C–H/N–H Activation

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Rhodium-Catalyzed Oxidative Annulation of Sulfoximines and Alkynes as an Approach to 1,2-Benzothiazines**

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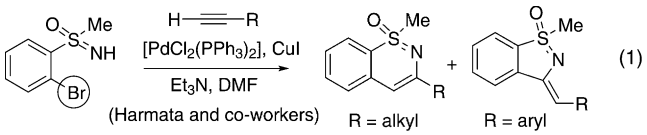
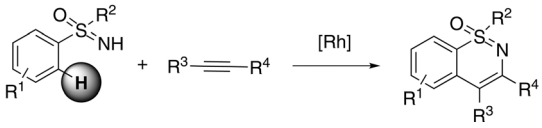
Within the last few years, oxidative activation reactions of C–H/N–H or C-H/O–H bond combinations with subsequent alkyne or alkene annulations have become the synthetically most useful C–C and C–X (X = N, O, etc.) bond-forming processes.[1] Various metals proved applicable, and complexes based on Pd^{II},[2] Rh^{III},[3] or Ru^{II}[4] have been utilized for the catalytic construction of a wide range of heterocycles. To the best of our knowledge, 1,2-benzothiazines have not been among the heterocyclic products, despite their usefulness as scaffolds in drug development[5] and as synthetic intermediates.[6] Harmata and co-workers have introduced the most advanced approaches towards 1,2-benzothiazines, including annulations of sulfonimidoyl chlorides with alkynes or alkenes,[7] palladium catalysis in domino reaction sequences starting with a Buchwald–Hartwig N-arylation,[6,8] and Sonogashira-type cross-coupling reactions of *S*-2-bromophenyl-*S*-methylsulfoximines with terminal alkynes [Eq. (1); DMF = *N*,*N*-dimethylformamide].[9] None of these 1,2-benzothiazine syntheses involve the oxidative C–H/N–H activation of simple alkyl aryl sulfoximines.

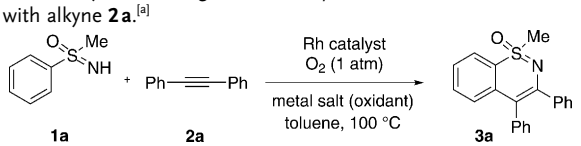


Stimulated by our recent findings on the copper-catalyzed direct arylation of N–H sulfoximines with heteroarenes[10a] and the oxidative cross-coupling of N–H sulfoximines with terminal alkynes[10b] and feeling challenged by the excellent work of Cramer and co-workers on the Rh^{III}-catalyzed oxidative C–H/N–H activation of *N*-acyl sulfonamides to afford benzosultams,[11] we wondered about an analogous strategy for the preparation of 1,2-benzothiazines from sulfoximines and alkynes [Eq. (2)]. We report herein our success with this approach.



To find suitable reaction conditions, we used the sulfoximine **1a** and diphenylacetylene (**2a**) as model substrates and examined the effect of the rhodium complex, oxidant, and solvent. The screening revealed that $[Cp^*Rh(MeCN)_3][BF_4]_2$ was most effective, with the formation of **3a** in 89% yield (Table 1, entry 1). The rhodium complexes $[\{RhCp^*Cl_2\}_2]$, $[\{Rh(OAc)_2\}_2]$, $[\{RhCl(cod)\}_2]$, and $[Rh(PPh_3)_3Cl]$ were less active (Table 1, entries 2–5). With respect to the oxidation system, a remarkable discovery was made: Under an atmosphere of molecular oxygen (1 atm), simple $Fe(OAc)_2$ (20 mol%) served as an effective mediator to give the desired product in 89% yield (Table 1, entry 1). To the best of our knowledge, this oxidant/mediator combination is unprecedented. Other iron and copper salts $[Fe(acac)_2$, $Fe(OTf)_2$, and $Cu(OAc)_2]$ were less effective (Table 1, entries 6–8), and the

Table 1: Catalyst screening for the C–H/N–H activation of sulfoximine **1a** with alkyne **2a**.[a]



1a **2a** **3a**

Entry	Catalyst	Metal salt/oxidant	Yield [%]
1	**$[Cp^*Rh(MeCN)_3][BF_4]_2$**	**$Fe(OAc)_2$**	**89**
2	$[\{RhCp^*Cl_2\}_2]$	$Fe(OAc)_2$	35
3	$[\{Rh(OAc)_2\}_2]$	$Fe(OAc)_2$	trace
4	$[\{RhCl(cod)\}_2]$	$Fe(OAc)_2$	–
5	$[Rh(PPh_3)_3Cl]$	$Fe(OAc)_2$	–
6	$[Cp^*Rh(MeCN)_3][BF_4]_2$	$Fe(acac)_2$	trace
7	$[Cp^*Rh(MeCN)_3][BF_4]_2$	$Fe(OTf)_2$	trace
8	$[Cp^*Rh(MeCN)_3][BF_4]_2$	$Cu(OAc)_2$	38
9	$[Cp^*Rh(MeCN)_3][BF_4]_2$	$PhI(OAc)_2$	–
10	$[Cp^*Rh(MeCN)_3][BF_4]_2$	$K_2S_2O_8$	–
11	–	–	–

[a] Reaction conditions: sulfoximine **1a** (0.30 mmol), alkyne **2a** (0.36 mmol), catalyst (5.0 mol%), metal salt/oxidant (20 mol%), toluene (2.5 mL), 100°C, 48 h. cod = 1,5-cyclooctadiene, Cp* = pentamethylcyclopentadiene.

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commonly applied oxidants $PhI(OAc)_2$ and $K_2S_2O_8$ proved inactive (Table 1, entries 9 and 10). When the reaction was carried out in the absence of the rhodium catalyst and the iron salt, no conversion occurred (Table 1, entry 11). Details of the solvent screening are reported in the Supporting Information.

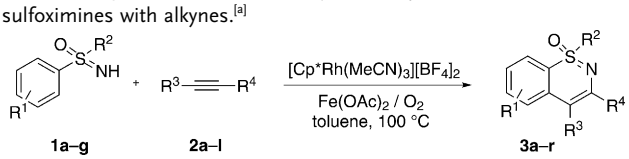
To evaluate the scope of the reaction, we treated substituted sulfoximines **1b–g** with **2a** under the optimized reaction conditions (Table 2). In general, all transformations proceeded well to afford the corresponding 1,2-benzothiazines in 72–89% yield (Table 2, entries 1–7). The reaction of the *meta*-substituted sulfoximine **1b** revealed high regioselectivity in favor of activation of the less hindered C–H bond to provide the two expected regioisomers **3b** and **3b′** in a 90:10 ratio in 88% combined yield (Table 2, entry 2). Comparison of the results for the conversion of the *para*-substituted sulfoximines **1c–f** shows that the influence of electronic effects induced by a methoxy, nitro, or halo group was minor and that chloro and bromo substituents were well tolerated (Table 2, entries 3–6). If the *S*-methyl group (as in **1a–f**) was changed to an *S*-phenyl substituent (as in **1g**), the yield of the resulting 1,2-benzothiazine (in this case **3g**) was essentially unaffected (85%; Table 2, entry 7).

Pleasingly, other alkynes also reacted well (as determined by reactions with **1a** as the coupling partner). In the series of symmetrically substituted diphenylacetylenes, the 4,4′-dimethoxy-, 4,4′-difluoro-, and 4,4′-dichloro derivatives all gave the corresponding products **3h–j** in high yields (up to 93%; Table 2, entries 8–10). When di(2-thienyl)acetylene (**2e**) was used, the 1,2-benzothiazine **3k** was obtained in 87% yield (Table 2, entry 11). With aliphatic alkyne substrates, the yields were slightly lower, as indicated by conversions of hex-3-yne (**2f**) and oct-4-yne (**2g**) to provide 1,2-benzothiazines **3l** and **3m** in 67 and 72% yield, respectively (Table 2, entries 12 and 13).

Unsymmetrically substituted alkynes were expected to lead to regioisomeric products. Depending on the substitution pattern, the regioselectivity was either high (up to 95:5) or nil (Table 2, entries 14–18). Thus, 1-phenyl-1-propyne (**2h**) and phenyl propiolate (**2i**) underwent the oxidative annulation effectively to give the two regioisomeric products (**3n**/**3n′** and **3o**/**3o′**) in high yields and isomer ratios of 85:15 and 95:5, respectively (Table 2, entries 14 and 15). The chemical identity of **3n** was established unequivocally by X-ray crystal-structure analysis (see the Supporting Information for details).[12] In contrast, no regioselectivity was observed when the unsymmetrical diaryl acetylenes **2j**, **2k**, and **2l** were used. Instead, the corresponding regioisomer pairs **3p**/**3p′**, **3q**/**3q′**, and **3r**/**3r′** were obtained in equal amounts in 90, 80, and 78% yield, respectively (Table 2, entries 16–18).

On the basis of earlier studies,[1,13] we deduced a reasonable mechanism for the transformation (Scheme 1). The catalytic cycle is most likely initiated by the transfer of an acetate group from $Fe(OAc)_2$ to $[Cp^*Rh(MeCN)_3][BF_4]_2$.[14] The reaction of the resulting rhodium species with the sulfoximine and subsequent activation of an *ortho* C–H bond forms a five-membered rhodacycle **II**. Coordinative insertion of alkyne **2** into the rhodium–carbon bond of intermediate **II** gives a seven-membered rhodacycle **IV**. Finally, reductive elimination affords the 1,2-benzothiazine and a Rh^I species. The iron salt mediates the reoxidation of this Rh^I species by molecular oxygen to regenerate the active Rh^{III} species, which enters the next catalytic cycle.

Table 2: Scope of the rhodium-catalyzed C–H/N–H activation of sulfoximines with alkynes.[a]



1a–g **2a–l** **3a–r**

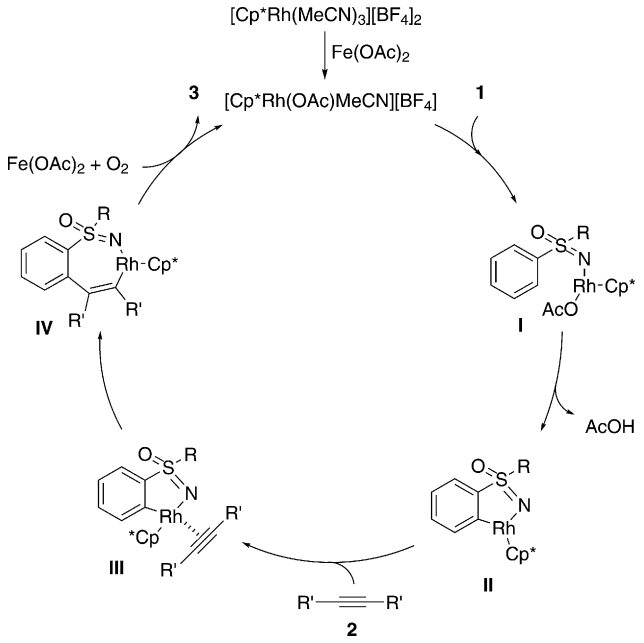
1a: R^1 = H, R^2 = Me
1b: R^1 = 3-Me, R^2 = Me
1c: R^1 = 4-MeO, R^2 = Me
1d: R^1 = 4-NO_2, R^2 = Me
1e: R^1 = 4-Cl, R^2 = Me
1f: R^1 = 4-Br, R^2 = Me
1g: R^1 = H, R^2 = Ph

2a: R^3, R^4 = Ph
2b: R^3, R^4 = 4-$MeOC_6H_4$
2c: R^3, R^4 = 4-FC_6H_4
2d: R^3, R^4 = 4-ClC_6H_4
2e: R^3, R^4 = 2-thienyl
2f: R^3, R^4 = Et

2g: R^3, R^4 = *n*Pr
2h: R^3 = Me, R^4 = Ph
2i: R^3 = CO_2Me, R^4 = Ph
2j: R^3 = Ph, R^4 = 4-$MeOC_6H_4$
2k: R^3 = Ph, R^4 = 4-$NO_2C_6H_4$
2l: R^3 = Ph, R^4 = 2-naphthyl

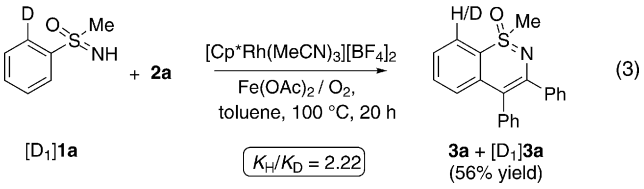
Entry	1	2	Product 3	Yield [%]
1	a	a	**3a**: R^1 = H	89
2	b	a	**3b**: R^1 = 3-Me	88[b]
3	c	a	**3c**: R^1 = 4-MeO	86
4	d	a	**3d**: R^1 = 4-NO_2	72
5	e	a	**3e**: R^1 = 4-Cl	79
6	f	a	**3f**: R^1 = 4-Br	81
7	g	a	**3g**	85
8	a	b	**3h**: R^3, R^4 = 4-$MeOC_6H_4$	93
9	a	c	**3i**: R^3, R^4 = 4-FC_6H_4	82
10	a	d	**3j**: R^3, R^4 = 4-ClC_6H_4	86
11	a	e	**3k**: R^3, R^4 = 2-thienyl	87
12	a	f	**3l**: R^3, R^4 = Et	67
13	a	g	**3m**: R^3, R^4 = *n*Pr	72
14	a	h	**3n** / **3n′**	85 (85:15)
15	a	i	**3o** / **3o′**	82 (95:5)
16	a	j	**3p**: R^3 = Ph, R^4 = 4-$MeOC_6H_4$ / **3p′**: R^3 = 4-$MeOC_6H_4$, R^4 = Ph	90 (50:50)
17	a	k	**3q**: R^3 = Ph, R^4 = 4-$NO_2C_6H_4$ / **3q′**: R^3 = 4-$NO_2C_6H_4$, R^4 = Ph	80 (50:50)
18	a	l	**3r**: R^3 = Ph, R^4 = 2-naphthyl / **3r′**: R^3 = 2-naphthyl, R^4 = Ph	78 (50:50)

[a] Reaction conditions: sulfoximine **1** (0.50 mmol), alkyne **2** (0.60 mmol), $[Cp^*Rh(MeCN)_3][BF_4]_2$ (5.0 mol%), $Fe(OAc)_2$ (20 mol%), toluene (3.0 mL), 100°C, 48 h. [b] Ratio of regioisomers **3b** and **3b′**: 90:10.



Scheme 1. Plausible catalytic pathway for the formation of 1,2-benzothiazines.

The intramolecular kinetic isotope effect (KIE) of $k_H/k_D = 2.22$ found by using [D$_1$]**1a** as a substrate [Eq. (3)] indicated that the C–H bond cleavage was directly involved in the product-determining cyclometalation step.[15]



(3)

The proposed intermediacy of a five-membered rhodacycle was substantiated by the isolation of a complex upon the heating of a mixture of **1a** and $[Cp^*Rh(MeCN)_3][BF_4]_2$ to 100 °C in toluene for 16 h. ^{1}H NMR, ^{13}C NMR, and IR spectroscopy in combination with mass spectrometry suggested the formation of rhodacycle **V** (Figure 1), in which L is a coordinated molecule of sulfoximine **1a**. The molecular structure of **V** was indirectly confirmed by X-ray crystal-structure analysis of rhodacycle **VI**,[12] which was obtained by the treatment of **V** with NaI in MeOH at room temperature for 30 min.

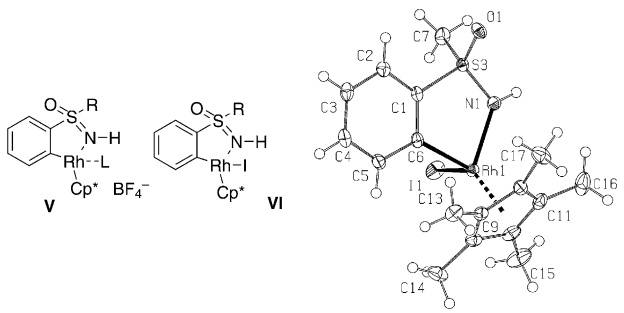
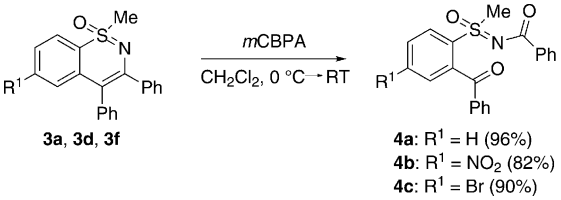


Figure 1. Structure of rhodacycles **V** and **VI** as well as an ORTEP diagram of complex **VI** (thermal ellipsoids are drawn at 50% probability).[12]

To demonstrate that such rhodacycles could be involved in the catalytic formation of 1,2-benzothiazines, we treated **V** with **2a** in the presence of $Fe(OAc)_2$ in toluene at 100 °C and obtained **3a** in high yield after 2 h. In the same manner, 1,2-benzothiazine **3a** was obtained from rhodacycle **VI** and **2a** in 78% yield after 15 h.

Finally, in the search for new synthetic applications of 1,2-benzothiazines, we discovered an unprecedented oxidative C–C bond-cleavage reaction. Thus, the treatment of **3a** with *meta*-chloroperoxybenzoic acid (*m*CPBA) in CH_2Cl_2 at 0 °C and warming to room temperature for 8 h led to *ortho*-benzoyl-*N*-benzoylsulfoximine **4a** in 96% yield. 1,2-Benzothiazines **3d** and **3f** reacted in an analogous manner to provide products **4b** and **4c**, respectively, in high yields [Eq. (4)].



(4)

In summary, we have developed a rhodium-catalyzed process for the synthesis of 1,2-benzothiazines from *N*H-sulfoximines and alkynes. The combination of simple $Fe(OAc)_2$ (20 mol%) and O_2 (1 atm) enables metal reoxidation to close the catalytic cycle. Mechanistically, the transformation is proposed to involve a one-pot C–H/N–H activation followed by an annulation of the alkyne. This hypothesis was substantiated by KIE studies and the isolation of a reactive rhodacycle. The method is high-yielding and suitable for the synthesis of small libraries of functionalized 1,2-benzothiazines.

Experimental Section

General procedure: The sulfoximine (0.5 mmol), the alkyne (0.6 mmol), $[Cp^*Rh(MeCN)_3][BF_4]_2$ (13.5 mg, 0.025 mmol, 5 mol%), and $Fe(OAc)_2$ (18 mg, 0.1 mmol, 20 mol%) were placed in a Schlenk tube (20 mL) with a stirring bar. Under an oxygen atmosphere (1 atm), dry toluene (3.0 mL) was added, and the reaction mixture was stirred at 100 °C for 48 h and then cooled to room temperature. The mixture was filtered through a short pad of Celite and washed with dichloromethane (3 × 20 mL). The filtrate was concentrated, and the product was purified by column chromatography on silica gel with a mixture of hexanes and ethyl acetate as the eluent.

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