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Iodine(III)-Mediated/Catalyzed Cycloisomerization–Amination Sequence of *N*-Propargyl Carboxamides

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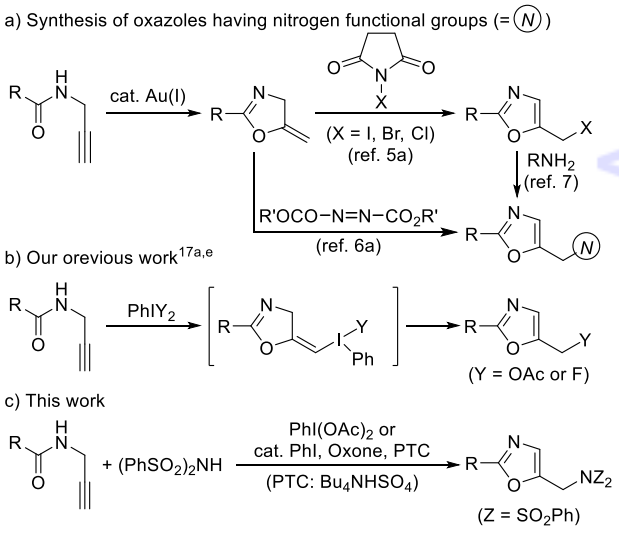
Abstract. (Diacetoxyiodo)benzene or iodine(III) catalyst, *in situ* generated from iodobenzene precatalyst with Oxone, promotes the cycloisomerization–amination sequence of *N*-propargyl carboxamides with bis(sulfonyl)imides under mild conditions, thereby leading to the direct formation of oxazoles bearing nitrogen functional groups.

Keywords: iodine; cycloisomerization; amination; amides; oxazoles

Tandem cycloisomerization-functionalization reactions of *N*-propargyl carboxamides provide one of the most effective approaches to the synthesis of functionalized oxazoles,[1] which are prevalent in many natural products and pharmaceutically active compounds.[2] For example, Pd-catalyzed methods lead to the construction of oxazole ring concomitant with the introduction of aryl and allyl groups into the side chain.[3] Also, Pd- or Hg-catalysts with oxidants bring about the formation of oxazoles bearing oxygen functional groups in a single operation.[4] Recently, Hashmi *et al.* reported a prospective and versatile synthesis of halogenated oxazoles based on the gold-catalyzed formation of alkylideneoxazolines from *N*-propargyl amides (Scheme 1a).[5] However, although such an one-pot, two-step method has been extended to oxazole synthesis methods with the introduction of nitrogen[6a,7] and other functional groups,[6b-h] an additional step for the introduction of heteroatomic functional groups except for oxygen functional groups is required in these syntheses of functionalized oxazoles.

In recent years, metal-catalyzed oxidative *vic*-diamination[8] and oxyamination reactions[9] of unsaturated compounds have been well studied for the effective introduction of nitrogen functional groups. Furthermore, these studies have led to the development of the cyclization-amination sequence of various alkenyl amines and alcohols catalyzed by Pd,[10] Cu[11] or Au complexes.[12] Nevertheless, the only formations of 3-amino-indoles or 3-amino-benzofurans have been known as the metal-catalyzed cyclization–amination sequences of alkynes.[13] Very recently, iodine(III) reagents prepared from $PhI(OAc)_2$ with bis(sulfonyl)imide by Muñiz *et al.*[14] have been employed in the metal-free synthesis of heterocycles based on the cyclization–amination reactions, which are mainly the reactions of alkenes.[15,16] On the other hand, through our studies on the metal-free synthesis of heterocycles based on the activation of alkynes by iodine(III) reagents,[17] we have previously found the cycloisomerization–acetoxylation and –fluorination sequence of propargyl amides (Scheme 1b).[17a,e] As further extension of cycloisomerization–functionalization reactions using iodine(III) reagents, herein, we report a direct formation of the oxazole possessing nitrogen functional groups from propargyl amides and bis(sulfonyl)imides (Scheme 1c).



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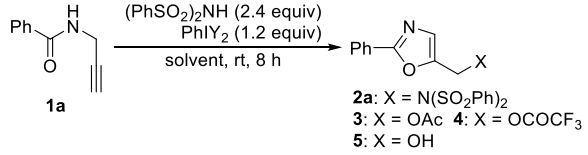
Scheme 1. Cycloisomerization-functionalization sequence of *N*-propargyl carboxamides.

In preliminary experiments, we found that the cycloisomerization–amination sequence of amide **1a** with $(PhSO_2)_2NH$ (1.2 equiv) using $PhI(OAc)_2$ (1.2 equiv) proceeded in dichloromethane (DCM) to give the desired oxazole **2a** in 59% yield at room temperature for 24 h (entry 1, Table 1). Since byproduct **3** having OAc group was detected in 11% yield in the case of entry 1, the amount of $(PhSO_2)_2NH$ was increased to 2.4 equiv, thereby leading to the improved yield of **2a** up to 66% along with the suppressed formation of **3** (5%, entry 2). On the other hand, the use of $PhI(OCOCF_3)_2$ instead of $PhI(OAc)_2$ reduced the yield of **2a** down to 24% due to the formation of **4** and **5** bearing oxygen functional groups in 37% and 17% yields, respectively (entry 3). When PhIO was employed, **2a** was slowly formed to recover **1a** in 18% (entry 4). Therefore, in the presence of $PhI(OAc)_2$, the screening of solvents was next examined in the reaction of **1a** and $(PhSO_2)_2NH$ (entries 5-8). Among the tested solvents, a mixed solvent of DCM and hexafluoroisopropanol (HFIP), particularly in a ratio of 3:1, showed good results, in which **2a** was obtained in 75% yield (entry 8).

Table 1. Optimization of the reaction conditions.

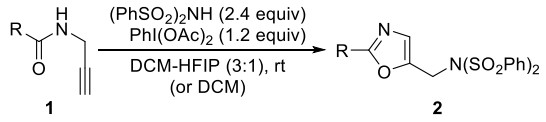


entry	$PhIY_2$	solvent	**2a** (%)[a]	
1[b]	$PhI(OAc)_2$	DCM	59[c]	(**3** 11)[d]
2	$PhI(OAc)_2$	DCM	66	(**3** 5)
3	$PhI(OCOCF_3)_2$	DCM	24[c]	(**4** 37)[e]
4	PhIO	DCM	32[c]	(**1a** 18)
5	$PhI(OAc)_2$	TFE	62	(**3** 6)
6	$PhI(OAc)_2$	HFIP	70	(**3** 5)
7[f]	$PhI(OAc)_2$	DCM-HFIP	74	(**3** 5)
8[g]	$PhI(OAc)_2$	DCM-HFIP	75	(**3** 5)

DCM, dichloromethane; TFE, 2,2,2-trifluoroethanol; HFIP, 1,1,1,3,3,3-hexafluoro-2-propanol. [a] Isolated yield, unless otherwise stated. Yields or values in parentheses were determined by ^1H NMR analysis. [b] $(PhSO_2)_2NH$: 1.2 equiv, reaction time: 24 h. [c] NMR yields. [d] **1a**: 6%. [e] **5**: 17%. [f] DCM:HFIP = 1:1. [g] DCM:HFIP = 3:1.

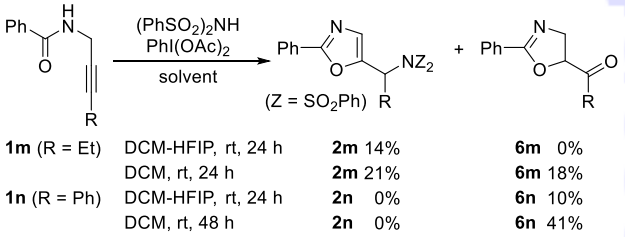
Under the optimized reaction conditions, the scope for the formation of oxazoles **2** from various *N*-propargyl carboxamides **1** is summarized in Table 2. Similar to benzamide **1a** (entry 1), regardless of electron-withdrawing or electron-donating properties, aromatic amides **1b-i** successfully reacted with $(PhSO_2)_2NH$ (2.4 equiv) in the presence of $PhI(OAc)_2$ (1.2 equiv) in DCM-HFIP at room temperature to give **2b-i** in 54-77% yields (entries 2-9). Also, the present method could be applied to the reactions of cinnamamide **1j** and aliphatic amides **1k**,**l** (entries 10-12). Notably, the sole use of DCM as a solvent improved the yields of **2d**,**e**,**l** by ca. 10% (entries 4, 5 and 12). On the other hand, in cases of internal alkynes **1m** and **1n**, the present methods in DCM-HFIP gave complex mixtures (Scheme 2). The reaction of **1m** in DCM led to the formation of the desired product **2m** in 21% yield along with ketone **6m** in 18% yield, whereas the reaction of **1n** provided **6n** as main product (41%). Furthermore, the treatment of **1a** with saccharin in the presence of $PhI(OAc)_2$ in 1,2-dichloroethane (DCE)-HFIP (3:1) afforded the desired product 7 in 60% yield, albeit under thermal conditions (Scheme 3, see Supporting Information for details).[14f,18]

Table 2. Reaction scope of *N*-propargyl carboxamides **1**.

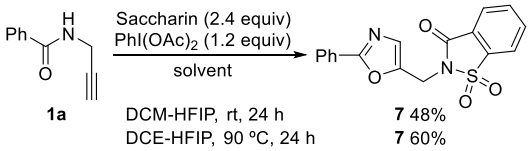


entry	**1**	R	time (h)	**2**	Yield (%)[a]
1	**1a**	Ph	8	**2a**	75 (66)
2	**1b**	2-ClC_6H_4	12	**2b**	72 (58)
3	**1c**	3-ClC_6H_4	12	**2c**	61 (61)
4	**1d**	4-ClC_6H_4	12	**2d**	59 (67)
5	**1e**	3-$NO_2C_6H_4$	12	**2e**	54 (62)
6	**1f**	4-$MeOC_6H_4$	8	**2f**	69 (55)
7	**1g**	4-MeC_6H_4	8	**2g**	75 (69)
8	**1h**	2-naphthyl	12	**2h**	77 (66)
9	**1i**	2-thienyl	12	**2i**	75 (51)
10	**1j**	(*E*)-styryl	8	**2j**	65 (47)
11	**1k**	^{t}Bu	8	**2k**	70 (59)
12	**1l**	$PhCH_2CH_2$	12	**2l**	44 (52)

[a] Isolated yield. Values in parentheses represent the yields in cases of DCM only as a solvent.



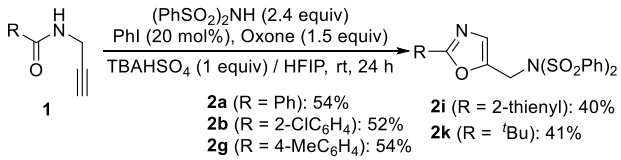
Scheme 2. Reactions of internal alkynes **1m** and **1n**.



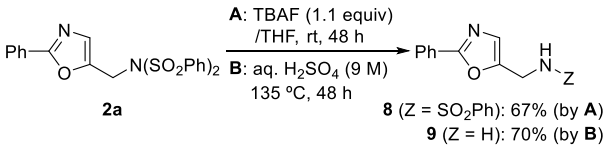
Scheme 3. Reaction of **1a** with saccharin.

To our delight, iodine(III) catalysts, which were *in situ* generated from PhI precatalysts (20 mol%) and

Oxone (1.5 equiv) in the presence of $TBAHSO_4$ (TBA: tetra-*n*-butylammonium, 1 equiv) in HFIP, were effective on the reactions of various amides **1** with $(PhSO_2)_2NH$ (2.4 equiv), thereby affording the corresponding oxazoles **2** in 40-54% yields (Scheme 4). Although *m*-chloroperoxybenzoic acid (*m*CPBA), which was employed in the iodine(III) catalysis of alkenyl amines with triflimide,[15a,19] worked as a terminal oxidant in the formation of **2a** (Supporting Information), **2a** could not be separated from byproduct. It should be mentioned that the deprotection of sulfonyl groups in the product **2a** could selectively lead to sulfonamide **8** and amine **9** (Scheme 5). Thus, **2a** was treated with TBAF in THF to give **8** in 67% yield (method **A**).[20a] Under acidic conditions at 135 ºC, **2a** was converted to **9** in 70% yield (method **B**).[10a,14f,20b]



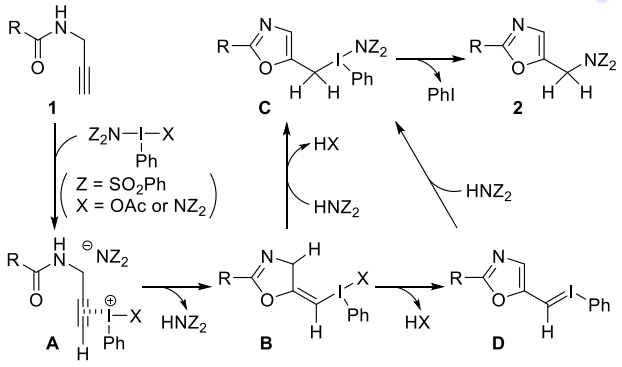
Scheme 4. Catalytic reactions of **1** with $(PhSO_2)_2NH$.



Scheme 5. Deprotection of sulfonyl groups.

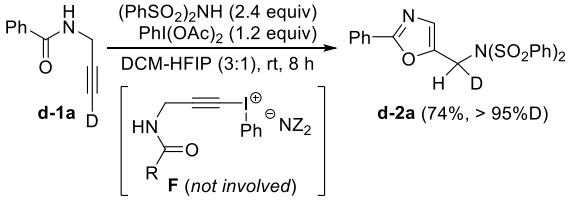
In order to gain additional information on the reaction mechanism, we carried out NMR studies using $PhI(OAc)_2$ and Ts_2NH in CD_2Cl_2 at room temperature (Fig. S-1, Supporting Information). $PhI(OAc)_2$ was treated with 1 equiv Ts_2NH for 30 min to afford a mixture of $PhI(OAc)_2$, $PhI(NTs_2)OAc$ and $PhI(NTs_2)_2$ in a ratio of 32:60:8. The similar results were reported by Minakata *et al*.[18e] $PhI(NTs_2)_2$ might be generated by the disproportionation of the main product, $PhI(NTs_2)OAc$. Furthermore, by the addition of 1 equiv Ts_2NH to the above-mentioned reaction mixture, the ratio was changed to 14:62:24. Thus, in both cases, $PhI(NTs_2)OAc$ and $PhI(NTs_2)_2$ were formed as a mixture.

On the basis of these observations and our previous reports about the I(III)-meditated cycloisomerization-functionalization sequence of *N*-propargyl amides,[17a,e] we proposed the reaction mechanism as shown in Scheme 6. That is, $PhI(NZ_2)X$ (Z = SO_2Ph, X = OAc and NZ_2), *in situ* generated from $PhI(OAc)_2$ and $(PhSO_2)_2NH$, would activate the triple bond of amides **1** to promote the cyclization of **1**. Subsequently, the formed intermediate **B** would be converted into the intermediate **C** via isomerization to oxazole ring by $(PhSO_2)_2NH$[21] and ligand exchange of OAc group. Alternatively, the intermediate **C** would be formed by the 1,4-elimination of HX in the intermediate **B** followed by the addition of $(PhSO_2)_2NH$ to the intermediate **D**. Finally, the reductive elimination of PhI in the intermediate **D** provides oxazoles **2** having nitrogen functional groups. The formation of ketones **6m** and **6n** from internal alkynes **1m** and **1n** might be due to low reactivities of intermediates like **B**, which would be more thermodynamically stable than less substituted **B**, for the isomerization to intermediates like **C** and **D**. Thus, the reductive elimination of PhI in the intermediates like **B** prior to the isomerization affords enemines and/or alkenyl ester, thereby leading to ketones **6m** and **6n** by hydrolysis during work-up (see Supporting Information for the details).



Scheme 6. Proposed reaction mechanism.

In the reactions of terminal alkynes using $PhI(NTs_2)OAc$, Muñiz *et al*. suggested the involvement of alkynyliodonium species as an intermediate.[16] Also, we proposed the alkynyliodonium intermediate like **F** (Scheme 7) would take part as a key intermediate as well as the intermediate like **A** in the cycloisomerization-acetoxylation of propargyl amides mediated by $PhI(OAc)_2$.[17a] However, the result of deuterium labelling experiment (Scheme 7) indicates no intervention of the intermediate **F** in the present reactions. Thus, the treatment of deuterated alkyne **d-1a** with $(PhSO_2)_2NH$ (2.4 equiv) in the presence of $PhI(OAc)_2$ (1.2 equiv) in DCM-HFIP under the optimized conditions afforded the deuterated oxazole **d-2a** in 75% yield without the detection of the undeuterated **2a**, which would be formed if alkynyliodane is involved.



Scheme 7. Deuterium labelling experiment.

In conclusion, we have developed a metal-free and direct synthesis of 5-[(*N*,*N*-disulfonylamino)methyl]-oxazoles based on the cycloisomerization–amination sequence of *N*-propargyl carboxamides with bis(sulfonyl)imides in the presence of $PhI(OAc)_2$. Also, this synthetic method could be successfully extended to the catalytic version by iodine(III) catalyst, which is *in situ* generated from iodobenzene precatalyst with Oxone as a terminal oxidant in the presence of $TBAHSO_4$ as a phase transfer reagent. Since such an introduction method of heteroatomic functional groups except for oxygen functional groups by iodine(III) catalysis have been less studied, our findings provide not only an attractive procedure for the access to the oxazoles bearing the nitrogen functional group, but also a new reactivity of the iodine(III) catalyst.

Experimental Section

Representative procedure for the cycloisomerization–amination of amide 1a with $(PhSO_2)_2NH$

$PhI(OAc)_2$ (154.6 mg, 0.48 mmol) was treated with $(PhSO_2)_2NH$ (285.4 mg, 0.96 mmol) in DCM-HFIP (3:1, 1.0 mL) at room temperature for 20 min. And then, to the reaction mixture was added a solution of **1a** (63.7 mg, 0.40 mmol) in DCM-HFIP (3:1, 1.0 mL). After being stirred at same temparature for 8 h, the reaction mixture was diluted with Et_2O and filtered through a short alumina column. Concentration of the filtrate to dryness and the subsequent purification of the residue by silica gel column chromatography (hexane/AcOEt = 3/1) gave **2a** (136.9 mg, 75%).

Representative procedure for the catalytic reaction of amide 1a with $(PhSO_2)_2NH$

To a suspension of Oxone (368.9 mg, 0.60 mmol) and $TBAHSO_4$ (135.8 mg, 0.40 mmol) in HFIP (2.0 mL) was added PhI (8.9 μL, 0.08 mmol), $(PhSO_2)_2NH$ (178.4 mg, 0.60 mmol) and **1a** (63.7 mg, 0.40 mmol) in turn at room temperature. After being stirred at same temperature for 24 h, the reaction mixture was diluted with Et_2O and filtered through a short alumina column. Concentration of the filtrate to dryness and the subsequent purification of the residue by silica gel column chromatography (hexane/AcOEt = 3/1) gave **2a** (98.6 mg, 54%).

Acknowledgements

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