

## Note

Photo-Induced Aziridination of Alkenes with *N*-Sulfonyliminoiodinanes

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**Activation of *N*-sulfonyliminoiodinanes was achieved by photo-irradiation at 375 nm, which enabled the reaction with several alkenes to afford the corresponding aziridines. Mechanistic studies suggested that the reaction would proceed through a stepwise mechanism *via* radical intermediates rather than through a concerted process.**

**Key words** aziridination; hypervalent iodine; iminoiodinane; photoreaction

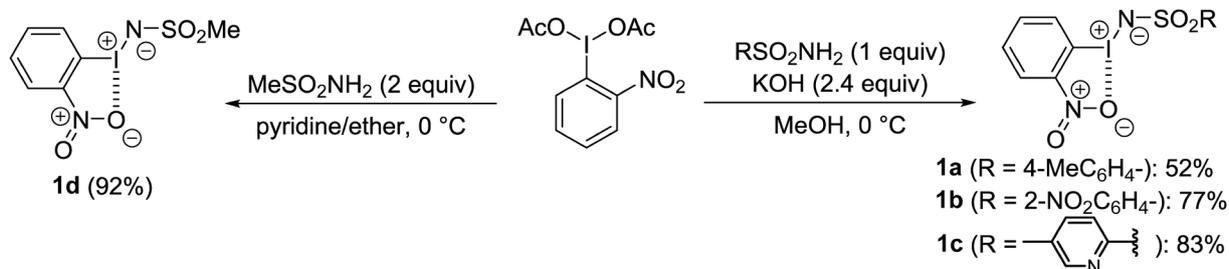
Aziridines are important synthetic intermediates for various nitrogen-containing compounds *via* ring opening<sup>1,2)</sup> and ring expansion reactions.<sup>3–6)</sup> Also, they are often found in natural products and biologically active compounds,<sup>7)</sup> and therefore a variety of methods have been developed for the synthesis of aziridines.<sup>8)</sup> Among them, transition-metal-catalyzed aziridination of alkenes is one of the most reliable approaches, where *N*-haloamine salts,<sup>9)</sup> organic azides,<sup>10,11)</sup> and iminoiodinanes<sup>12–15)</sup> were employed as nitrene precursors. Recently, metal-free aziridination<sup>16–19)</sup> and catalyst-free aziridination<sup>20–22)</sup> of alkenes have emerged as greener alternatives, but only limited approaches are available and there still remains to be solved for the development of this research area. Very recently, we have developed newly designed *N*-acyliminoiodinanes, which were found to be activated under photo-irradiation conditions and utilized as *N*-acylnitrene equivalent.<sup>23)</sup> The coordination of the oxygen atom of *ortho*-substituent (–OMe, –CH<sub>2</sub>OMe) to the iodine atom seemed to be essential for the photo-activation of *N*-acyliminoiodinanes as well as *N*-sulfonyliminoiodinanes, and silyl enol ethers were successfully  $\alpha$ -aminated using those iminoiodinanes under photo-irradiation. We envisioned that such *ortho*-substituted iminoiodinanes could be similarly applied to a photo-induced aziridination of alkenes without using any catalysts. We also anticipated that iminoiodinanes bearing *ortho*-nitro substituents would be applicable to photoreactions due to the coordination of the *ortho*-nitro group to the iodine atom,<sup>24)</sup> and that electron-withdrawing property of the *ortho*-nitro substituents would increase the electrophilicity of iminoiodinanes, leading to high reactivity toward alkenes. Herein, we report a catalyst-free aziridination of alkenes using *ortho*-substituted

(–CH<sub>2</sub>OMe, –NO<sub>2</sub>) iminoiodinanes under photo-irradiation at 375 nm.

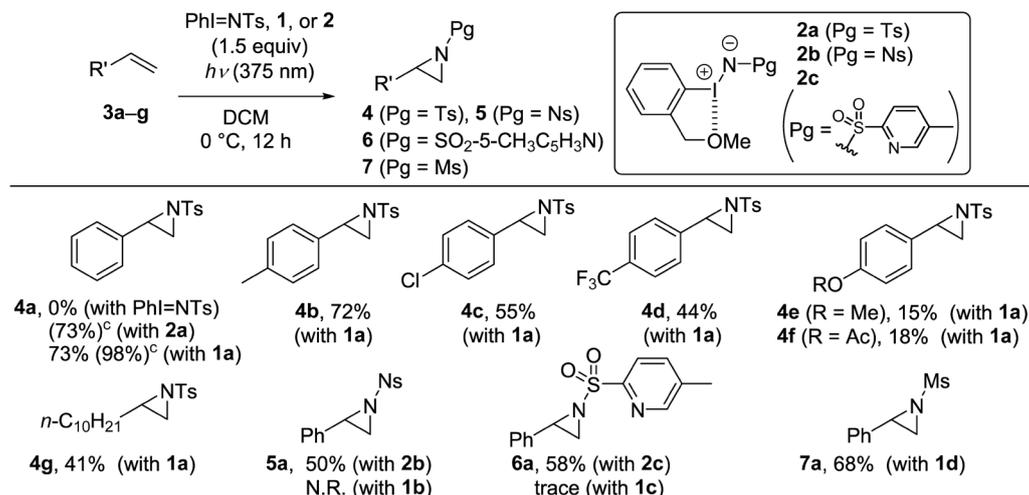
We first synthesized several *N*-sulfonyliminoiodinanes bearing *ortho*-nitro substituents (Chart 1). According to the synthesis of *N*-tosyliminoiodinane **1a**,<sup>24)</sup> new iminoiodinanes **1b**, **c** bearing 2-nitrobenzenesulfonyl- and 5-methylpyridine-2-sulfonyl groups were successfully obtained in high yields from 2-nitroiodobenzene diacetate with the corresponding sulfonamides in basic methanol solution (Chart 1). These *N*-sulfonyl groups would increase the reactivity of the corresponding aziridines and allow it easier to be deprotected from the nitrogen atom.<sup>25,26)</sup> In addition, new iminoiodinane **1d** was prepared from 2-nitroiodobenzene diacetate and methanesulfonamide in pyridine–ether solution. Although **1b** (*o*-Ns) showed low solubility in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, the other iminoiodinanes **1c**, **1d** exhibited enough solubility to take NMR in CDCl<sub>3</sub>. It is worth noting that these resulting off-white or yellow solid could be stored for several months at room temperature.

We next investigated the aziridination of alkenes with the synthesized iminoiodinanes under photo-irradiation conditions (Table 1). The reaction of styrene **3a** under the previously reported conditions<sup>23)</sup> (with iminoiodinane **2a**<sup>27)</sup> in dichloromethane under photo-irradiation at 375 nm) gave the corresponding aziridine **4a** in 73% yield, while the use of PhI=NTs<sup>12–15)</sup> gave no desired product. To our delight, replacement of iminoiodinane **2a** with **1a** improved the chemical yield of **4a** to 98%.

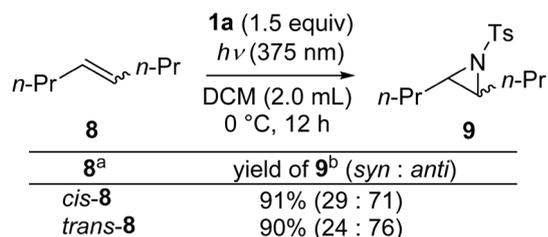
With these optimized conditions in hand, we next investigated the substrate scope of the photo-induced aziridination of alkenes **3a–g** (Table 1). Styrenes having several substituents on the aromatic rings **3b–d** were tolerant to the photo-

Chart 1. Synthesis of Iminoiodinanes **1a–d**

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Table 1. Substrate Scope of Photo-Induced Aziridination of Alkenes with Iminoiodinanes<sup>a,b</sup>

<sup>a</sup> Reaction conditions: styrene (0.1 mmol), iminoiodinane (0.15 mmol), dichloromethane (2 mL), 0 °C, 12 h. <sup>b</sup> Yields of isolated products unless otherwise noted. <sup>c</sup> Yields in parenthesis were determined by <sup>1</sup>H-NMR using dimethylsulfone as internal standard.



<sup>a</sup> Reaction conditions: **8** (0.1 mmol), **1a** (0.15 mmol)  
<sup>b</sup> Determined by <sup>1</sup>H-NMR analysis of crude products.

Chart 2. Reaction of *cis*- or *trans*-**8**

irradiation conditions to afford the corresponding aziridines **4b-d** in 44–72% yields. However, substrates **3e** and **3f** having electron-rich aromatic rings gave the desired products **4e** and **4f** in low yields, presumably due to their instability during purification on silica gel column chromatography.<sup>17,28</sup> Importantly, the aliphatic alkene **3g** was also applicable to the catalyst-free reaction to give aziridine **4g** in 41% yield. Furthermore, the aziridines bearing different *N*-sulfonyl groups **5a–7a** were successfully obtained in 50–68% yields using **2b**,<sup>23</sup> **2c**,<sup>23</sup> and **1d** as nitrogen source, respectively, although newly synthesized iminoiodinanes **1b** and **1c** did not furnish the corresponding products because of their poor solubility in dichloromethane.

Aziridination using *cis*- and *trans*-alkene provided stereochemical insight into the photoreaction of iminoiodinane **1a** (Chart 2). The photo-induced reaction of *cis*-**8** gave the corresponding aziridine **9** in 91% overall yield with *syn/anti* ratio of 29:71, whereas *trans*-**8** gave **9** in 90% yield with 24:76 *syn/anti* ratio. These results strongly suggest that photo-induced aziridination of alkenes with **1a** would proceed via a stepwise mechanism<sup>23</sup> rather than via a concerted process.<sup>29</sup>

In conclusion, we have developed a novel catalyst-free aziridination of alkenes using *ortho*-substituted iminoiodinanes under photo-irradiation conditions. We believe that this procedure could contribute the development of greener synthetic methodology of various *N*-containing compounds. Further applications are under investigation in our laboratory.

## Experimental

Styrene **3a** (0.10 mmol, 10.4 mg) and iminoiodinane **1a** (0.15 mmol, 62.7 mg) were suspended in dichloromethane (2.0 mL), and the reaction mixture was stirred at 0 °C for 12 h under photo-irradiation by light-emitting diode (LED) light (peak wavelength 375±3 nm). After the resulting yellow solution was concentrated under reduced pressure, the crude products were directly purified by silica gel column chromatography to give aziridine **4a** (19.9 mg, 73%).

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**Conflict of Interest** The authors declare no conflict of interest.

**Supplementary Materials** The online version of this article contains supplementary materials.

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