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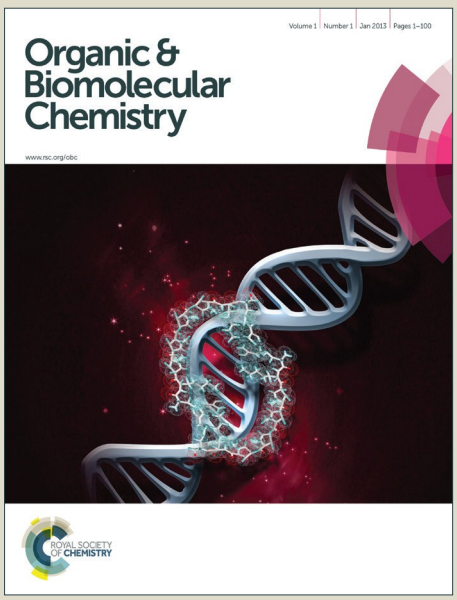

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COMMUNICATION

Visible-light-promoted chloramination of olefins with *N*-chlorosulfonamide as both nitrogen and chlorine sources

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A visible-light-promoted chloramination of olefins is reported. *N*-chlorosulfonamides serve as both nitrogen and chlorine sources. These reactions provide a simple, efficient, regioselective, and atom-economic method for the preparation of vicinal haloamine derivatives under mild conditions. A variety of olefins were tolerated, and chloroamidation products were obtained with good yields.

Vicinal haloamine derivatives are versatile synthetic intermediates for the synthesis of functional materials and biologically active compounds by replacement of the halogen atom with multifarious nucleophiles.[1] Among the synthetic routes to these 1,2-haloamines, the direct 1,2-functionalization of olefins is a practical method, due to the fact that the starting materials are readily available olefins.[2] Particularly, highly regioselective and stereoselective aminohalogenation of olefins remains important, but challenging to organic chemists.[3,4] In the literatures, vicinal haloamines is mainly achieved *via* nucleophilic attack to a halogenium intermediate with an amide nucleophile (Figure 1a). In this step, the nucleophile is normally an externally added amide.[3] The *in situ* generated amide anion derived from the *N*-halogenic reagents after delivering the halogenium ion may also participate in the nucleophilic addition, and this process is highly atom economic since both of the halogen and nitrogen moiety are preserved in the haloamination product (Figure 1b).[4] A notable limitation with these processes is the poor yield and selectivity in terms of product distribution.[3b,3d,4d,4g]

Nitrogen-centered radicals have been involved in a wide variety of useful organic transformations, which has received increasing attention from synthetic community.[5] We[6] and some other groups[7] recently reported visible-light-induced C-H bond amidations of arenes and heteroarenes using different nitrogen sources. The key intermediates in these transformations are nitrogen-centered amidyl radicals generated from different precursors under visible light irradiation.[8] Furthermore, our group[9] also reported a visible-light-induced remote C(sp3)-H amidation and chlorination of *N*-chlorosulfonamides. *N*-chlorosulfonamides could serve as nitrogen-centered radical precursors with the assistance of visible light and a photocatalyst. Inspired by these works, as well as recent research on photoredox catalytic 1,2-functionalization of olefins,[10] we envisaged that vicinal haloamidation of olefins could be achieved using *N*-chlorosulfonamides as both nitrogen and halogen sources under photoredox catalysis.

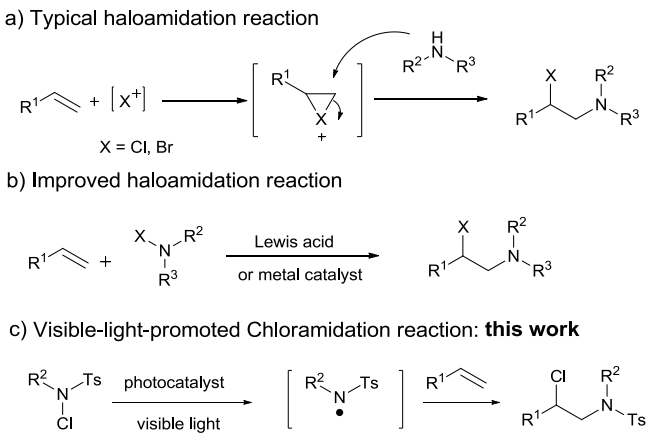

Figure 1. Major strategies for haloamination reaction.

Our efforts toward this goal focused on the use of 1-methoxy-4-vinylbenzene (**1a**) and *N*-chlorosulfonamide **2a** as model substrates. When a solution of **1a** and **2a** in CH_3CN was irradiated by white LED strips in the presence of photocatalyst $Ir(ppy)_3$ (**I**) and Na_2HPO_4 for 6 h, the desired chloramination product **3a** was obtained in 48% NMR yield as one regioisomer (Table 1, entry 1). Base was proved unnecessary (entry 2).

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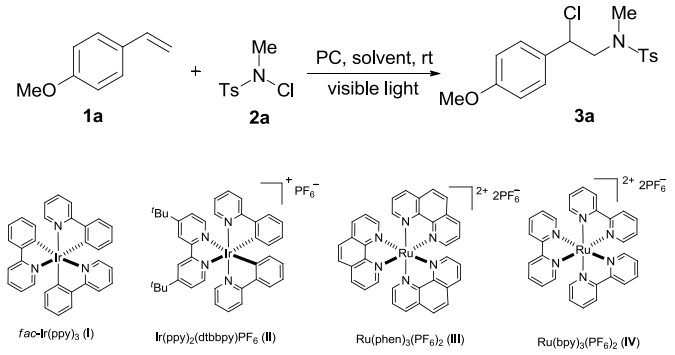
~~However, irradiation and the photocatalyst were crucial to this transformation (entries 3-4).~~ Various solvents, such as toluene, DMF, CH_2Cl_2, DMSO, THF and CH_3OH, could not give improved results (entries 3-7). Fortunately, the yield could be increased to 63% when DCE was used as the solvent (entry 8). Other photocatalysts, such as $Ir(ppy)_2(dtbbpy)PF_6$ (**II**), $Ru(phen)_3(PF_6)_2$ (**III**) and $Ru(bpy)_3(PF_6)_2$ (**IV**) were then examined. To our delight, 86% NMR yield (81% isolated yield, entry 9) was achieved when $Ir(ppy)_2(dtbbpy)PF_6$ (**II**) was used as the photocatalyst. The loading of photocatalyst had little impact on the outcome of this transformation (entries 12-13). Control experiments verified the necessity of the irradiation and photocatalyst (entries 14–15).

Table 1. Reaction conditon optimization[a]

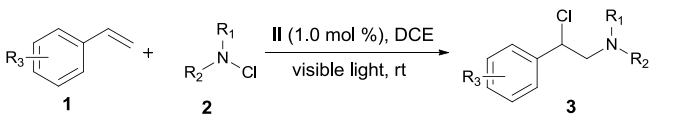


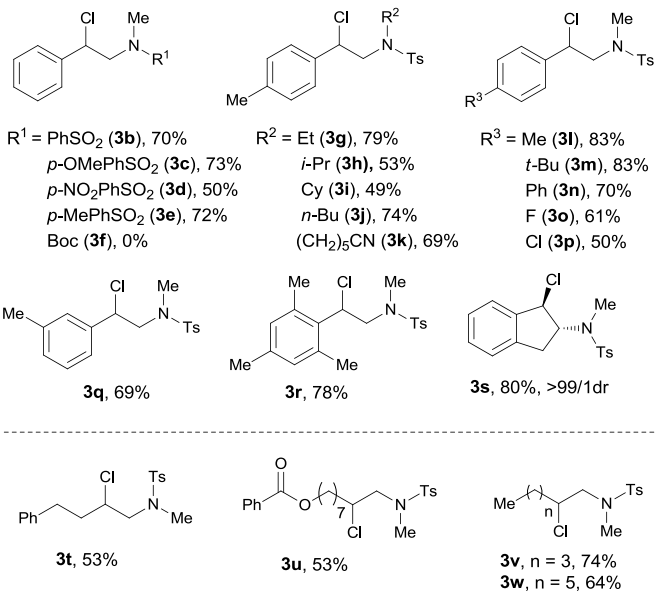
Entry	Photocatalyst	Solvent	Yield[b]
1[c]	**I** (1.0 mol %)	CH_3CN	48
2	**I** (1.0 mol %)	CH_3CN	51
3	**I** (1.0 mol %)	DMF	25
4	**I** (1.0 mol %)	CH_2Cl_2	54
5	**I** (1.0 mol %)	DMSO	NR
6	**I** (1.0 mol %)	THF	NR
7	**I** (1.0 mol %)	CH_3OH	NR
8	**I** (1.0 mol %)	DCE	63
9	**II** (1.0 mol %)	DCE	86(81[d])
10	**III** (1.0 mol %)	DCE	54
11	**IV** (1.0 mol%)	DCE	78
12	**II** (0.5 mol %)	DCE	68
13	**II** (2.0 mol %)	DCE	81
14	none	DCE	NR
15[e]	**II** (1.0 mol %)	DCE	NR

[a]Reaction conditions: A solution of **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), and photocatalyst (0.001 mmol, 1.0 mol %) in the indicated solvent (2.0 mL) was irradiated by white LED strips for 6 h. [b]Yields were determined by ^1H NMR using CH_2Br_2 as an internal standard. [c]Na_2HPO_4 used as base. [d]Isolated yield. [e]No irradiation. NR = no reaction.

After optimized conditions were established, we next explored the substrate scope of this visible-light-mediated aminohalogenation reaction (Table 2). The protecting groups of nitrogen atom were examined firstly. Relatively electron-rich benzenesulfonamide (**3c**, 73% yield) gave slightly better result than its electron-neutral counterpart (50% yield for **3b** and 72% yield for **3e**). Relatively electron-deficient benzenesulfonamide gave significantly worse yield (50% yield for **3d**). *N*-chlorocarbamate was ineffective under these conditions and the starting materials could be fully recovered. The alkyl groups of *N*-chlorosulfonamides were changable. Various alkyl groups, such as Et (**3g**, 79% yield), *n*-Bu (**3j**, 74% yield) and $(CH_2)_5CN$ (**3k**, 69% yield), gave good yields. Isopropyl (**3h**, 53% yield) and cyclohexyl (**3i**, 49% yield) groups gave lower yields due to steric hinderance. A variety of styrene derivatives were tested with *N*-chlorosulfonamide **2a**. All the substituted styrenes tested so far have worked quite well to give the corresponding products **3l**-**3s** in satisfactory yields (50-83%). Aliphatic olefins were also suitable coupling partners in this transformation, but with slightly less efficiency than their aromatic counterparts. The corresponding products **3t**-**3w** were isolated in 53-74% yields. This methods were not applicable to electron-deficient olefins. It is worthy to note that all the chloramides were isolated in one regioisomer.

Table 2. Substrate scope[a]

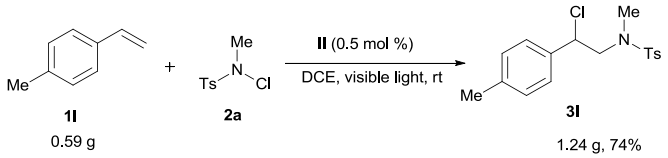




[a]Reaction conditions: A solution of **1** (0.1 mmol, 1.0 equiv), **2** (0.15 mmol, 1.5 equiv), and **II** (0.001 mmol, 1.0 mol %) in DCE (2.0 mL) was irradiated by white LED strips for 6 h. The yields were isolated yields.

As a demonstration of scalability, chloroamination of 4-methylstyrene (**1l**) with *N*-chlorosulfonamide **2a** was carried out on a gram scale in the presence of as little as 0.5 mol % of

the photocatalyst **II**. The product **3l** (1.24 g) was isolated in a 74% yield (Scheme 1).



Scheme 1. Gram-Scale Preparation of **3l**.

To understand the mechanism of this reaction, a series of control reactions were conducted. First, the reaction could be terminated completely when TEMPO was introduced to the reaction mixture, which implies the single-electron-transfer pathway. A light off/on and time profile experiment was carried out to investigate the mechanism details of this photoredox chloramination of Olefins (For details, see ESI). It was observed that the reaction progressed smoothly with light irradiation and there was little further conversion when the light resource was removed. This experiment verified the necessity of light, which suggested that regeneration of the photocatalyst was necessary for the full consumption of olefins.

Based on these observations, a possible catalytic cycle is proposed for this transformation (Figure 2). First, the photocatalyst Ir^{III} is irradiated to the excited state Ir^{III*}. The excited state Ir^{III*} is then oxidatively quenched by *N*-chlorosulfonamide **2a** with generation of Ir^{IV} and the nitrogen-centered radical **4** respectively. The radical **4** adds to olefin **1l** to produce the alkyl radical intermediate **5**. The radical **5** is oxidized to carbocation **6** by Ir^{IV} with regeneration of Ir^{III}. Cation **6** is finally trapped by chloride anion to give chloramination product **3l** (path A). Radical chain mechanism can be a competitive pathway (path B). The radical **5** can abstract chlorine atom from **2a** to give the final product **3l** and regenerate the nitrogen-centered radical **4**.

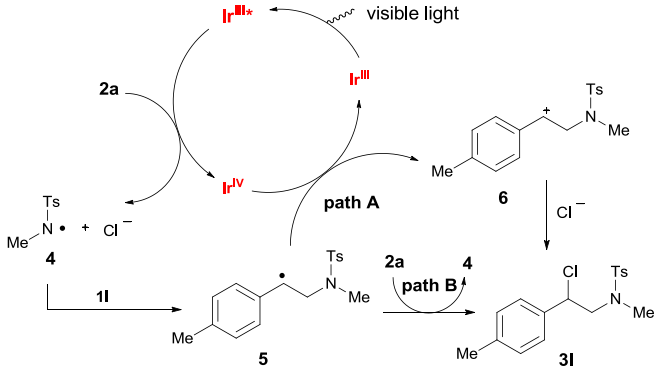


Figure 2. Proposed mechanism.

In summary, we have described a visible-light-promoted and regioselective 1,2-chloramination of olefins. *N*-chlorosulfonamides serve as both nitrogen and chlorine sources. This is a simple, efficient, and highly atom-economic method for the preparation of vicinal haloamine derivatives.

Acknowledgements

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