Diastereoselective Aminooxygenation and Diamination of Alkenes with Amidines by Hypervalent Iodine(III) Reagents

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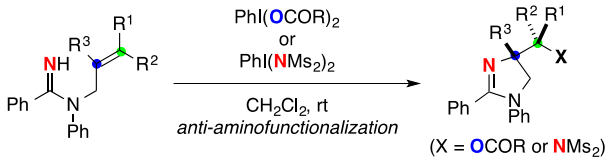
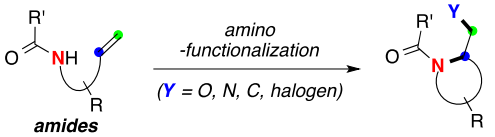
Supporting Information Placeholder



ABSTRACT: Diastereoselective *anti*-aminooxygenation and *anti*-diamination of alkenes with amidines were enabled by hypervalent iodine(III) [I(III)] reagents such as $PhI(OCOR)_2$ and $PhI(NMs_2)_2$, respectively. The present transformation offers diastereochemically pure dihydroimidazoles divergently from *E*- and *Z*-alkenes.

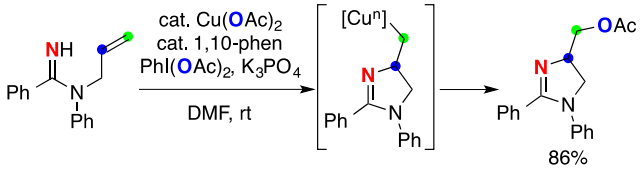
Difunctionalization of alkenes is one of the most powerful processes for chemical manipulations in organic synthesis. Represented by the Sharpless dihydroxylation[1] and aminohydroxylation,[2] a variety of strategies enabling stereo- and chemoselective difunctionalization of alkenes have been exploited to construct diverse molecular complexity.[3] Among them, intramolecular amino-difunctionalization of alkene has offered promising synthetic tactics for regio- and stereoselective construction of nitrogen-containing heterocycles (azaheterocycles), which are omnipresent in potent pharmaceutical drugs.[4] Within this arena, use of alkenyl amides/sulfonamides is the mainstream of methodology development under various oxidative reaction conditions (Scheme 1 for a typical example with *exo*-cyclization).

Scheme 1. Intramolecular amino-difunctionalization of alkenyl amides for azaheterocycle synthesis.



On the other hand, oxidative amino-difunctionalization of alkene installed on amidine moieties exhibits distinct trends and aspects in the synthesis of nitrogen-containing molecules, as (1) the intrinsic electron-rich nature of amidines might result in unique and unprecedented modes of the reaction processes for alkene difunctionalization;[5] (2) the azaheterocycle products, cyclic amidines such as dihydroimidazoles, include 1,3-diamino functionality and further reductive ring-opening of them would offers the construction of highly functionalized amines.[6] Herein, we report diastereoselective *anti*-aminooxygenation[7,8] and *anti*-diamination[9,10] of alkenes with amidines mediated by hypervalent iodine(III) reagents.

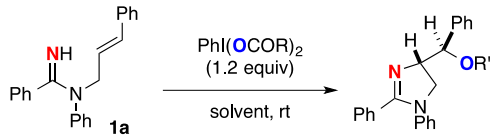
Scheme 2. Cu-catalyzed aminooxygenation of alkenes with amidines (previous works)



We have recently developed Cu-catalyzed-$PhI(OAc)_2$-mediated aminooxygenation (aminoacetoxylation) of *N*-allylamidines for construction of 4-acetoxymethyl-4,5-dihydroimidazoles, which proceeded presumably via alkene aminocupuration followed by acetoxylation of the putative organocopper intermediates (Scheme 2).[5b,11] However, this aminoacetoxylation strategy was amenable only to functionalization of the terminal alkene, which limited the substrate scope and the potential application. For example, the reaction of amidine **1a** having an internal *E*-alkenyl moiety under the optimized reaction conditions [15 mol% of $Cu(OAc)_2$-1,10-phen, 1.2 equiv of $PhI(OAc)_2$, 1 equiv of K_3PO_4 in DMF at room temperature] provided a complex mixture of unidentified compounds (Table 1, entry 1). Continuous investigation of the mixture could lead to isolation of a very small amount of amino-acetoxylation product **2a** (<10% yield) as a single diastereomer. The structure of **2a** could be secured by X-ray crystallographic analysis of the corresponding deacetylated alcohol **3a** (see Table 1, entry 7),[12] showing that *anti*-aminooxygenation takes place during the process. With the inherently electron-rich nature of amidines in mind, we envisioned that the amidine moiety could be activated (oxidized) only with hypervalent iodine(III) reagents under metal-free reaction conditions.[13,14] Indeed, it was found that the reaction of **1a** only with $PhI(OAc)_2$ in the absence of $Cu(OAc)_2$, could provide the same *anti*-aminoacetoxylation product **2a** in 15% yield, along with a mixture of unidentified compounds (Table

1, entry 2). Further screening of solvents for the $PhI(OAc)_2$-mediated reaction of amidine **1a** revealed that choice of the solvent noticeably affects the reaction efficiency (entries 3-6). Although the reactions in MeCN and toluene gave only poor yields of **2a** (entries 3 and 4), the reactions in trifluoroethanol (CF_3CH_2OH) and dichloromethane (CH_2Cl_2) enabled formation of **2a** in good yields with full conversion of amidine **1a** (entries 5 and 6). The best result was obtained from the reaction in CH_2Cl_2, affording **2a** in 79% yield (entry 6). We next investigated the effect of carboxylate ions on the present alkene amino-oxygenation event. More electron-deficient iodobenzene bis(trifluoroacetate) [$PhI(OCOCF_3)_2$] accelerated the reaction with amidine **1a**, leading to full conversion within 7 h to give *anti*-aminohydroxylation product **3a** in 82% yield (entry 7). In this process, the initially installed trifluoroacetyl group was labile and thus removed during the processes of aqueous work-up and purification through silica-gel chromatography. On the other hand, use of iodobenzene bis(benzoate) [$PhI(OCOPh)_2$] resulted in a slower reaction probably due to the steric hindrance of $PhI(OCOPh)_2$, forming benzoate **4a** in 71% yield with recovery of **1a** in 11% yield even after running for 38 h (entry 8).

Table 1. Optimization of the reaction conditions[a]

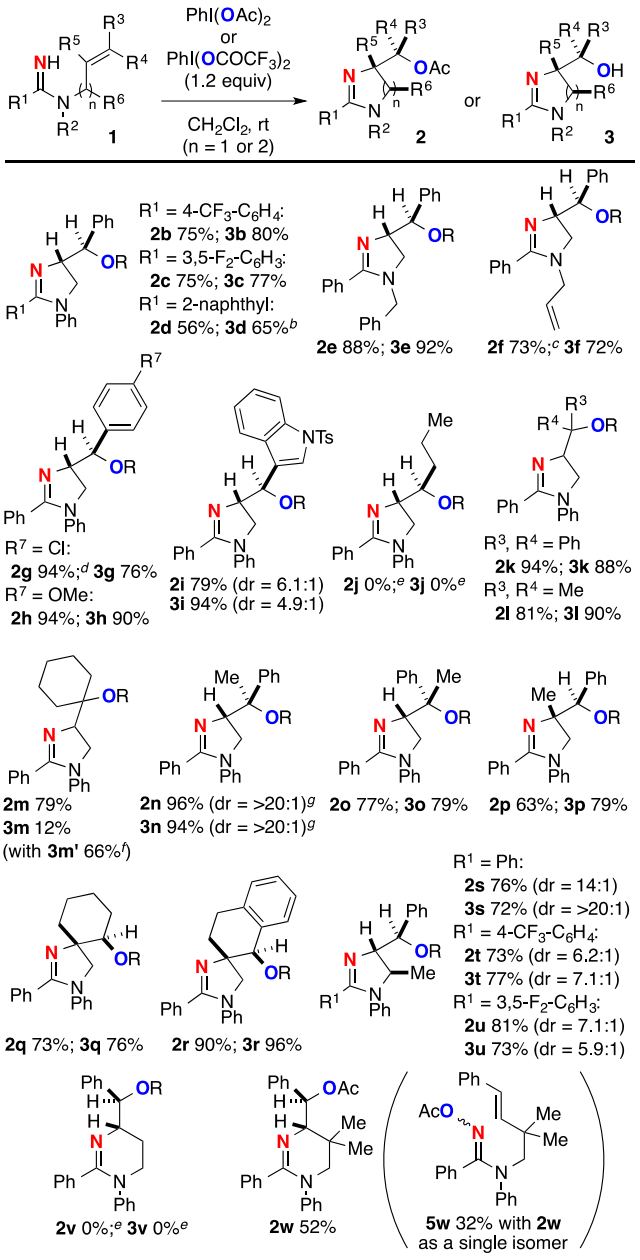


entry	R	solvent	time/h	products	yield [%][b]
1[c]	Me	DMF	20	**2a** (R' = Ac)	10
2	Me	DMF	20	**2a** (R' = Ac)	15
3	Me	MeCN	24	**2a** (R' = Ac)	45
4	Me	toluene	24	**2a** (R' = Ac)	19 (32)[d]
5	Me	CF_3CH_2OH	24	**2a** (R' = Ac)	70
6	Me	CH_2Cl_2	20	**2a** (R = Ac)	79[e]
7	CF_3	CH_2Cl_2	7	**3a** (R' = H)	82[e]
8	Ph	CH_2Cl_2	38	**4a** (R' = Bz)	71[e] (11)[d]

[a] The reactions were carried out using 0.3 mmol of **1a** in solvent (0.1 M) at room temperature. [b] ^1H NMR yields. [c] The reaction was carried out using $Cu(OAc)_2$ (15 mol%), 1,10-phenanthroline (15 mol%), $PhI(OAc)_2$ (1.2 equiv), and K_3PO_4 (1 equiv). [d] Recovery yield of **1a**. [e] Isolated yields.

With these optimized reaction conditions in hand, the substrate scope of amidines **1** for the present *anti*-aminooxygenation of alkene was then investigated using $PhI(OAc)_2$ and $PhI(OCOCF_3)_2$ (Scheme 3). We first investigated substituent compatibility of R^1 and R^2 on the amidine moiety as well as R^3 on the *E*-alkene part. By varying R^1, the reactions allowed installing electron-deficient benzene rings having trifluoromethyl (for **1b**) or 3,5-difluoro (for **1c**) substituents to provide the corresponding dihydroimidazoles in good yields, while the reaction with amidine **1d** bearing a 2-naphthyl group as R^1 resulted in moderate yields of aminooxygenation products **2d** and **3d**. Replacement of R^2 from phenyl to benzyl (for **1e**) did not affect the present *anti*-aminooxygenation, providing **2e** and **3e** in good yields. By installing allyl at R^2 (for **1f**), the reactions provided **2f** and **3f** as sole products through *anti*-aminooxygenation of the 3-phenylallyl moiety, demonstrating intriguing chemoselectivity of the present process. Investigation of the substituent effect of R^3 on the *E*-alkene revealed that 4-chloro- (for **1g**) and 4-methoxyphenyl (for **1h**) groups could be installed to afford **2g-h** and **3g-h** in good yields. Amidine **1i** having a 3-indolyl moiety as R^3 also performed well, while another diastereomer, *syn*-aminooxygenation product, was generated as a minor component [6.1:1 with $PhI(OAc)_2$; 4.9:1 with $PhI(OCOCF_3)_2$] (see the Supporting Information for discussion about the generation of minor diastereomer). Unfortunately, it was found

Scheme 3. Aminooxygenation of amidines 1[a]



[a] All the reactions were conducted using 0.3 mmol of *N*-allylamidines **1** in CH_2Cl_2 (3 mL) under a N_2 atmosphere. See Table S1 in the Supporting Information showing starting materials and products of each entry. [b] 1.5 equiv of $PhI(OCOCF_3)_2$ was used. [c] 1.4 equiv of $PhI(OAc)_2$ was used. [d] 1.3 equiv of $PhI(OAc)_2$ was used. [e] Complex mixtures of unidentified compounds were formed. [f] **3m'**: R = $COCF_3$. [g] Alkene **1n** contains small amount of *Z*-isomer (*E*:*Z* = 21:1).

that the present reaction did not proceed with amidine **1j** bearing a propyl group as R^3.

We then became interested in the reactions of amidines **1k-m** with 3,3-disubstituted allyl moieties. It is worthy of note that in all cases, the aminooxygenation proceeded smoothly and selectively to afford dihydroimidazoles **2k-m** and **3k-m** bearing a quaternary carbon and a newly formed C-O bond. The reaction of **1m** with $PhI(OCOCF_3)_2$ provided trifluoroacetate **3m'** as a major product along with hydrolyzed alcohol **3m** only in 12% yield.

Having obtained these promising results on the present aminooxygenation, we next prepared amidines **1n** and **1o** having *E*- and *Z*-alkenyl moieties, respectively. As expected, the present *anti*-aminooxygenation led to the formation of **2n**/**3n** and **2o**/**3o** from *E*- and *Z*-alkenes, respectively, in good yields, showing diastereo-divergency of the process.

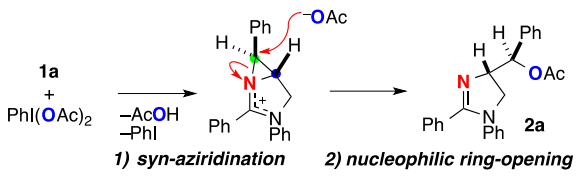
The reactions of amidine **1p** having a methyl group as R^5 at the C2 allyl position could construct another quaternary carbon at the C4 position of dihydroimidazoles **2p** and **3p** in diastereoselective fashion. Similarly, the present strategy was successfully applied for construction of spirocyclic dihydroimidazoles **2q**/**3q** and **2r**/**3r**.

The effect of a methyl substituent installed at the C1 allylic position (as R^6) on the diastereoselectivity of the present cyclization was also investigated. The reactions of **1s-u** were performed to construct three successive stereogenic centers in good diastereoselectivity and chemical yields, in which the C–N bond forming cyclization occurs selectively from the opposite side of the methyl group.

We next investigated the reactivity of *N*-butenylamidine **1v** for construction of 6-membered ring (tetrahydropyrimidine). In contrast to the above successful examples of *anti*-aminooxygenation observed for a series of *N*-allylamidines, the reaction of **1v** with either $PhI(OAc)_2$ or $PhI(OCOCF_3)_2$ resulted in formation of a complex mixture of unidentified compounds. Installation of the dimethyl functionality at the allylic position turned out to be crucial to achieve the desired *anti*-aminooxygenation. The reaction of amidine **1w** with $PhI(OAc)_2$ afforded tetrahydropyrimidine **2w** in 52% yield as a single diastereomer, while *O*-acetyl amidoxime **5w** was also formed in 32% yield.

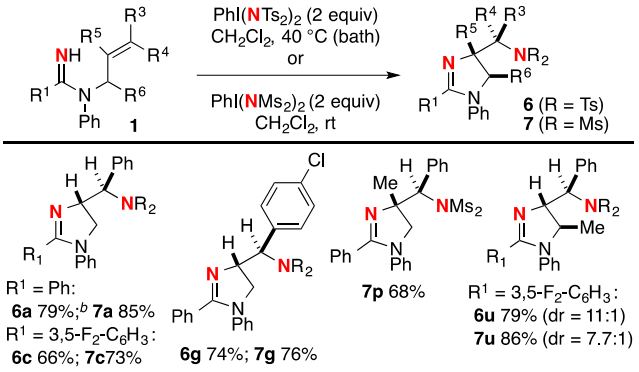
Based on these observations, the present process proceeded via stepwise sequence of *syn*-aziridination of alkenes[8e,8f] and nucleophilic ring-opening of aziridinium ions with counter carboxylate ions, necessarily resulting in *anti*-aminooxygenation of alkenes (Scheme 4).[15]

Scheme 4. A proposed mechanistic possibility



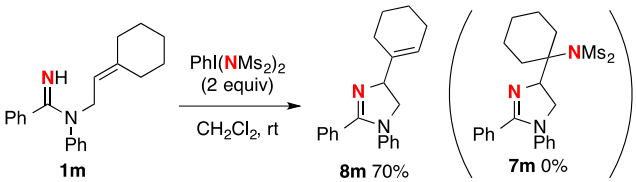
It is worth noting that $PhI(NTs_2)_2$ and $PhI(NMs_2)_2$ were capable of realizing diastereoselective *anti*-diamination of **1a**, affording **6a** and **7a** in good yields, respectively (Scheme 5). The reaction with sterically less hindered $PhI(NMs_2)_2$ was smoother than that with $PhI(NTs_2)_2$ at room temperature. The scope of the *anti*-diamination reaction was then investigated. Amidines having a disubstituted alkene (for **1c, 1g**) provided the corresponding products **6** and **7** in good-moderate yields. Diamination of the (*E*)-2-methyl-3-allyl moiety proceeded well, resulting in formation of the C4-quaternary carbon in dihydroimidazole **7p**. Diastereoselective construction of three successive stereogenic centers was also achieved in the diamination of amidine **1u**. However, the reaction of 3,3-disubstituted allylamidines such as **1m** with $PhI(NMs_2)_2$ did not form the expected diamination product **7m**, but provided cyclohexenyl dihydroimidazole **8m** in 70% yield (Scheme 6) (see the Supporting Information for the proposed mechanism for generation of alkene **8m**).

Scheme 5. Diamination of amidine 1a with $PhI(NTs_2)_2$ and $PhI(NMs_2)_2$[a]



[a] All the reactions were conducted using 0.3 mmol of *N*-allylamidines **1** in CH_2Cl_2 (3 mL) under a N_2 atmosphere. [b] The reaction was conducted at room temperature and **1a** was recovered in 9% yield.

Scheme 6. The reaction of amidine **1m** using $PhI(NMs_2)_2$.



In summary, we have developed a method for diastereoselective *anti*-aminooxygenation and *anti*-diamination of *N*-allylamidines that is mediated solely by hypervalent iodine(III) reagents. We anticipate that this strategy is capable of supplying various polyamine compounds useful for medicinal, materials, and catalysis applications. Further investigation to elucidate the detailed reaction mechanism and application of this strategy for other types of amino-functionalization of alkenes are currently in progress in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(6) We have demonstrated conversion of several dihydroimidazole products to polyamines by the AlH_3 reduction, see the Supporting Information.

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(11) For an account on our Cu-catalyzed aerobic molecular transformation for synthesis of azaheterocycles, see: Chiba, S. *Bull. Chem. Soc. Jpn*. **2013**, *86*, 1400.

(12) The structures of compounds **3a**, **3i**, **3n**, **3o**, **3s**, and **6a** were determined by X-ray crystallographic analyses. See the Supporting Information for more details. The structures of the other products were speculated from these results.

(13) Long and Zhu independently reported hypervalent I(III)-mediated sp^2 aromatic C–H amination with amidines for synthesis of benzimidazoles, see: (a) Lin, J.-P.; Zhang, F.-H.; Long, Y.-Q. *Org. Lett*. **2014**, *16*, 2822. (b) Huang, J.; He, Y.; Wang, Y.; Zhu, Q. *Chem. Eur. J*. **2012**, *18*, 13964.

(14) For reviews on application of hypervalent iodine reagents in organic synthesis, see: (a) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem*. **2013**, 5769. (b) Zhdankin, V. V. *J. Org. Chem*. **2011**, *76*, 1185. (c) Liang, H.; Ciufolini, M. A. *Angew. Chem., Int. Ed*. **2011**, *50*, 11849. (d) Duschek, A.; Kirsh, S. F. *Angew. Chem., Int. Ed*. **2011**, *50*, 1524. (e) Yusubov, M. S.; Maskaev, A. V.; Zhdankin, V. V. *Arkivoc* **2011**, *i*, 370. (f) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed*. **2009**, *48*, 9052. (g) Uyanik, M.; Ishihara, K. *Chem. Commun*. **2009**, 2086. (h) Dohi, T.; Kita, Y. *Chem. Commun*. **2009**, 2073. (i) Zhdankin, V. V.; Stang, P. J. *Chem. Rev*. **2008**, *108*, 5299. (j) Ochiai, M.; Miyamoto, K. *Eur. J. Org. Chem*. **2008**, 4229. (k) Deprez, N. R.; Sanford, M. S. *Inorg. Chem*. **2007**, *46*, 1924. (l) Ochiai, M. *Chem. Rec*. **2007**, *7*, 12. (m) Wirth, T. *Angew. Chem., Int. Ed*. **2005**, *44*, 3656.

(15) Deatailed discussion on the proposed mechanism especially for *syn*-aziridination was described in the Supporting Information.