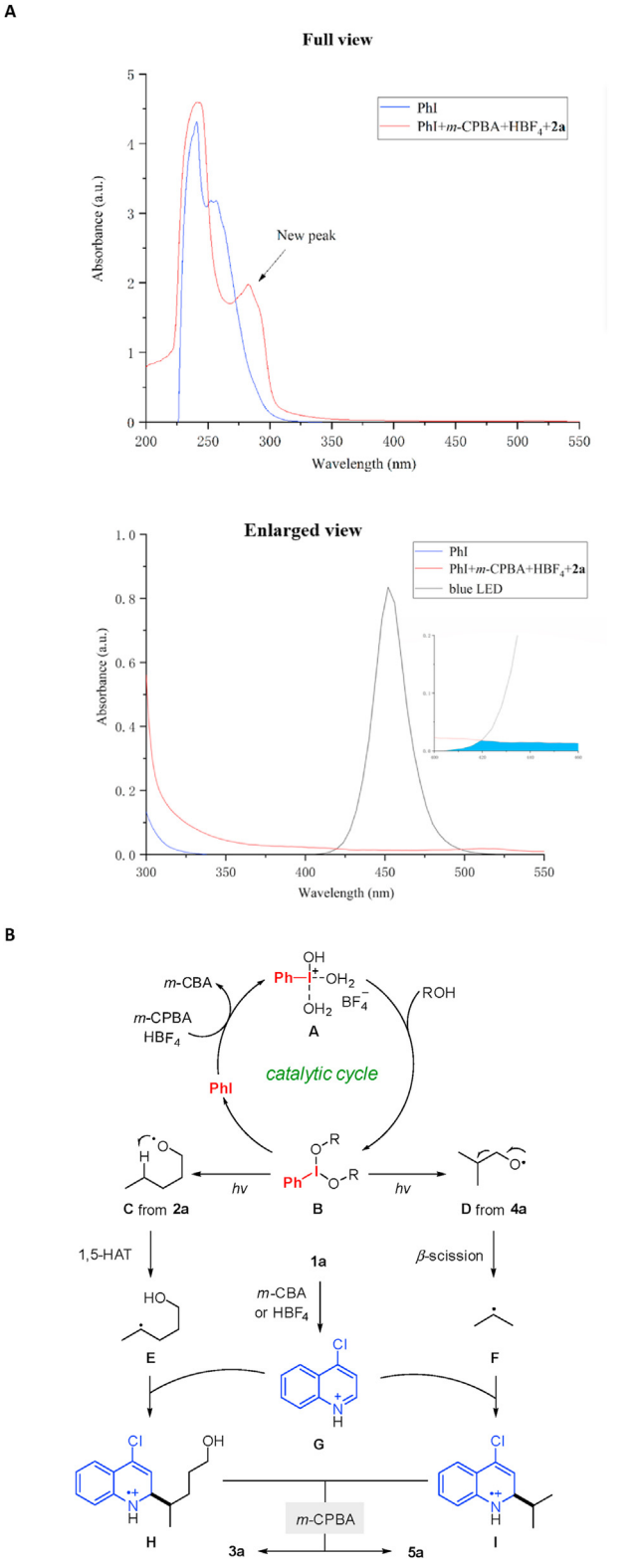


Scheme 4. Scale-up preparation.

and aliphatic alcohol gives rise to an intermediate (**B**) with reactive iodine-oxygen bonds, which then undergoes homolysis under blue light irradiation to deliver alkoxy radical (**C**) (from **2a**) or **D** (from **4a**) [11]. Meanwhile, iodobenzene is regenerated, continuing the catalytic cycle. The conversion of **C** to **E** via 1,5-HAT or **D** to **F** via *β*-C-C scission and



Scheme 5. Radical trapping experiment.



Scheme 6. (**A**) UV-VIS experiments. (**B**) Proposed mechanisms.

subsequent interception of the alkyl radical (**E** or **F**) by the protonated heteroarene (**G**) gives rise to radical cation **H** or **I**, respectively. Single-electron oxidation of **H** or **I** by excess *m*-CPBA furnishes the final product **3a** or **5a**.

3. Conclusion

We are reporting an unprecedented protocol of iodobenzene-catalyzed Minisci-type reactions. The radical heteroarylation of C–H and C–C bonds in aliphatic alcohols proceeds readily under visible-light irradiation, and the inexpensive *m*-CPBA oxidizes iodobenzene to hypervalent iodine species, perpetuating the catalytic cycle. Many Minisci-type adducts have been obtained in synthetically useful yields. The protocol has many merits, including the use of a non-metallic organocatalyst, broad substrate scope, excellent regioselectivity, ability to expand the scale, and direct functionalization of complex structures. It should be mentioned that iodobenzene-catalyzed radical transformation is at a very early stage, and this approach opens up a new avenue for this research area.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tchem.2022.100031.

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