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Synthesis of Benzothiadiazine-1-oxides by Rhodium-Catalyzed C−H Amidation/Cyclization

Peng Shi, Yongliang Tu, Chenyang Wang, Deshen Kong, Ding Ma, and Carsten Bolm*

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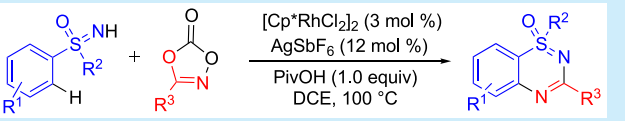
ABSTRACT: A rhodium-catalyzed C−H amidation/cyclization sequence provides benzothiadiazine-1-oxides from sulfoximines and 1,4,2-dioxazol-5-ones in good yields. The reaction is characterized by a high functional group tolerance and, in contrast to most previous transformations of this type, is well-suited for *S*-alkyl-*S*-aryl-substituted sulfoximines.



In past decades, sulfoximines have extensively been used in organic synthesis,[1] agricultural science,[2] and medicinal chemistry.[3] Due to their unique structure and biological properties, cyclic derivatives such as benzothiadiazine-1-oxides have caught particular attention, leading to a range of pharmaceutical agents, including Gö 4962,[4] NSC 287474,[5] and an analogue of the adrenergic receptor blocker Prazosin (Figure 1).[6]

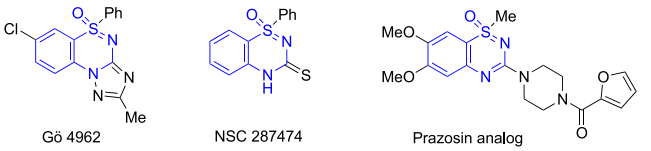
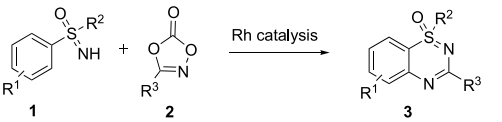


Figure 1. Benzothiadiazine-1-oxides with biological activity.

Although various synthetic approaches toward benzothiadiazine-1-oxides have already been developed, most of them reveal severe preparative limitations and a restricted substrate scope. For example, using 2-azido-,[7] 2-amido-,[8] or 2-bromosulfoximines[9] as starting materials can be effective, but those compounds require multiple-step syntheses. Transition-metal-catalyzed C−H bond functionalizations of *S*-aryl sulfoximines[10] offer an attractive alternative. Aiming at synthesizing benzothiadiazine-1-oxides with this approach, Chen introduced a microwave-assisted cobalt catalysis with 1,4,2-dioxazol-5-ones as amidation agents as early as 2017.[11] Unfortunately, only *S*,*S*-diaryl sulfoximines reacted well, whereas *S*-alkyl-containing substrates proved unreactive. Subsequently, Dong reported rhodium and iridium catalyses with benzylazides and *N*-alkoxyamides, respectively, as nitrogen sources.[12] With this work, the substrate scope was enlarged, but most of the products had a rather specific molecular scaffold. Here, we report a more general approach toward benzothiadiazine-1-oxides using a rhodium-catalyzed direct C−H bond amidation/cyclization with 1,4,2-dioxazol-5-ones as amidation agents,[13] allowing a wide structural variation of the targeted heterocycles (Scheme 1).

Scheme 1. Catalytic Synthesis of Benzothiadiazine-1-oxides Reported Here



Guided by the previous work,[10] we initiated the current study using sulfoximine **1a** and 3-phenethyl-1,4,2-dioxazol-5-one (**2a**)[14] as representative starting materials. To our delight, applying both molecules in a 1.0:1.5 ratio and using $Rh(cod)Cl_2$ (3 mol %) in combination with $AgSbF_6$ (12 mol %) as catalyst in DCE (1.0 mL) at 100 °C for 10 h did indeed give product **3a**, but the yield was only 11% (Table 1, entry 1). $CuCl_2$ and $PdCl_2$ were ineffective (Table 1, entries 2 and 3). With $[Cp^*RhCl_2]_2$, the yield of **3a** increased to 75% (Table 1, entry 4). As a solvent, DCE proved superior over acetone, THF, toluene, and DCM (Table 1, entries 4−8). Whereas the addition of NaOAc and $NaHCO_3$ significantly decreased the yield of **3a**, the presence of weak acids showed positive effects (Table 1, entries 9−13). Finally, the yield of **3a** reached 91% with 1.0 equiv of pivalic acid as the additive. Performing the catalysis under argon or increasing the amount of **2a** from 1.5 to 2.0 equiv had only minor effects on the reaction outcome (Table 1, entries 14 and 15).

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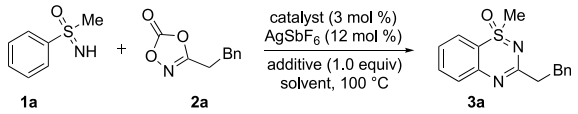
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	additive	solvent	yield (%)
1	$Rh(cod)Cl_2$		DCE	11
2	$CuCl_2$		DCE	trace
3	$PdCl_2$		DCE	trace
4	$[Cp^*RhCl_2]_2$		DCE	75
5	$[Cp^*RhCl_2]_2$		acetone	60
6	$[Cp^*RhCl_2]_2$		THF	45
7	$[Cp^*RhCl_2]_2$		toluene	38
8	$[Cp^*RhCl_2]_2$		DCM	65
9	$[Cp^*RhCl_2]_2$	NaOAc	DCE	11
10	$[Cp^*RhCl_2]_2$	$NaHCO_3$	DCE	trace
11	**$[Cp^*RhCl_2]_2$**	**PivOH**	**DCE**	**91**
12	$[Cp^*RhCl_2]_2$	CH_3COOH	DCE	13
13	$[Cp^*RhCl_2]_2$	1-AdCOOH	DCE	80
14[b]	$[Cp^*RhCl_2]_2$	PivOH	DCE	88
15[c]	$[Cp^*RhCl_2]_2$	PivOH	DCE	87

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), catalyst (3 mol %), $AgSbF_6$ (12 mol %), and additive (0.10 mmol) in the given solvent (1 mL) at 100 °C for 10 h. [b]Under argon atmosphere. [c]Use of 2.0 equiv of **2a** (0.20 mmol).

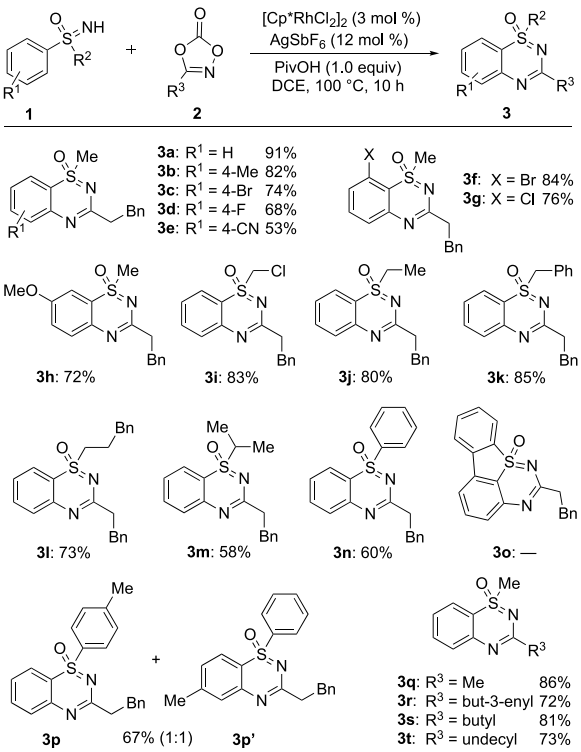
Under the optimized conditions (Table 1, entry 11), the substrate scope was evaluated. As shown in Scheme 2, the process was very general, allowing a wide range of both sulfoximines **1** and dioxazolones **2** to be converted with high structural diversity. In the series of *S*-aryl-*S*-methylsulfoximines, reactions with **2a** proceeded well, providing the corresponding products **3a**–**h** in yields ranging from 53 to 91%. Although the number of examples was limited, the presence of electron-withdrawing substituents on the arenes appeared to have a slight negative effect on the yields of the corresponding products [for example, 82% of **3b** (with 4-Me) versus 53% of **3e** (with 4-CN)]. Steric crowding played a minor role, as revealed by the yields of **3f**–**h** (72–84%). Noteworthy, for 3-methoxy-substituted **3h**, only one regioisomer was observed, presumably due to a higher reactivity of the less congested C–H bond site. Sulfoximines with *S*-alkyl groups other than methyl also reacted well, as shown in the results for *S*-alkyl-*S*-phenylsulfoximines **3i**–**m** with yields of 58–85%. In light of the high reactivity of *S*-chloromethyl- and *S*-benzyl-substituted sulfoximines,[15] the data for **3i** and **3k** with yields of 83 and 85%, respectively, are remarkable. Branching at the *S*-alkyl substituent as in **3m** bearing an *S*-isopropyl group seemed to hamper the product formation (58% yield). The applicability of *S*,*S*-diarylsulfoximines was shown in conversions of **2a** with **1n** and **1p**, which afforded **3n** and **3p**/**3p′** in yields of 60 and 67%, respectively. The latter product was obtained as a 1:1 mixture of positional isomers. The attempt to react dibenzothiophene sulfoximine (**1o**) under the optimized conditions failed, and thus, **3o** remained inaccessible. This result was in line with previous observations which revealed a very particular reaction behavior of compounds of this type.[16] Using *S*-methyl-*S*-phenylsulfoximine (**1a**) as the reaction partner, the applicability of other dioxazolones **2** was tested. Again, the catalyses proceeded smoothly, providing the expected products **3q**–**t** in yields ranging from 72% (for **3r**) to 86% (for **3q**).

On a 1 mmol scale, the reaction between **1a** and **2a** led to **3a** in 81% yield.

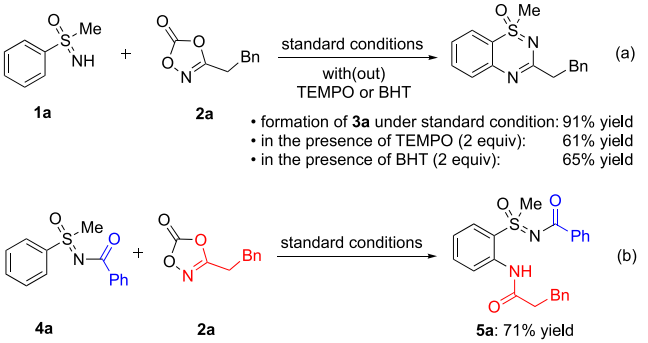
To further understand the reaction pathway, several control experiments were performed. Under standard conditions with **1a** and **2a** as substrates, the presence of 2 equiv of TEMPO or BHT decreased in yield of **3a** from 91% (Table 1, entry 11) to 61 and 65%, respectively, indicating that the reaction did not involve free radicals being trappable by such typical radical scavengers (Scheme 3, reaction a). Reacting benzoyl-substituted sulfoximine **4a** with **2a** gave amidated product **5a** in 71% yield (Scheme 3, reaction b) showing that N-substituted sulfoximines could also be applied in this C–H bond activation process with **2a** and that, in the original system, the free *N*H group of the sulfoximine was essential for the benzothiadiazine-1-oxide formation.

Based on these results and previous reports,[10,17] a plausible catalytic cycle is proposed in Scheme 4. Cationic rhodium complex **I** generated by anion exchange of $[Cp^*RhCl_2]_2$ with

Scheme 2. Substrate Scope with Respect to Sulfoximines and 1,4,2-Dioxazol-5-ones (0.1 mmol Scale)



Scheme 3. Control Experiments



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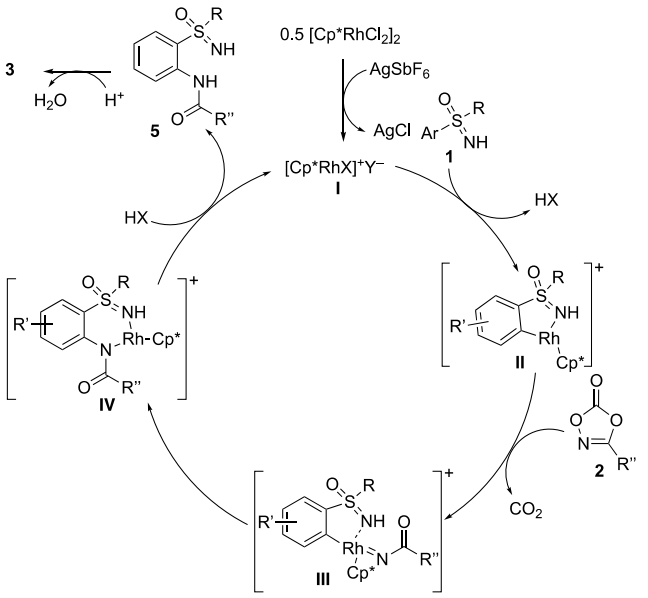
Scheme 4. Plausible Mechanism



$AgSbF_6$ reacts with sulfoximine **1** to give five-membered rhodacycle **II** by loss of HX.[18] Stronger acids such as AcOH can compete with the sulfoximine, thereby affecting the formation of intermediate **II**.[19] After coordination of 1,4,2-dioxazol-5-one **2** and loss of CO_2, rhodium nitrenoid **III** is formed. Subsequent C−N bond formation leads to **IV**, which is protonated to give amidated product **5**. In this step, [Cp*RhX]Y is regenerated, closing the catalytic cycle.[20] Finally, dehydrative ring closure of **5** leads to the observed benzothiadiazine-1-oxide **3**. If the sulfoximine nitrogen is substituted (as in **4a**), the reaction sequence is identical except that last step cannot occur and compounds such as **5a** are the final products.

In conclusion, we developed an efficient rhodium catalysis for the synthesis of benzothiadiazine-1-oxide starting from *NH*-sulfoximines and 1,4,2-dioxazol-5-ones.[21] It proceeds with high functional group tolerance, allowing the preparation of a wide range of products including unsymmetrical ones, which proved difficult to prepare with previously reported protocols.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03212.

Experimental details, characterization data, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Carsten Bolm − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany;* orcid.org/0000-0001-9415-9917; Email: carsten.bolm@oc.rwth-aachen.de

Authors

Peng Shi − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Yongliang Tu − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Chenyang Wang − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Deshen Kong − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Ding Ma − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c03212

Notes

The authors declare no competing financial interest.

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(18) A representative complex of this type has been characterized by X-ray crystal structure analysis. See ref 10a.

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(20) For analogous amidations of arylamides performed under solvent-free mechanochemical conditions see: Hermann, G. N.; Bolm, C. Mechanochemical Rhodium(III)-Catalyzed C−H Bond Amidation of Arenes with Dioxazolones under Solventless Conditions in a Ball Mill. *ACS Catal.* **2017**, *7*, 4592−4596.

(21) Here, all sulfoximines were racemic. As the stereogenic center at sulfur remains unaffected in the formation of the heterocycle, we assume that enantiomerically pure products can stereospecifically be accessed from the corresponding enantiopure starting materials.

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