Zitierweise: *Angew. Chem. Int. Ed.* **2024**, *63*, e202413181
doi.org/10.1002/anie.202413181

Synthetic Methods | Hot Paper

Mechanochemical Conditions for Intramolecular N–O Couplings via Rhodium Nitrenoids Generated from *N*-Acyl Sulfonimidamides

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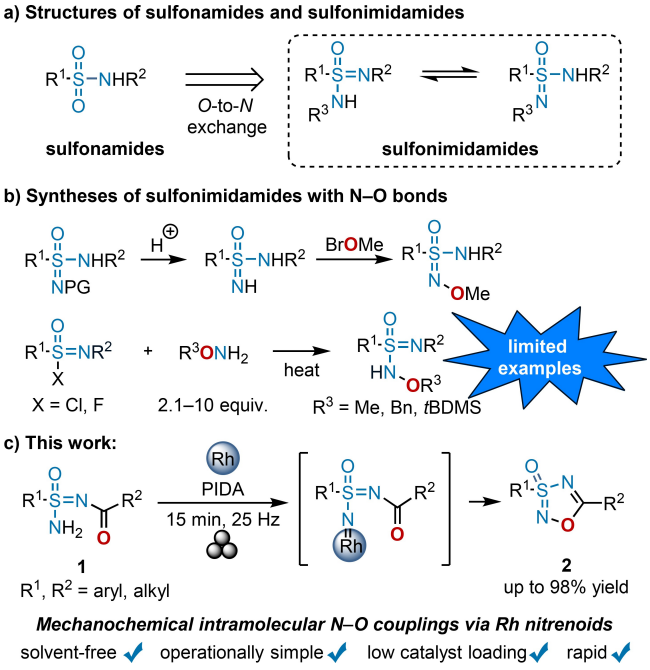
Abstract: Starting from *N*-acyl sulfonimidamides, mechanochemically generated rhodium nitrenoids undergo intramolecular N–O couplings to provide unprecedented 1,3,2,4-oxathiadiazole 3-oxides in good to excellent yields. The cyclization proceeds efficiently with a catalyst loading of only 0.5 mol% in the presence of phenyliodine(III) diacetate (PIDA) as oxidant. Neither an inert atmosphere nor additional heating is required in this solvent-free procedure. Under heat or blue light, the newly formed five-membered heterocycles function as nitrene precursors reacting with sulfoxides as exemplified by the imidation of dimethyl sulfoxide.

Sulfonimidamides, the aza-analogues of sulfonamides, have recently garnered significant interest due to their wide applicability in organic synthesis,[1] and chemistry related to medicine[2] and agriculture.[3] Potential variations of the substituents at the sulfur core and the two nitrogens lead to a great structural diversity of sulfonimidamides resulting in a wide range of adjustable chemical, physical, and biological properties.

While the construction of N–O bonds has been extensively studied for accessing compounds such as isoxazolidines,[4] isoxazoles,[5] and oxadiazoles,[6] analogous transformations of sulfonimidamides leading to heterocyclic products are unknown. For the preparation of acyclic sulfonimidamides with N–O bonds, two strategies have been developed (Scheme 1b). However, both of them have remained rather underexplored. The first one can be found in a patent, where methyl hypobromite was employed as a methoxy source to react with deprotected sulfonimidamides.[7] The second, more common approach starts from sulfonimidoyl halides which undergo substitutions with N–OR-type nucleophiles.[8] Apparently, the latter sequence is attractive because it circumvents the challenging direct N–O bond formation but typically it requires the use of excessive amounts of nucleophiles and a high reaction temperature. Furthermore, only methyl-, benzyl-, and *tert*-butyldimethylsilyl(*t*-BDMS)-substituted hydroxylamines have yet been applied.



Scheme 1. a) Core structures. b) General synthetic strategies to access sulfonimidamides with N–O bonds. c) Oxidative N–O couplings of *N*-acyl sulfonimidamides under mechanochemical conditions.

The nucleophilic attack of amines to electrophilic nitrenes has emerged as a promising N–N coupling strategy for the preparation of hydrazides under transition-metal catalysis.[9] In contrast, the analogous N–O bond formation involving a nitrene or nitrenoid intermediate is relatively unexplored.[10] In general, such studies focus on the use of vinyl nitrenes generated from 2*H*-azirines, providing isoxazoles[10a–d] and oxime ethers[10e–h] by ring expansion and intermolecular addition reactions, respectively. Oxidants, particularly hypervalent iodine reagents, were found to promote the formation of isoxazoles via nitrene or nitrenium ion pairs.[11] Independently, Dauban and Malacria identified sulfonimidamides with NH_2 substituents at sulfur as efficient nitrenoid precursors with attractive applications in rhodium-

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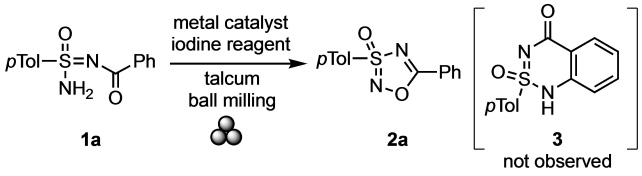
catalyzed C–H aminations,[12] olefin aziridinations,[13] and sulfur iminations.[14]

Mechanochemical synthesis is a promising tool in organic chemistry, offering several advantages over traditional solution-phase methods.[15] These include the solvent-free and air-insensitive nature of the process and the potential for higher or alternative chemoselectivity. Recently, we reported an efficient iron-catalyzed mechanochemical approach to synthesizing *N*-acyl sulfonimidamides **1** from sulfinamides and dioxazolones.[16] While exploring the product reactivity under such less common mechanochemical conditions we discovered a so far unreported reaction path of sulfonimidamide-derived rhodium nitrenoids leading to unprecedented heterocycles by intramolecular N–O bond formation (Scheme 1c). The results of this study are presented here.

The discovery was made while studying mechanochemical transformations of *N*-[amino(oxo)(*p*-tolyl)-λ^6-sulfaneylidene] benzamide (**1a**). Those experiments were carried out in a 10 mL stainless steel jar with a 10 mm stainless steel ball in a mixer mill at 25 Hz for 60 min, and following previous observations,[16,17] talcum was added as a lubricant. Milling of **1a** in the presence of PIDA was hypothesized to generate an iminoiodinane-type intermediate, which we expected to undergo intramolecular C(sp^2)–H amination[18] to yield heterocycle **3** (Table 1). However, neither in the absence nor in the presence of a (Rh or Cu) catalyst did such cyclization occur, and product **3** was never detected. Instead, to our surprise, five-membered heterocycle 1,3,2,4-oxathiadiazole 3-oxide **2a** was formed.

Table 1: Optimization of the reaction conditions.[a]



Entry	Metal catalyst	Iodine reagent[c]	Milling time [min]	Yield of **2a** [%][b]
1	–	PIDA	60	33
2	–	PIFA	60	trace
3	–	PhIO	60	21
4	$Rh_2(OAc)_4$	PIDA	60	60
5	$Rh_2(OCOC_3F_7)_4$	PIDA	60	19
6	$Rh_2(esp)_2$	PIDA	60	63
7	$Rh_2(Oct)_4$	PIDA	60	83
8	$[Cp^*RhCl_2]_2$	PIDA	60	18
9	$Cu(OTf)_2$	PIDA	60	trace
10[d]	$Rh_2(Oct)_4$	PIDA	60	87
11[e]	$Rh_2(Oct)_4$	PIDA	60	87
12[e]	**$Rh_2(Oct)_4$**	**PIDA**	**15**	**89**
13[e]	$Rh_2(Oct)_4$	PIDA	5	87
14[e]	$Rh_2(Oct)_4$	–	15	0
15[e,f]	$Rh_2(Oct)_4$	PIDA	15	79

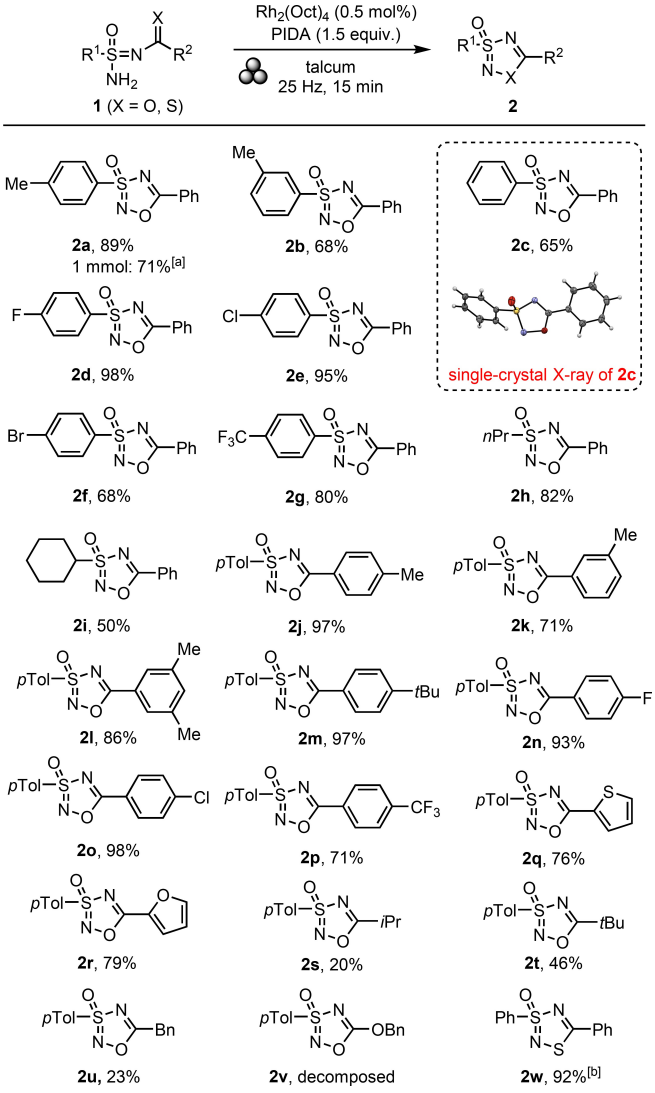
[a] Reaction conditions: **1a** (0.2 mmol), iodine reagent (0.3 mmol, 1.5 equiv.), metal catalyst (3 mol%), and talcum (60 mg) were added into a stainless steel jar (10 mL) with one stainless steel ball (diameter: 10 mm, weight: ca. 3.5 g) under air and milled at 25 Hz for 5–60 min. [b] After chromatography. [c] PIDA: phenyliodine(III) diacetate. PIFA: phenyliodine bis(trifluoroacetate). [d] Use of 1 mol% of rhodium catalyst. [e] Use of 0.5 mol% of rhodium catalyst. [f] Without talcum.

In the initial experiments (Table 1, entries 1–3), no metal catalyst was added, and as oxidants, PIDA, PIFA, and PhIO (1.5 equiv.) were used. In each case, **2a** was formed, but the amounts varied from a trace (for PIFA) to a yield of 33% for PIDA. With the intention to optimize the PIDA-based process, various metal catalysts (in 3 mol% quantities) were applied. Rhodium catalysts proved to be most effective, leading to **2a** in yields ranging from 18% to 83% (Table 1, entries 4–8). In this series, the best result was obtained with $Rh_2(Oct)_4$ as catalyst, while $Cu(OTf)_2$ gave only a trace amount of the product (Table 1, entries 7 and 9). Reducing the catalyst loading from 3 mol% to 1 mol% or 0.5 mol% did not significantly decrease the yield of **2a**. Hence, in the subsequent screening experiments 0.5 mol% of $Rh_2(Oct)_4$ was used. Varying the reaction times showed that the transformation was very fast during the initial five minutes and complete after 15 minutes (Table 1, entries 12 and 13). This is consistent with results from $^{19}F\{^1H\}$ NMR studies where the reaction was conducted in a deuterated solvent (for further details, see the Supporting Information). No product was formed in the control experiment without the iodine reagent, confirming the indispensable role of the oxidant (Table 1, entry 14). Without the addition of talcum, the yield of **2a** dropped from 89% to 79% (Table 1, entry 15).

With the optimized mechanochemical conditions in hand, the scope of the reaction was investigated. The results are summarized in Scheme 2.

First, *S*-aryl sulfonimidamides with various substituents on the *S*-arene were explored. In addition, all compounds had an unsubstituted *N*-benzoyl group. In each case, the corresponding 1,3,2,4-oxathiadiazole 3-oxide **2a–g** was obtained in a good to excellent yield. Sulfonimidamide **1a** with an electron-donating methyl group at the *para*-position afforded the product (**2a**), in a higher yield (89%) than compound **1b** with a methyl group at *meta*-position, which gave **2b** in 68% yield. When *S*-phenyl sulfonimidamide **1c** was applied, **2c** was obtained in 65% yield. The molecular structure of **2c** was confirmed by single-crystal X-ray diffraction and is depicted in Scheme 2.[19] *S*-Arenes with electron-withdrawing substituents (**1d–g**) were converted smoothly into products **2d–g** in yields ranging from 68–98%. Sulfonimidamides with *S*-*n*-propyl and *S*-cyclohexyl groups reacted well too, providing the corresponding products **2h** and **2i** in yields of 82% and 50%, respectively.

Next, the influence of the *N*-aroyl group on the 1,3,2,4-oxathiadiazole 3-oxide formation was tested. The respective sulfonimidamides **1j–v** had *S*-tolyl substituents. Substrates with methyl-, *tert*-butyl-, halo-, and trifluoromethyl-containing *N*-aroyl groups reacted well leading to **2j–p** in yields of 71–98%. Thiophenyl- and furyl-substituted sulfonimidamides afforded **2q** and **2r** in 76% and 79% yields, respectively. Compared with the *N*-aroyl sulfonimidamides, their alkyl-based counterparts were less reactive. Hence, the *iso*-propyl-, *tert*-butyl-, and benzyl-substituted *N*-acyl sulfonimidamides provided the corresponding products **2s–u** in



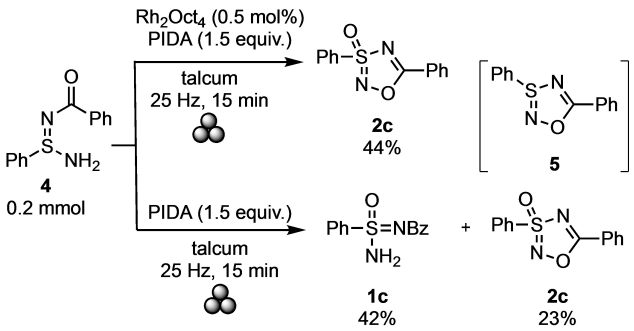
Scheme 2. Substrate scope of substituted sulfonimidamides **1a–w**.[19] Reaction conditions: **1** (0.2 mmol), $Rh_2(Oct)_4$ (0.5 mol%), PIDA (0.3 mmol), and talcum (60 mg) were added into a stainless steel jar (10 mL) with one stainless steel ball (diameter: 10 mm, weight: ca. 3.5 g) and milled at 25 Hz for 15 min. [a] The reaction was conducted on a 1 mmol scale in a 20 mL stainless steel jar. [b] Use of 1.0 equiv. of PIDA.

yields of only 20–46 %. When *N*-benzyloxyacyl sulfonimidamide **1v** was tested, the expected product **2v** was not obtained due to the decomposition of the starting material. Noteworthy, also an oxidative N–S bond coupling worked well as demonstrated with benzothioamide derivative **1w** as starting material. The corresponding product **2w** was isolated in 92 % yield. Here, a reduced amounts of PIDA (1.0 equiv.) was employed to avoid a potential further oxidation of **2w**. An upscaling option was demonstrated by conducting the cyclization reaction of **1a** on a 1 mmol scale in a 20 mL stainless steel jar, leading to **2a** in 71 % yield.

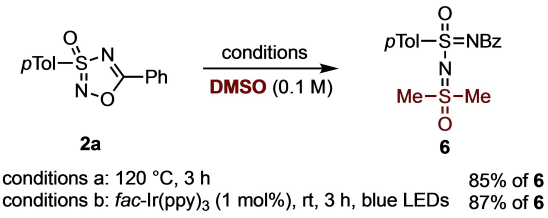
As suspected, *N*-[amino(phenyl)-λ^4-sulfaneylidene]benzamide (**4**) did not give an analogous cyclized product **5**, and instead, **2c** was obtained in 44 % yield under standard conditions (Scheme 3). In the absence of the rhodium catalyst, sulfinamidine **4** afforded sulfonimidamide **1c** as the major product (42 % yield) together with **2c**, which was isolated in 23 % yield. Also in this case, **5** was not found. These results suggest an initial oxidative conversion of sulfinamidine **4** to sulfonimidamide **1c** by PIDA[20] followed by the aforementioned intramolecular N–O bond formation leading to **2c**.

Realizing the potential of N–O bond activations in preparative organic chemistry under transition metal catalysis or photocatalysis,[21] possible synthetic applications of the newly prepared products **2** were investigated (Scheme 4). Compound **2a** was selected as a representative substrate. To our delight, it was activated by both heat and photocatalysis reacting with DMSO to give *S*-iminated product **6** in 85 % and 87 % yields, respectively (Scheme 4).[22] Apparently, **2** had reacted as nitrene precursors. Attempts to expand the ring of **2a** by reacting it with an ynamide or a diazo ester remained unsuccessful. (For further details, see the Supporting Information.)

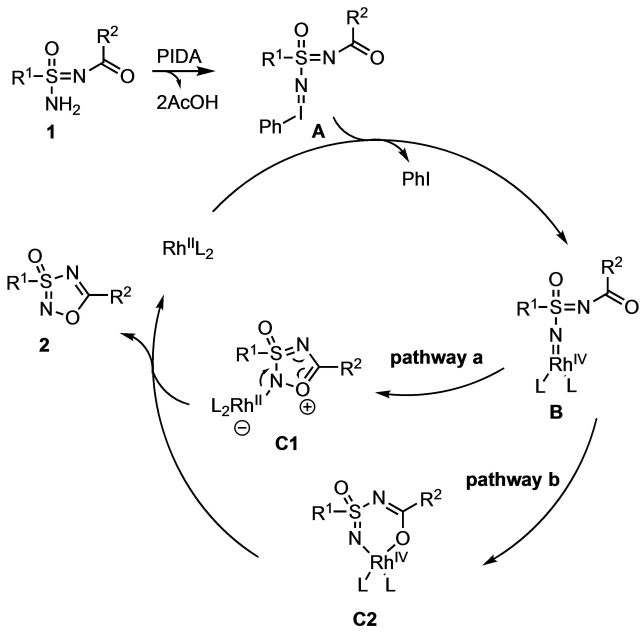
ESI-MS analysis of a reaction mixture that was milled for 1 min revealed the formation of various intermediates complexed to $Rh_2(Oct)_4$. (For details, see the Supporting Information.) On the basis of the previous work,[9,10] we propose two possible pathways involving five- and six-membered cyclic intermediates (Scheme 5). Both start with the reaction of sulfonimidamide **1** with PIDA, which leads to iminoiodinane-type intermediate **A**. When the rhodium catalyst reacts with **A**, phenyl iodide is expelled and rhodium nitrenoid **B** is formed. In **B**, the benzoyl oxygen reacts as a nucleophile leading to either rhodium-tethered five-membered heterocycles **C1** (pathway a) or six-membered rhodacycle **C2** (pathway b). Both intermediates (**C1**



Scheme 3. Reactions of sulfinamidine **4**.



Scheme 4. Activation of the N–O bond of **2a** by heat and photocatalysis.



Scheme 5. Proposed mechanism.

and **C2**) lead to product **2** upon loss of a $Rh^{II}L_2$ species, which re-enters the catalytic cycle.

In summary, we discovered a rhodium-catalyzed mechanochemical intramolecular N–O coupling of *N*-acyl sulfonimidamides leading to unprecedented 1,3,2,4-oxathiadiazole 3-oxide derivatives in up to 98 % yield. The catalyst loading is low [0.5 mol % of $Rh_2(Oct)_4$], and the process is solvent-free. Under standard conditions, sulfinamidines react directly to 1,3,2,4-oxathiadiazole 3-oxides. In addition, the feasibility of analogous oxidative N–S bond couplings was demonstrated. Potential synthetic applications of the resulting products as nitrene precursors were demonstrated by a reaction with DMSO under heat or blue light. Mechanistically, the cyclization is suggested to proceed via rhodium nitrenoids. Further studies on intramolecular nitrogen-hetero bond couplings of sulfonimidamides and syntheses of compounds with different ring sizes are under investigation.

Acknowledgements

S.P. and P.W. are grateful to the China Scholarship Council (CSC) for predoctoral stipends, and we acknowledge the Alexander von Humboldt Foundation for support of K.R. (AvH research award). Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article. The authors have cited additional references within the Supporting Information.[16,20,22–32]

Keywords: Cyclization · Mechanochemistry · Nitrenoids · N–O Coupling · Rhodium

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Manuscript received: July 12, 2024
Accepted manuscript online: October 9, 2024
Version of record online: November 9, 2024