

## Sulfoximidation

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## Synthesis of Sulfoximidoyl-Containing Hypervalent Iodine(III) Reagents and Their Use in Transition-Metal-Free Sulfoximinations of Alkynes

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Dedicated to Professor K. Barry Sharpless on the occasion of his 75th birthday

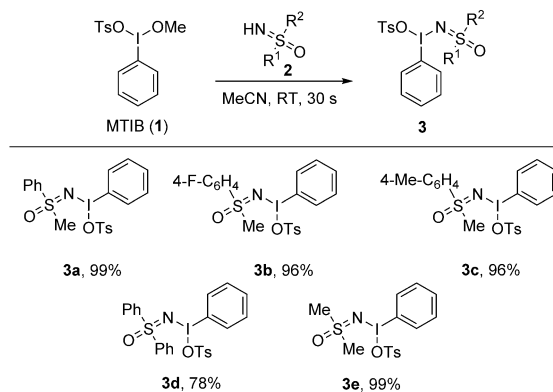
**Abstract:** Well-defined hypervalent iodine(III) reagents incorporating transferable sulfoximidoyl groups were obtained through ligand exchange reactions of methoxy-(tosyloxy)iodobenzene (MTIB) with NH sulfoximines in good to excellent yields. The solid-state structure of a representative product was characterized by X-ray crystallography. Utilizing these reagents in synthesis provides a new, transition-metal-free approach towards *N*-alkynylated sulfoximines.

Hypervalent iodine(III) compounds are attractive reagents for preparative organic chemistry.<sup>[1,2]</sup> The use of nitrogen-containing derivatives has led to valuable synthetic methods for oxidative intermolecular carbon–nitrogen bond forming processes. In this context, azidoiodanes have been utilized for the introduction of azido groups,<sup>[3]</sup> and iodonium imides (ArIN=R) have been applied as nitrene precursors in catalytic aziridinations and metal-free amination reactions.<sup>[4]</sup> Various methods for the use of amidoiodanes are known, and they often involve in situ preparation of the reagent.<sup>[5]</sup> In 2011, Muñiz and co-workers reported oxidative diaminations of alkenes through utilizing hypervalent iodine(III) species containing a bisulfonimide group.<sup>[6]</sup> Although, the reactive amidoiodane was generated in situ, a hypervalent iodine(III) species could be characterized by X-ray crystallography, thus indicating the existence of a I<sup>III</sup>–N covalent bond. Soon afterwards, the same group isolated analogous reagents with the general formula PhI(OAc)N(SO<sub>2</sub>R)(SO<sub>2</sub>R') and applied them in direct aminations of acetylenes and in allylic aminations.<sup>[7]</sup> Recently, Kiyokawa, Minakata, and co-workers utilized hypervalent iodine(III) reagents containing a phthalimide group for the oxidative amination of *N,N*-dimethylanilines, trialkylamines, and enamines.<sup>[8]</sup>

Sulfoximines are important compounds for asymmetric synthesis, crop protection, and medicinal chemistry.<sup>[9]</sup> Finding new synthetic approaches towards such compounds and modifying existing structures with sulfoximidoyl motifs has long been a focus of our research.<sup>[10]</sup> In this context, we have introduced various catalytic and metal-free methods for

oxidative sulfoxide-to-sulfoximine conversions with hypervalent iodine reagents as key reaction components.<sup>[4d,11–13]</sup> We now conceived the application of our expertise in sulfoximine chemistry to the development of novel hypervalent iodine(III) reagents with the aim of producing compounds with transferable sulfoximidoyl groups. A proof-of-concept study is reported herein.

Inspired by reported procedures,<sup>[8,14]</sup> a ligand-exchange approach was envisaged for accessing the target compounds. Various iodobenzoacetates and tosylates with acetate, hydroxy, or chloro substituents were treated with NH-sulfoximine **2a** (2 with R<sup>1</sup> = Me, R<sup>2</sup> = Ph) as nucleophiles, but none of these attempts led to success (see Table S1 in the Supporting Information). To our delight, however, **2a** reacted with methoxy-(tosyloxy)iodobenzene (MTIB, **1**)<sup>[15]</sup> in acetonitrile to afford the desired product **3a** as a precipitate in essentially quantitative yields (99%) within 30 s at room temperature (Scheme 1). The same reactivity was observed



**Scheme 1.** Syntheses of hypervalent iodine reagents **3**.

with other NH sulfoximines, leading to the corresponding hypervalent iodine(III) compounds **3b–e** in high to excellent yields (Scheme 1). Notably, the reaction of **1** and **2a** could be scaled up (to 15 g) without affecting the outcome (quantitative yield of **3a**).

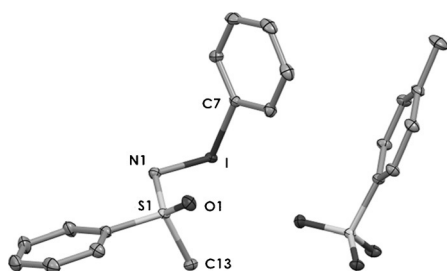
NMR spectroscopy revealed that products **3** were stable compounds that could be stored in the solid state or in solution at ambient temperature over an extended period of time (see the Supporting Information). Good solubility was observed in halogenated and highly polar solvents such as dichloromethane, water, and DMSO. In acetonitrile, compounds **3** were only slightly soluble, and toluene, ethyl acetate,

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THF, and acetone proved unsuited as solvents. These observations suggest an ionic nature of **3a**. This notion was supported by results from  $^1\text{H}$  NMR spectroscopy, which showed a significantly downfield-shifted signal for the sulfoximine methyl group protons resulting from the presence of a strong electron-withdrawing substituent at the imine nitrogen.

Single-crystal X-ray diffraction analysis of compound **3a** (Figure 1)<sup>[16]</sup> provided unambiguous evidence for the proposed structure and revealed important molecular details. First, it confirmed the presence of an  $\text{I}^{\text{III}}\text{--N}$  covalent bond.

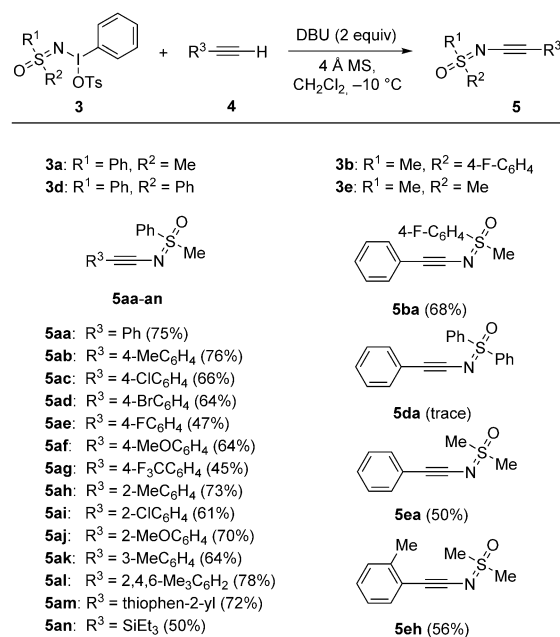


**Figure 1.** X-ray crystal structure of **3a** in the solid state (thermal ellipsoids are drawn at 50% probability). Selected bond lengths [Å] and angles [°]: I–C7 2.097(1), I–N1 2.016(1), S1–N1 1.561(1); C7–I–N1 95.43(4), O1–S1–N1 120.43(6), C13–S1–N1 112.55(6).

The experimental N–I distance of 2.016(1) Å for **3a** in the solid state was not too different from that of 2.126 Å calculated for the isolated molecule by using the DGDZVP basis set and inclusion of the correlation energy by employing the MP2 method.<sup>[17]</sup> A striking feature of the solid-state structure of **3a** was the short distance between the iodine atom and one oxygen atom of the tosyl group of 2.6326(9) Å. Since the van der Waals radii of iodine and oxygen are given as 2.15 Å<sup>[18a]</sup> and about 1.5 Å,<sup>[18b]</sup> the measured distance clearly indicates a bonding interaction between the oxygen atom of the tosyl moiety and the iodine atom. This distance was even reduced to 2.318 Å when **3a** was subjected to structural optimization with the DGDZVP basis set. An NBO analysis<sup>[19]</sup> of the DGDZVP wave function resulted in two subunits for the molecule, OTs (**A**) and PhMeS(O)NI (**B**), with no significant covalent bonding between them. The strongest second-order interaction<sup>[20]</sup> between **A** and **B** of  $-43 \text{ kcal mol}^{-1}$  occurred between a lone pair of an oxygen atom of the OTs group and the antibonding orbital of the N–I bond of **B**. Much weaker ( $-4.2 \text{ kcal mol}^{-1}$ ) was the second-order interaction between the same lone pair and the C–I antibond. Additional geometry optimizations were then performed for subunits **A** and **B** at the MP2/DGDZVP level, which led to an energy of formation of **3a** from **A** and **B** of  $-101.7 \text{ kcal mol}^{-1}$ . Summation of the natural atomic charges of **A** and **B** resulted in a significant charge separation, with  $-0.86\text{e}$  for **A** and a corresponding positive charge for **B**. Based on the lack of significant covalent bonding and only small second-order interactions between **A** and **B**, we concluded that bonding between the subunits is mostly through electrostatic (coulombic) interactions.<sup>[21]</sup>

In 2013, we reported the first synthesis of *N*-alkynylated sulfoximines (“yne-sulfoximines”), and since then, the synthetic chemistry related to such compounds has steadily been progressed.<sup>[22]</sup> To date, all preparative approaches have involved copper catalysis. In light of the findings by Muñiz and co-workers, who found that hypervalent iodine(III) reagents with bisulfonimido substituents [such as  $\text{ArI}(\text{OAc})\text{N}(\text{SO}_2\text{R})_2$ ] couple with alkynes to give yne-amides,<sup>[7b]</sup> we wondered about analogous reactions with compounds **3**. If successful, a new, metal-free access to yne-sulfoximines through  $\text{C}_{\text{sp}}\text{--N}$  coupling can be foreseen.

For testing the hypothesis, iodine reagent **3a** and phenylacetylene **4a** were chosen as representative starting materials. After significant optimization, the intended coupling could indeed be realized (Scheme 2). Under the optimized reaction

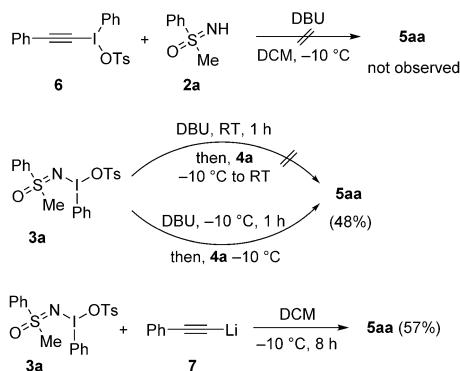


**Scheme 2.** Syntheses of *N*-alkynylated sulfoximines from alkynes and **3**.

conditions (see the Supporting Information), *N*-alkynylated sulfoximine **5aa** was obtained in 75% yield. Without 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), no reaction occurred. Analogously, other aryl alkynes reacted with **3a**. On the phenylacetylenes, both electron-donating and electron-withdrawing substituents were tolerated, affording the corresponding yne-sulfoximines **5aa–5al** in moderate to good yields. The position and number of substituents at the phenyl group of the alkyne did not significantly affect the yield of the process. Acetylenes **4m** and **4n**, which carry a thiophen-2-yl and triethylsilyl group, respectively, led to the corresponding *N*-alkynylated products in 72% (**5am**) and 50% (**5an**) yield. Aliphatic alkynes did not react. Next, the sulfoximidoyl portion of the iodine(III) reagent was structurally varied. Utilizing **3b** and **3e** as coupling partners for phenylacetylene **4a** led to the corresponding products in good yields (**5ba**: 68%, **5ea**: 50%, and **5eh**: 56%). To our surprise, **3d**, which

has an *S,S*-diphenylsulfoximidoyl substituent, did not participate in the reaction.

In order to elucidate the mechanism of the coupling process, a number of control experiments were performed. First, the intermediacy of an alkynyl iodine(III) compound (**6**)<sup>[23]</sup> was tested (Scheme 3, top). However, subjecting

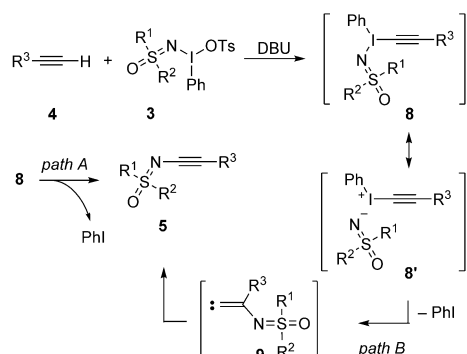


**Scheme 3.** Mechanistic investigations.

preformed **6** to a solution of **2a** in dichloromethane in the presence of DBU (1 equiv) at  $-10^{\circ}\text{C}$  did not lead to product **5aa**, and the starting material **2a** was fully recovered. We can thus exclude compound **6** as intermediate in the reaction process.

Stirring **3a** in the presence of DBU for 1 h at room temperature followed by addition of **4a** at  $-10^{\circ}\text{C}$  and subsequent warming to room temperature led to complete decomposition of the iodine reagent (Scheme 3, middle). Performing the entire experiment at  $-10^{\circ}\text{C}$  allowed the isolation of **5aa** in 48% yield. These results reveal that **3a** is sensitive to base at elevated temperature and indicate that the role of DBU is related to the deprotonation of **4a** (proceeding at  $-10^{\circ}\text{C}$ ), thereby increasing the nucleophilicity of this coupling partner.<sup>[24]</sup> This hypothesis was confirmed by applying the alkynyl lithium species **7** in the reaction with **3a** (in DCM at  $-10^{\circ}\text{C}$ ), which led to **5aa** in 52% yield after 6 h (Scheme 3, bottom).

Based on these observations and literature precedence, we propose the mechanism depicted in Scheme 4. The process is initiated by deprotonation of alkyne **4** by DBU. The



**Scheme 4.** Possible reaction pathways.

resulting anion reacts with iodine(III) reagent **3** to give an intermediate of type **8**. Subsequent expulsion of phenyliodide gives product **5**. With respect to the last step, two reaction paths can be considered. Either it occurs by direct ligand–ligand coupling under loss of PhI (path A), or it proceeds via alkylidenecarbene **9** generated from ionic species depicted as **8'** (path B).<sup>[25]</sup>

In summary, we prepared novel sulfoximidoyl-containing hypervalent iodine(III) salts and characterized their structural properties by X-ray crystal structure analysis, NMR spectroscopy, and DFT calculations. Furthermore, their reactivity was studied in transformations with alkynes and their use led to *N*-alkynylated sulfoximines through an unprecedented transition-metal-free route.

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**Keywords:** alkynes · amidation · hypervalent iodine(III) · sulfoximination · sulfoximine

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