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Metal-Free Aminoiodination of Alkynes Under Visible Light Irradiation for the Construction of a Nitrogen-Containing Eight-Membered Ring System

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Abstract: A method for the synthesis of dihydrodibenzo[*c*,*e*]azocine derivatives via a regioselective intramolecular aminoiodination of alkynes under visible light irradiation has been developed. This protocol uses a combination of iodine and hypervalent iodine to realize a sulfonamidyl radical, followed by intramolecular addition to alkyne to form a vinyl radical. Subsequent trapping of iodine radical affords an 8-membered heterocycle. Applications of the obtained iodinated 8-membered heterocycles in the Suzuki-Miyaura coupling and deiodination are also demonstrated.

Keywords: Metal-Free Synthesis; Aminoidodination; Hypervalent Iodine; Alkynes; Dibenzazocines

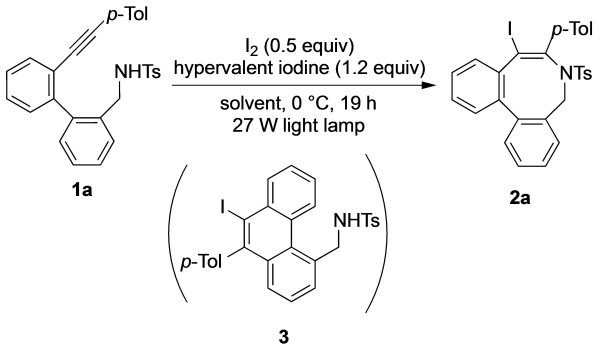
The regioselective aminohalogenation of alkynes, alkenes and allenes is a powerful method for synthesizing 1,2-aminohalogenated compounds, which are of paramount importance in organic synthesis.[1] A large number of reactions using transition-metal catalysts have been reported to access halogen-functionalized acyclic amines as well as nitrogen-containing heterocycles.[2] To avoid the problems associated with organometallic reagents such as toxicity and difficulties in purification, metal-free conditions for aminohalogenation have also been developed.[3–5]

In comparison to the aminohalogenation of alkenes,[3] 1,2-difunctionalization of alkynes via the addition of both amine and halogen moieties under metal-free conditions has been less studied. In fact, only a few examples have been reported to achieve the intermolecular aminohalogenation of alkynes under transition metal-free conditions.[4] In contrast, the intramolecular aminohalogenation of alkynes is more studied, and was used to construct a variety of 5- and 6-membered heterocycles such as indoles, isoindolinones, isoquinolines, and benzimidazoles.[5] These aminohalogenation reactions that have been reported to access 5- and 6-membered heterocycles proceed via electrophilic cyclization, and no involvement of radical species was reported. To the best of our knowledge, the synthesis of 8-membered heterocycles via an aminohalogenation reaction has not been reported.

Medium-sized nitrogen-containing heterocycles are important intermediates in organic synthesis and have interesting biological properties.[6] For example, dibenzoazocines such as Imipramine and Desipramine are useful psychotropic drugs. Moreover, the dibenzazocine core is found in alkaloid natural products such as Apogalanthamine and Buflavine.[6c–d] Medium-sized ring compounds are mainly synthesized by ring-expansion reactions, cyclization of acyclic compounds and ring-closing metathesis.[7] Despite the availability of these methods, the limited scope of substrates, the need for expensive reagents and harsh conditions urge the development of further reactions for the synthesis of medium-sized heterocycles.

Based on the above background and our continuing interest in the development of efficient organic reactions using metal-free conditions,[8] as well as the synthesis of medium-sized heterocycles,[9] herein we present a regioselective intramolecular reaction for the synthesis of 5,6-dihydrodibenzo[*c*,*e*]azocine derivatives using iodine and hypervalent iodine under visible light irradiation. We began our studies by evaluating the intramolecular reaction of compound **1a**, which

Table 1. Optimization of the Reaction Conditions.[a]



Entry	Hypervalent iodine	Solvent	Yield[b]
1[c]	$PhI(OAc)_2$	DCE	85
2	$PhI(mCBA)_2$	DCE	82
3[d]	$PhI(OCOCF_3)_2$	DCE	N.D.
4[e]	PhI(OH)(OTs)	DCE	N.D.
5	$PhI(OAc)_2$	THF	23
6	$PhI(OAc)_2$	MeCN	74
7	$PhI(OAc)_2$	$MeNO_2$[f]	59
8[g]	$PhI(OAc)_2$	DCE	80
9[h]	$PhI(OAc)_2$	DCE	84
10[i]	$PhI(OAc)_2$	DCE	65
11[j]	$PhI(OAc)_2$	DCE	0
12[k]	$PhI(OAc)_2$	DCE	N.R.
13[l]	–	DCE	N.R.

[a] Reaction conditions: Unless otherwise stated, **1a** (0.05 mmol), I_2 (0.50 equiv.), hypervalent iodine (1.20 equiv.), dehydrated solvent (3.50 mL) at 0 °C for 19 h under 27 W fluorescent light irradiation.
[b] Isolated yields.
[c] Conducting by 0.10 mmol scale.
[d] Compound **3** was obtained in 70% (NMR yield).
[e] Compound **3** was obtained in 73% (NMR yield).
[f] Using non-dehydrated $MeNO_2$.
[g] At rt.
[h] Ceiling light irradiation.
[i] Using NIS.
[j] Under darkness.
[k] Without I_2, 17 h.
[l] 17 h. DCE: 1,2-dichloroethane, MeCN: acetonitrile. N.D.: Not detected, N.R.: No reaction.

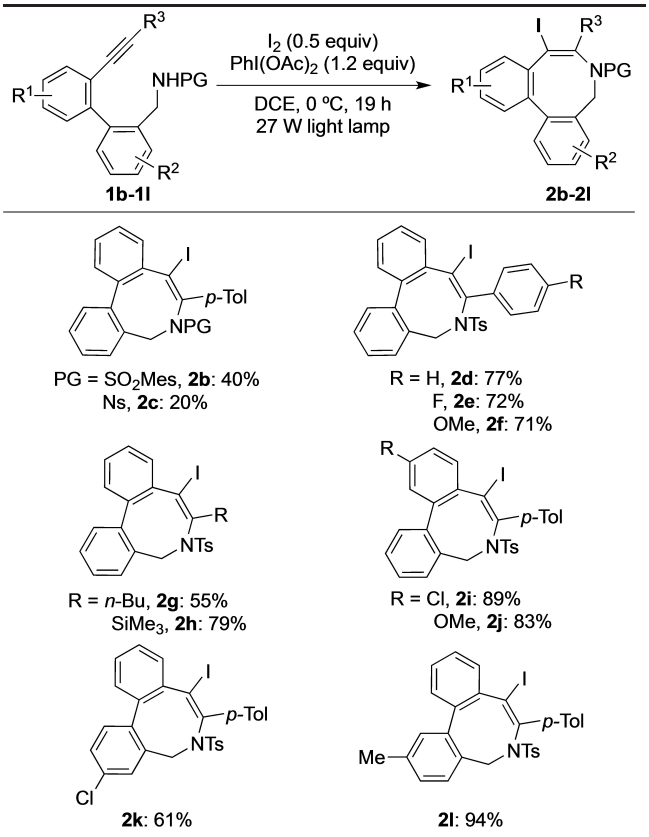
Figure 1. X-ray Structure of **2a** (Thermal ellipsoids shown at 50% probability).

contains alkynyl and sulfonamide groups, under various conditions (Table 1). First, when compound **1a** was treated with iodine (0.5 equiv) and phenyliodine (III) diacetate (PIDA) (1.2 equiv) in 1,2-dichloroethane (DCE) under 27 W fluorescent light irradiation at 0 °C for 19 h, the desired 8-membered heterocycle **2a** was obtained in 85% isolated yield (entry 1). The structure of **2a** was characterized by NMR and mass spectra, and the eight-membered ring structure was finally determined by a single-crystal X-ray diffraction analysis (Figure 1). Although phenyliodine(III) bis(*m*-chlorobenzoate) ($PhI(mCBA)_2$) also gave the desired product **2a** in 82% yield (entry 2), the desired 8-membered heterocycle could not be detected when phenyliodine (III) bis(trifluoroacetate) (PIFA) or Koser's reagent (PhI(OH)(OTs)) was used (entries 3, 4). In contrast, compound **3** was obtained in respective yields of 70 and 73%. A survey of solvents revealed that the aminoiodination reaction also proceeded in the presence of THF, MeCN and $MeNO_2$, albeit in lower yields compared to DCE (entries 5–7 vs 1). The reaction also proceeded smoothly at rt, or under ceiling light irradiation to afford **2a** in respective yields of 80% and 84% (entries 8, 9). A reaction conducted using *N*-iodosuccinimide (NIS) as an iodide source was also successful and gave dibenzazocine **2a** in 65% yield (entry 10). Notably, control experiments proved that the presence of visible light, an iodine source, and hypervalent iodine were crucial for the intramolecular aminoiodination to proceed (entries 11–13). Based on these optimization results, the conditions in entry 1 were chosen to examine the substrate scope.

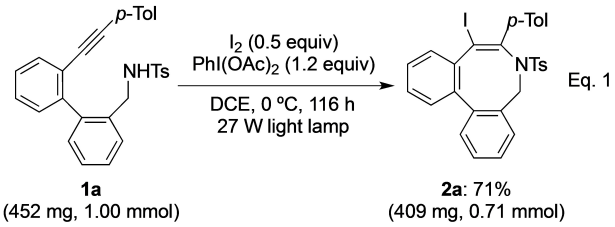
With the optimized conditions in hand, the scope of substrates was determined (Table 2). When the *N*-protecting group was changed from tosyl to mesitylsulfonyl (Mes) or nosyl (Ns) group, cycloadducts **2b** and **2c** were obtained in lower yields. The aryl group of the alkynyl moiety could be changed to a phenyl, 4-fluorophenyl or 4-methoxyphenyl group without much decrease in yield, as demonstrated in the synthesis of compounds **2d**–**2f**. Apart from aryl groups, substrates containing alkynes substituted with *n*-butyl (**1g**) and trimethylsilyl (**1h**) groups also participated in the intramolecular aminoiodination reaction to afford desired 8-membered heterocycles **2g** and **2h** in moderate and high yields, respectively. Various electron-withdrawing and electron-donating groups such as chloro, methoxy and methyl groups on the tethering aryl motifs were also tolerated and gave desired products **2i**–**2l** in 61–94% yields. These results mean that iodinated 5,6-dihydrodibenzo[*c*,*e*]azocines with various functionalities can be smoothly synthesized using the present protocol. But terminal alkyne (R^3 = H) was not available and the corresponding cycloadduct was not detected.

To demonstrate the practicality, we conducted the present intramolecular aminoiodination on a larger

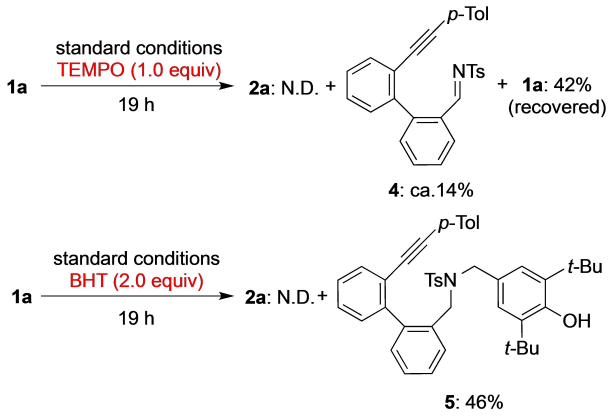
Table 2. Scope for Aminoiodination of Alkynes: Synthesis of 5,6-Dihydrodibenzo[*c*,*e*]azocine.



scale using **1 a** (ca. 0.5 g). Although it required a longer reaction time, the desired dibenzazocine **2 a** was obtained in good yield along with the recovery of a small amount of the substrate (ca. 10%) (Eq. 1).

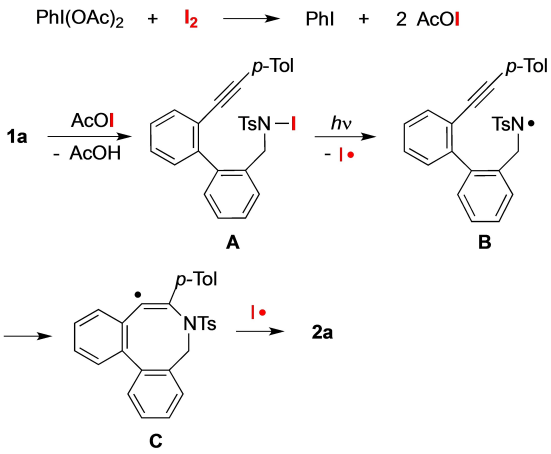


Most previous aminoiodination reactions of alkynes were demonstrated to proceed via an electrophilic halogenation mechanism.[5] To gain insight into the species involved in our intramolecular aminohalogenation reaction, we conducted two reactions using radical trapping additives (Scheme 1). First, we conducted a reaction in the presence of 1.0 equivalent of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as a radical scavenger: formation of the desired product **2 a** was completely halted, and imine **4** was obtained in ca. 14% yield as an oxidation product. Next, when the reaction of **1 a** was conducted under the optimized conditions in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT), formation of the desired product **2 a** was also halted. Compound **5**, possibly formed by the reaction of sulfonamidyl radical with BHT, was obtained in 46% yield after purification.[10] These observations mean that the present reaction most likely proceeds via a radical mechanism.



Scheme 1. Mechanism Study Using TEMPO and BHT.

Based on the above observations, previous studies[11] and our previous report,[8c] a representative mechanism using substrate **1 a** is shown in Scheme 2. The reaction mechanism is initiated by the reaction of iodine with $PhI(OAc)_2$ to give acetyl hypoiodite (AcOI). The hypoiodite then reacts with sulfonamide **1 a** to give an iodosulfonamide intermediate **A** with the concomitant formation of AcOH. The nitrogen-iodine bond of **A** undergoes light-induced homolytic cleavage to form sulfonamidyl radical **B**, which is stabilized by the electron-withdrawing sulfonyl group. Next, sulfonamidyl radical **B** adds to the alkynyl motif regioselectively to afford a vinyl radical species **C**. Finally, the vinyl radical **C** couples with the iodine radical to give desired iodinated 5,6-dihydrodibenzo[*c*,*e*]azocine **2 a**. Since the present reaction requires light irradiation and was halted by radical scavengers such as TEMPO



Scheme 2. Plausible Reaction Mechanism.

and BHT, a mechanism initiated by activation of the alkynyl moiety by acetyl hypoiodite,[12] followed by intramolecular sulfonamide addition is not feasible.

To elucidate the selective 8-*endo-dig* cyclization over 7-*exo-dig* one, we conducted DFT calculations starting from the nitrogen radical. The geometry optimizations were carried out at the UωB97X-D[13] level of theory with a basis set of 6-31 + G(d). Single point energy calculations were carried out at the same level of theory with 6-311 + + G(2d,2p) and solvation effects DCE (ε = 10.125000) using IEFPCM model.[14] According to the energy diagram (Figure 2), the activation energy of 8-*endo-dig* cyclization was 10.2 kcal/mol and that of 7-*exo-dig* cyclization was 13.5 kcal/mol. These results mean that the 8-*endo-dig* cyclization preferentially proceeds under the reaction conditions and that the present reaction is kinetically controlled.

We further investigated the non-covalent interaction in the **TS-8-*endo*** by NCI[15] analysis using multiwfn[16] and visualized by VMD.[17] Figure 3 clearly shows the steric repulsion around the *ortho* positions of the biaryl moiety colored by orange. Moreover, the π–π stacking between tosyl group and the substituent of alkyne terminus can be found, which is colored by green. Actually a control experiment using a monoaryl-tethered substrate gave the corresponding product, yet

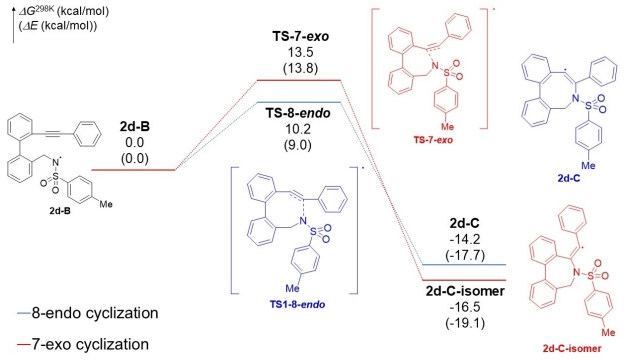


Figure 2. Free Energy Diagram of Radical Cyclization.

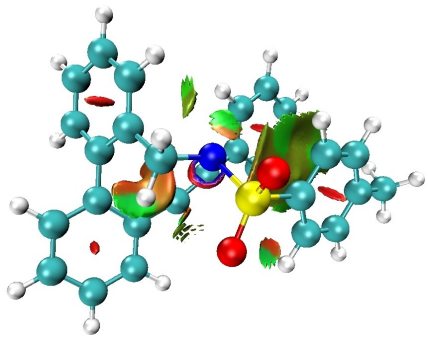
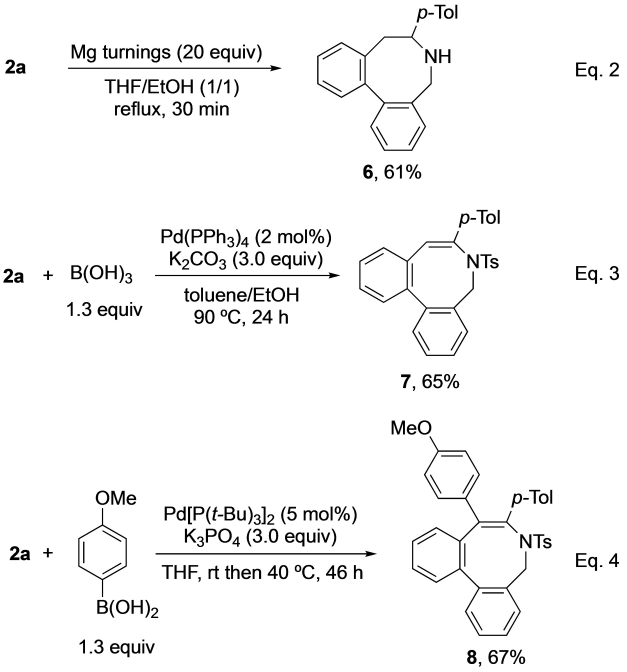


Figure 3. Non-Covalent Interactions in the **TS-8-*endo***.

in low yield with low 8-*endo*/7-*exo* selectivity (see supporting information in detail), which shows that the biaryl moiety is crucial for the efficient and regioselective cyclization.

Finally, we conducted three synthetic conversions using **2a** as a representative 5,6-dihydrodibenzo[*c*,*e*]azocine. First, the reaction of **2a** in the presence of Mg turnings in refluxed THF/EtOH resulted in removal of the tosyl group, reduction of the alkene moiety and deiodination in a single pot (Eq. 2). As a result, dibenzo[*c*,*e*]azocine **6**, which possess the core structure of Apogalanthamine and Buflavine natural products, was obtained in 61% yield. A palladium-catalyzed removal of the iodine moiety of **2a** using boric acid proceeded to give compound **7** in 65% yield (Eq. 3). Finally, Suzuki-Miyaura coupling of **2a** with 4-methoxyphenylboric acid successfully gave diarylated 5,6-dihydrodibenzo[*c*,*e*]azocine **8** in 67% yield (Eq. 4).



In conclusion, we have demonstrated an intramolecular regioselective aminoiodination reaction of alkynes for the synthesis of a variety of iodinated dihydrodibenzo[*c*,*e*]azocine derivatives under visible light irradiation using iodine and a hypervalent reagent. The reaction tolerates a variety of functional groups to give highly functionalized 8-membered heterocycles, which are normally difficult to synthesize. We also elucidated that the reaction proceeded via a radical mechanism. The preferential 8-*endo-dig* cyclization over 7-*exo-dig* one was supported by DFT calculations. A few synthetic applications were also demonstrated and gave the desired products in good yields.

Experimental Section

General procedure for intramolecular aminoiodination: alkyne **1 a** (22.6 mg, 0.05 mmol), phenyliodine(III) diacetate ($PhI(OAc)_2$) (19.4 mg, 0.06 mmol), and iodine (6.4 mg, 0.025 mmol) were placed into a Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was evacuated and backfilled with argon (3 ×). After the addition of 1,2-dichloroethane (1.75 mL), the Schlenk tube was capped, and the reaction mixture was stirred for 19 h at 0 °C under 27 W fluorescent light irradiation. It was quenched with sat. $Na_2S_2O_3$ aq. solution and washed with sat. $NaHCO_3$ aq. solution. The crude material was then purified using preparative TLC (toluene/ethyl acetate = 19/1) to give dibenzazocine **2 a**.

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COMMUNICATIONS

Metal-Free Aminoiodination of Alkynes Under Visible Light Irradiation for the Construction of a Nitrogen-Containing Eight-Membered Ring System

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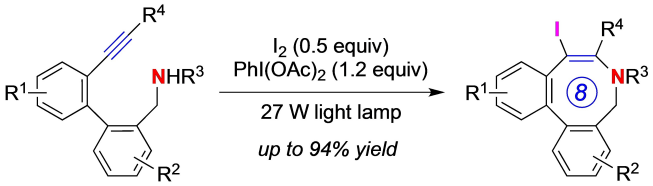

- Synthesis of 8-membered heterocycles
- Regioselective aminoiodination
- Mild conditions and simple procotol