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Imination of sulfoxides mediated by IBX with $Sc(OTf)_3$ as catalyst

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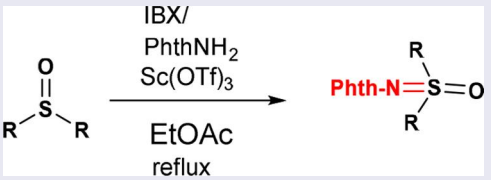
ABSTRACT

Herein we utilized, for the first time, 2-iodoxybenzoate along with scandium triflate as a specific oxidant for $PhthNH_2$ to create sulfoximines. This method efficiently effects imination of aryl, benzyl, cyclic and alkyl substituted S=O bonds with good to excellent yields. In addition, sterically encumbered sulfoxides have been studied and found that the present protocol is the worthy choice. This facile method does not require either inert atmosphere or anhydrous solvents.

GRAPHICAL ABSTRACT



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KEYWORDS
Hypervalent iodine; IBX; *N*-aminophthalimide; scandium triflate; sulfoximination

Introduction

Sulfoximines, monoaza analogs of sulfone, have widely been used as a structural constituent in pseudopeptides[1] and as building blocks for chiral ligands.[2] In 1992, Bolm et al., reported the application of sulfoximines as chiral ligands for enantioselective C–C bond formation reactions.[2a] In light of that, variety of successful applications of sulfoximines have been reported in asymmetric catalyzes such as Diels-Alder,[2b] hetero Diels-Alder,[2c,d] Mukaiyama aldol,[2e] ene-reaction,[2f,g] asymmetric hydrogenantion,[2h] and asymmetric allylation (Fig. 1).[2i]

In addition, recently, sulfoximines have gained great attention in drug discovery. They have been examined as antibiotics,[3a] tumor metastasis inhibitors[3b] and antithrombotics.[3c] Importantly, several sulfoximines derivatives exhibit improved bioactivity in the case of CDK inhibitor for,[3d] HIV-1 protease inhibitor,[3e] and as selective inhibitors of human neutrophil elastase (Fig. 2).[3f] Sulfoximine has also fascinated synthetic chemists[4] with its ability to stabilize the adjacent carbanions. Moreover, this

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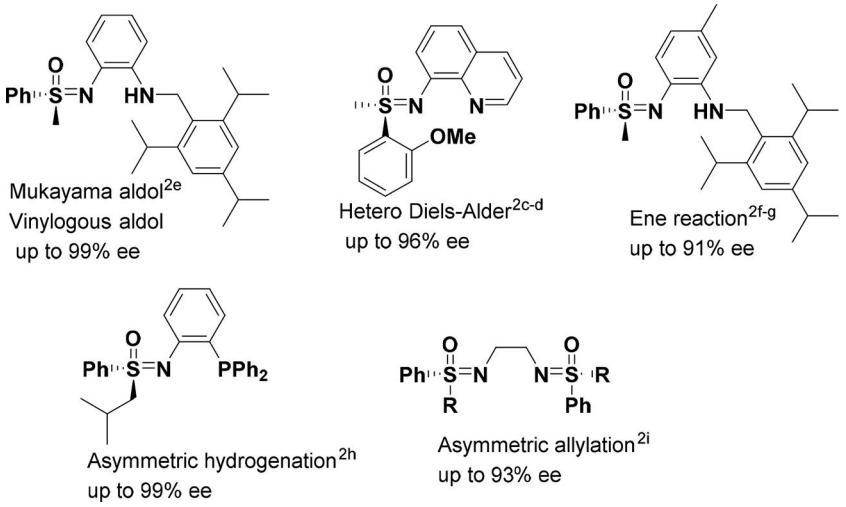


Figure 1. Structures of sulfoximine chiral ligands.

could serve as leaving group in the presence of nucleophiles. Based on these facts, the term *Chemical Chameleons* was coined.[4]

Number of methods to prepare sulfoximines have been reported. Different kinds of oxidants can be used for the oxidative sufloximination of sulfoxides such as *N*-tosylimino phenyl iodinane and catalytic CuOTf,[5a] $BocN_3$ with $FeCl_2$,[5b] *o*-mesitylene sulfonyl hydroxylamine,[5c] *N*-amino-substituted compounds with $Pb(OAc)_4$,[5d] TsN_3,[5e] and *tert*-butyl hypochlorite with aromatic amines.[5f] In 2004, Bolm et al. reported an efficient method to convert sulfoxides and sulfides into their corresponding sulfoximines and sulfilimines, respectively, using $Rh_2(OAc)_4$ as catalyst, trifluoroacetamide as the amine source and (diacetoxyiodo)benzene (DIB) in combination with MgO.[5g] Yudin et al. proposed an

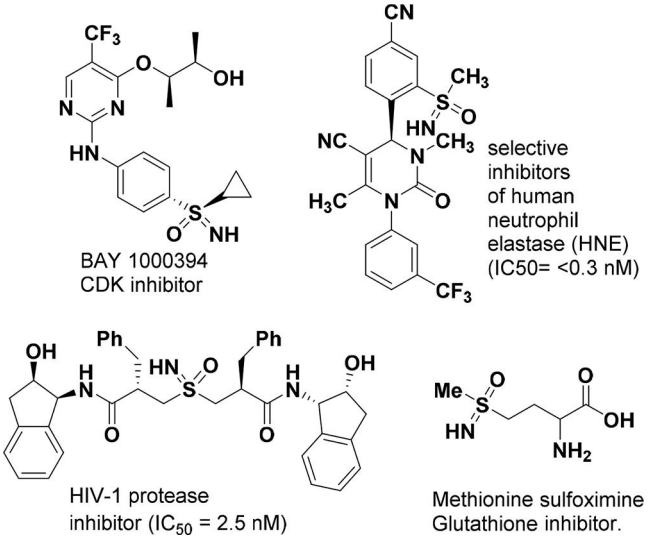
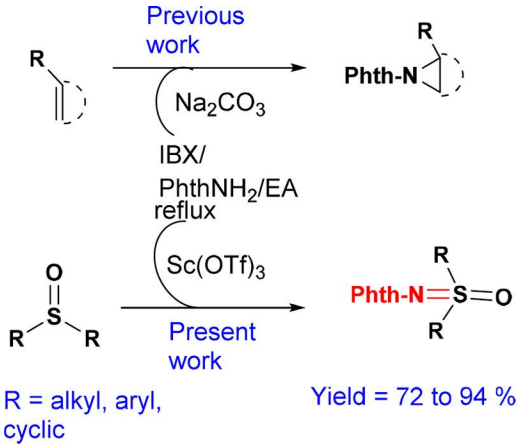


Figure 2. Structures of biologically important sulfoximine molecules.

electro chemical method on contrary to conventional chemical reaction to generate sulfoximines.[5h] They also reported the preparation of sulfoximine from sulfoxides using diacetoxy iodobenzene as oxidant and *N*-aminophthalimide as amine source.[5j]

Most of these methods involve toxic oxidants and/or toxic amine source and anhydrous conditions. In light of our continual focus on the total synthesis of various biologically important molecules,[6] we are in demand of alkylidene transfer reagent to prepare epoxide from ketone. Sulfoximines are the best choice for this requirement.[4a] Accordingly, it appeared necessary to develop a condition which is economic and eco-friendly. Therefore, the search for a new catalytic protocol without toxic oxidant and amine source, which is highly suitable for broad range of substrates such as aryl, alkyl and cyclic sulfoxides, continues to stimulate much thought from a synthetic point of view. 2-iodoxy benzoic acid (IBX),[7] an inexpensive,[7b] innocuous, readily available and stable oxidizing reagent evinces a plethora of applications in organic chemistry. In addition to IBX, its derivatives such as stabilized-IBX (SIBX), modified IBX (MIBX), TetrafluroIBX, Dess-Martin periodinane (DMP), and polystyrene supported IBX gained significant interest and demonstrate some useful transformations. Importantly, useful transformations have been reported by utilizing IBX with *N*-methyl morpholine[7c] and 2-hydroxypyridine (HyP).[7d] Recently we also explored aziridination of olefin using IBX with Na_2CO_3 (Scheme 1).[7e] Nevertheless, the reactivity of IBX with metal triflates are unfocused and it requires investigation. In light of our earlier invention,[7e] here we demonstrate an alternative method for making sulfoximine using $Sc(OTf)_3$ as a catalyst, IBX as oxidant and *N*-amino phthalimide as amine source that avoids usage of poisonous oxidants and amine source (Scheme 1). Importantly, Xue et al. investigated the effect of N–H bond dissociation energies of various amine sources with DIB as a oxidant. Interestingly, they were identified $PhthNH_2$ as one of the most preferable choice.[4h]

In this highly proliferating field, the emergence of a catalytic system with hypervalent iodine reagents to transfer nitrene has offered unique opportunities culminating with the development of new methods for simple and direct introduction of nitrogen into several substrates. In parallel, a catalytic system to introduce nitrogen to sulfoxides affords useful sulfoximines. Recently scandium triflate catalyzed functional group transformation



Scheme 1. Schematic illustration of our study toward the aziridination and sulfoximination.

reactions have been developed.[8] However, the present report offers a novel application of scandium triflate as a catalyst, which allows efficient imination of sulfoxides without formation of byproduct sulfone.

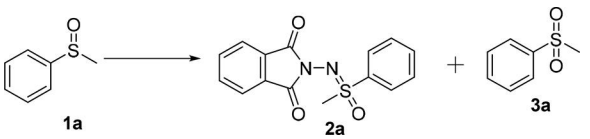
Results and discussion

For the initial screening and optimization, we chose methylphenyl sulfoxide (**1a**) as substrate and a nitrogen source generated *in situ* from $PhthNH_2$. For exploring iodine (V) reagents mediated sulfoximination reaction conditions, we carefully examined the reaction of **1a** and $PhthNH_2$ with a broad range of oxidants for instance, SIBX (Table 1, entry 1), DMP (entry 2), IBX-HyP (entry 3), IBX (entry 4), IBX-Na_2CO_3 (entry 5), and IBX-NMO (entry 6). Inspection of optimization entries 1–6 (Table 1) unveils that the intermolecular sulfoximination of **1a** with IBX as oxidant is the best choice than other iodine (v) reagents or their combinations.

In addition, in the search to find efficient and selective conjugate base we examined various bases such as TEA (entry 7), pyridine (entry 8), DBU (entry 9), DMAP (entry 10), and K_2CO_3 (entry 11). Unlike our aziridination method,[7e] we did not observe the expected product in the presence of base (entries 5–11). We found that the addition of a base slows this transformation. Furthermore, we also investigated the utilization of various solvents at different temperatures to improve reaction yield. Previously reported sulfoximination methods predominantly used toxic halogenated solvents. We found that, among various solvents examined, ethyl acetate (EtOAc) is the most effective.

Moreover, we examined the addition of acidic additives (Table 2, entries 1–9). It does not improve the yield at a satisfactory level, in this S-N bond formation. On contrary,

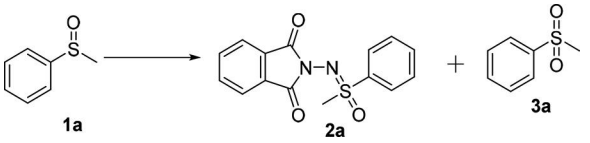
Table 1. Optimization of reaction conditions for sulfoximination of sulfoxide **1a**.[a]



Entry	Oxidant (equiv.)	$PhthNH_2$ (equiv.)	Solvent	Hours	Additives	Yield[b] **2a** (%)	Yield[b] **3a** (%)
1	SIBX (2.8)	3	CH_2Cl_2	16	–	14	16
2	DMP (2.8)	3	CH_2Cl_2	12	–	17	9
3	IBX-HyP (2.8)	3	CH_2Cl_2	24	–	7	13
4	IBX (2.8)	3	CH_2Cl_2	24	–	39	6
5	IBX-Na_2CO_3 (2.8)	3	CH_2Cl_2	24	–	–	–
6[c]	IBX-NMO (2.8)	3	CH_2Cl_2	24	–	–	Trace
7[c]	IBX (2.8)	3	CH_2Cl_2	16	TEA	–	–
8[c]	IBX (2.8)	3	CH_2Cl_2	16	Pyridine	–	–
9[c]	IBX (2.8)	3	CH_2Cl_2	16	DBU	–	–
10[c]	IBX (2.8)	3	CH_2Cl_2	16	DMAP	–	–
11[c]	IBX (2.8)	3	CH_2Cl_2	16	K_2CO_3	–	–
12	IBX (2.8)	3	EtOAc	16	–	63	16
13	IBX (2.8)	3	can	16	–	44	20
14	IBX (2.8)	3	1,4-dioxane	16	–	29	15

[a]Reactions were performed in 1 mmol scale.
[b]Isolated yield.
[c]Reaction was performed with 2.8 equiv. of base.
DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DMAP, 4-dimethylaminopyridine; DMP, Dess-Martin periodinane; IBX, 2-iodoxy benzoic acid; SIBX, stabilized IBX; TEA, triethylamine.

Table 2. Optimization of reaction conditions for sulfoximination of sulfoxide **1a**.[a]



Entry	IBX (equiv.)	$PhthNH_2$ (equiv.)	Hours	Additives	Yield[b] **2a** (%)	Yield[b] **3a** (%)
1	2.8	3	12	SiO_2	67	12
2	2.8	3	1	SiO_2, H_2O, HCl	Decompose	–
3	2.8	3	14	$MgSO_4$	44	21
4	2.8	3	8	TFA (0.1 equiv.)	33	20
5	2.8	3	6	TFA (1.0 equiv.)	46	16
6	2.8	3	3	TMSCl	17	10
7	2.8	3	16	Ac_2O	32	17
8	2.8	3	16	TFAA	12	10
9	2.8	3	16	$Yb(OTf)_3$	49	7
10	2.8	3	16	$In(OTf)_3$	55	5
11	2.8	3	13	AgOTf	69	9
12	2.8	3	76	$Cu(OTf)_2$	69	11
13	2.8	3	48	$Ln(OTf)_3$	69	10
14	2.8	3	26	$Yb(OTf)_3$	69	8
15	2.8	3	19	TfOH (0.1 equiv.)	69	10
16	2.8	3	6	TfOH (0.5 equiv.)	69	7
17	2.8	3	36	$Sc(OTf)_3$	76	Trace
18	IBX (0.7 × 3)	0.8 × 3	15 + 6	$Sc(OTf)_3$	84	–

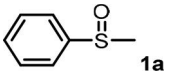
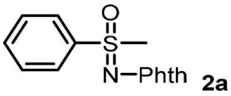
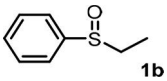
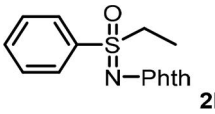
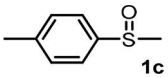
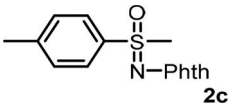
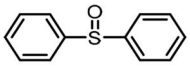
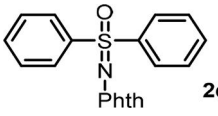
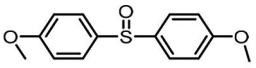
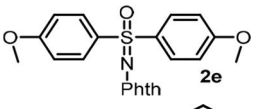
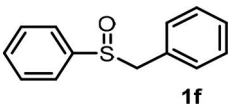
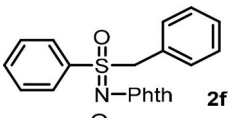
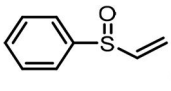
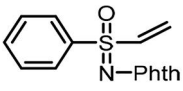
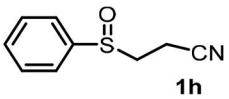
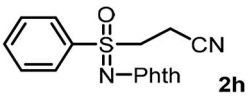
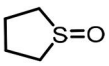
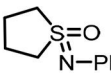
[a]Reactions were performed in 1 mmol scale in EtOAc.
[b]Isolated yield.
IBX, 2-iodoxy benzoic acid; TFA, trifluoroacetic acid.

the addition of metal triflate shows significant improvement in product (**2a**) formation and reduction of yield in sulfone (**3a**) formation (entries 10–16). Interestingly, $Sc(OTf)_3$ highly enhances the reactivity and selectivity of this system. Importantly, addition of 10 mol% of $Sc(OTf)_3$ greatly reduced the formation of undesired sulfone. Treatment of **1a** with IBX (2.8 equiv.), $PhthNH_2$ (3 equiv.) and $Sc(OTf)_3$ (10 mol%) in EtOAc (entry 17) produced the desired adduct **2a** with 76% isolated yield. Gratifyingly, the reaction yield was further increased by the lot wise addition of IBX and $PhthNH_2$. We found that, reacting **1a** with IBX (0.7 × 3 equiv.), $PhthNH_2$ (0.8 × 3 equiv.), and $Sc(OTf)_3$ (7.5 mol%) in EtOAc (entry 18) produced the desired adduct **2a** with 84% isolated yield without formation of undesired sulfone. Importantly, either reducing or increasing the concentration of this reaction leads to diminutive yield. We also got discontented results while increasing or decreasing the equivalents of IBX, $PhthNH_2$, and $Sc(OTf)_3$.

Having established this ripest novel sulfoximine procedure, its generality with respect to the structure of sulfoxides was investigated. We were delighted to find that the chemistry was suitable for a diverse range of sulfoxides. Its applicability to the imination of more challenging substrates such as sulfoxides bearing benzylic, alkyl, vinyl, and nitrile substituents (Table 3) were found to be excellent. In other words, functional group tolerance is excellent in this protocol. In general, aryl substituted sulfoxides were found to have proceeded better than other kinds of sulfoxides.

Exposing **1a** and **1b** to the $Sc(OTf)_3$/IBX/$PhthNH_2$ system gave 84 and 82% yield of **2a** and **2b**, respectively (Table 3, entries 1 and 2). The sulfoximination reaction of methylphenyl sulfoxide directly scales up; thus, sulfoximine **2a** was obtained with 81%

Table 3. Scandium triflate catalyzed sulfoximination of sulfoxide.[a]

Entry	Substrate	Product	Yield[b]
1	 **1a**	 **2a**	84 81[c]
2	 **1b**	 **2b**	82
3	 **1c**	 **2c**	86
4	 **1d**	 **2d**	91
5	 **1e**	 **2e**	94
6	 **1f**	 **2f**	84
7	 **1g**	 **2g**	79
8	 **1h**	 **2h**	72
9	 **1i**	 **2i**	81
10	 **1j**	 **2j**	78

[a]All the reactions were performed in 1 mmol scale at reflux temperature.
[b]Isolated yield.
[c]Reaction was performed in 10 mmol scale.

yield on a 10-mmol scale (entry 1). Presence of activating groups over aryl ring influences the reactivity of sulfoxides. For example, due to the presence of a methyl group on aryl ring, the formation of sulfoximine was found to be better in methyl-*p*-methylphenyl sulfoxide (**1c**) than methylphenyl sulfoxide (**1b**) (entries 1 and 3). Similar trend was observed in the case of diphenyl sulfoxide (**1d**) and di-*p*-methoxypheyl sulfoxide (**1e**) (entries 4 and 5). Interestingly, the presence of a coordinating group, for instance, a methoxy group did not inhibit the reaction, and sulfoximine **2e** was obtained with excellent yield (entry 5). Sulfoximination onto benzyl phenyl sulfoxide (**1f**) was also found to be effective (entry 6). In the case of phenyl vinyl sulfoxide **1g** (entry 7), no aziridination product was observed, indicating the possibility of achieving chemo selective nitrene equivalent transfer to the sulfoxide moiety. To further ascertain the viability of this system, the

sulfoxide **1h** was studied under optimum conditions and gave desired product **2h** (entry 8). With an eye on extending these observations to other kinds of sulfoxides, we explored the sulfoximination of acyclic and cyclic sulfoxides. Either dimethyl sulfoxide **1i** or tetramethylene sulfoxide **1j** reacted efficiently with $Sc(OTf)_3$/IBX/$PhthNH_2$ derived sulfoximination reagent to render 81% and 78% yield of the desired sulfoximination adducts **2i** and **2j**, respectively (Table 3, entries 9 and 10). Many of the products (Table 3) were found to yield higher than the previously reported procedures. Left unanswered by this proposal is the specific oxidizing property of IBX-$Sc(OTf)_3$ toward amine over sulfoxide. Further mechanistic insights are clearly required before any definite conclusion can be reached.

Conclusion

We have developed and demonstrated a simple and straightforward method, based on the novel combination of $Sc(OTf)_3$/IBX/$PhthNH_2$, for preparing sulfoximines from sulfoxides. We have extended our hypervalent Iodine mediated nitrogen transfer methodology to the synthesis of sulfoximines from sulfoxides. Sulfoxides can also be used as a nucleophilic trap for the *in situ* generated nitrene equivalent. In total, the rational approach described here for the formation of sulfoximines from sulfoxides has several advantages over the previously reported procedures. The reagents involved are easy to handle, mild, nonexplosive, and stable toward atmospheric moisture and oxygen. Thus, neither an inert atmosphere nor anhydrous reagents are demanded. Further mechanistic insights are certainly necessary to understand the role of $Sc(OTf)_3$ with IBX, which facilitates the formation of sulfoximine over sulfone. In addition, novel reactivity of IBX with Lewis acid opened the gates of multifarious chemistry, those are the subject of ongoing research.

Experimental section

General procedure for sulfoximination of sulfoxides

$Sc(OTf)_3$ (0.075 mmol) was added to the suspension of IBX (0.75 mmol) and $PhthNH_2$ (0.8 mmol) in EtOAc (4 mL) under nitrogen atmosphere. After stirring for 10 min at rt, sulfoxide (1 mmol) was added. The RM was stirred at reflux for 3 h, allowed to reach rt. IBX (0.75 mmol) and $PhthNH_2$ (0.8 mmol) were added to RM and stirred at reflux for 5 h, allowed to reach rt. IBX (0.75 mmol) and $PhthNH_2$ (0.8 mmol) were added to RM and stirred at reflux for 13 h, allowed to reach rt. The RM was quenched with saturated solution of Na_2CO_3. The separated organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using Hexane: EA (2.5:1) to afford sulfoximine.

Acknowledgments

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