CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700352

Comparative Study of Metal-Catalyzed Iminations of Sulfoxides and Sulfides

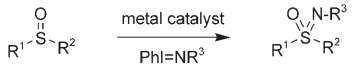
Olga García Mancheño and Carsten Bolm*[a]

Abstract: A comparative study of the imination of sulfur compounds with various metal catalysts in combination with isolated or in situ generated iminoiodinanes (PhI=NR) as nitrogen sources is presented. The influence of the metal catalyst towards the imination of a variety of substituted sulfoxides has been evaluated. Moreover, the effect of the different oxidation states of sulfur on the reactivity and selectivity of the nitrogen transfer redox process in the formation of sulfilimines and sulfoximines was studied. Depending on both the specific metal catalyst as well as the employed nitrene precursor, the sulfide/sulfoxide imination ratio varied in transformations of thianthrene-5-oxide and substituted *para*-thio phenylsulfoxides.

Keywords: homogeneous catalysis · iminations · sulfilimines · sulfoximines · sulfur

Introduction

Sulfilimines and, particularly, sulfoximines are interesting intermediates and building blocks for the preparation of chiral ligands[1] and pseudopeptides.[2] However, despite the interest that these kinds of molecules have lately generated, there is still a need to develop general and efficient methods for their synthesis. Though a number of synthetic approaches have been described,[3] the most straightforward is the imination of the corresponding sulfoxide (or sulfide) using either toxic and potentially explosive hydrazoic acid (generated in situ from NaN_3 and H_2SO_4)[4] or *O*-mesitylene sulfonyl hydroxylamine (MSH).[5] Alternatively, iminoiodinanes such as PhI=NTs can be employed under metal catalysis (Scheme 1).



Scheme 1. General metal-catalyzed imination of sulfoxides.

Recently, significant progress has been made in metal-catalyzed sulfur iminations, however, most of the methods lead to *N*-tosyl sulfoximines which are difficult to transform into the synthetically more useful NH-derivatives.[6] Major improvements in this area were reported by several research groups.[7] For example, Bach found that $FeCl_2$-catalyzed iminations of sulfides and sulfoxides with $BocN_3$.[8] Although the catalytic efficiency of this system was rather limited and its use involved a potentially explosive azide, the resulting *N*-Boc protected products could be easily transformed into the corresponding NH-sulfoximines. At the same time, Müller reported that CuOTf was an efficient catalyst for sulfoxide iminations with PhI=NTs.[9] Subsequently, we,[10] Nakayama[11] and Tye,[12] published Cu^I-catalyzed reactions with $CuPF_6$, which proved to be a more efficient catalyst. Notably, Tye described the application of modified iminoiodinanes such as PhI=NNs (Ns = *para*-nitrobenzenesulfonyl) and PhI=NSes (Ses = trimethylsilylethylsulfonyl) having easily removable protecting groups. Finally, Malacria reported that the more stable and reasonably priced $Cu(OTf)_2$ was also an active catalyst.[13]

In 2004, we discovered a mild oxidative imination using $[Rh_2(OAc)_4]$ as catalyst with a combination of sulfonamides or trifluoroacetamide and iodobenzenediacetate $[PhI(OAc)_2]$.[14] The corresponding protected sulfoximines were formed in good yield and the resulting *N*-$COCF_3$ sulfoximines were easily hydrolyzed to the synthetically interesting NH-sulfoximines. However, the high cost of the rhodium catalyst limited large-scale syntheses using this protocol.[15] After further studies it was found that the less costly silver nitrate in combination with 4,4′,4″-tri-*tert*-butyl-

[a] Dr. O. García Mancheño, Prof. Dr. C. Bolm
Institute of Organic Chemistry, RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
Fax: (+49) 241-809-2391
E-mail: carsten.bolm@oc.rwth-aachen.de

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: ^1H and ^{13}C NMR spectra for **3**–**8**, **12**–**14**, **16**, **17** and NH-**3**.

2,2′:6′,2″-terpyridine (tBu$_3$tpy) as ligand was an efficient catalyst for sulfur imination reactions using mixtures of *p*-nitrobenzenesulfonyl amide (nosyl amide, $NsNH_2$) and PhI(OAc)$_2$.[16] Recently, we discovered that [Fe(acac)$_3$] was also capable of catalyzing the imination of sulfides and sulfoxides with sulfonyl amides as nitrogen sources.[17]

With the goal of evaluating the generality and the effectiveness of the methodologies cited above, we investigated the influence of the metal catalyst in the imination of simple and substituted sulfoxides as well as their reactivity in comparison with sulfides.

Results and Discussion

First, the generally unproblematic imination of methyl phenyl sulfoxide (**1**) with nosyl amide was examined in more detail (Table 1). Besides the rhodium-, silver-, and iron-based catalytic systems that we recently reported for this transformation, the use of other simple copper, cobalt and manganese catalysts was explored.[18] Initially, the reactions were performed at room temperature generating the nitrene source in situ from PhI(OAc)$_2$ or iodosylbenzene (PhI=O) and Ns-NH$_2$ (method **A**, entries 1–8).

The best conditions described for the iminations with rhodium,[14] silver,[16] iron[17] and copper(II)[13] were used, which implies the use of 2.5 mol% of [Rh$_2$(OAc)$_4$] in dichloromethane, 8 mol% of AgNO$_3$/tBu$_3$tpy ligand, and 10 mol% of [Fe(acac)$_3$] or Cu(OTf)$_2$ in acetonitrile at room temperature. Although the rhodium, silver and iron catalysts gave excellent yields of the desired sulfoximine **2** (83–97%, Table 1, entries 1–4), the AgNO$_3$/tBu$_3$tpy system showed a significant lower reactivity, requiring longer reaction times (16 h vs 0.5–6 h). On the other hand, as previously observed, the use of PhI=O instead of PhI(OAc)$_2$ in the iron-catalyzed imination gave an important improvement in terms of yield and reaction time (entry 4). In contrast, [Mn(acac)$_3$] and [Co(acac)$_3$] gave no conversion after 24 h under these conditions (entries 7–8), and Co(ClO$_4$)$_2$ and Cu(OTf)$_2$ afforded **2** in very low yields after prolonged reaction times (25–28%, entries 5–6).

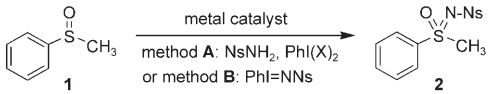
Considering that the copper-catalyzed iminations described to date always utilize a preformed iminoiodinane, we next carried out the metal-catalyzed iminations with PhI=NNs (method **B**, Table 1, entries 9–15). As expected, the use of this preformed iminating agent led to faster reactions with rhodium, silver and iron catalysts (1–8 h, 85–93%, entries 9–11). Moreover, Cu(OTf)$_2$ turned out to be an active catalyst, giving sulfoximine **2** in 81% yield after 16 h (entry 12). Unfortunately, no improvement was observed in the manganese- or cobalt-catalyzed iminations within this reagent (entries 13–15).

Next, as part of our continuing efforts to broaden the scope of this transformation, we turned our attention toward a comparative metal-catalyzed imination of different heteroaromatic sulfoxides (Table 2). This transformation is very appealing because it leads to functionalized sulfoximines, but it has the difficulty of the possible inactivation of the metal catalyst by coordination to the heteroatoms on the aromatic substituent.

In order to comparatively determine the effect of the heterocycle, the methyl group of the sulfoxide was retained and the aromatic substituent varied. Thus, iminations of various sulfoxides containing six-membered nitrogenated cycles such as 2-pyridine, 2-pyrimidine and 2-pyrazine, and different five-membered rings such as 2-benzothiazole, 2-*N*-methyl imidazole and a 1,3,4-oxadiazole were explored.

As a result, the iminations with the rhodium catalyst using method **A** turned out to be inefficient, leading to moderate to poor conversions to the desired sulfoximines **3**–**8** (<10–52% yield). In contrast, a similar pattern of reactivity as with the model sulfoxide **1** was observed with silver and iron catalysts. Additionally, in the iron-catalyzed imination of methyl 2-pyridyl sulfoxide and methyl 2-pyrazinyl sulfoxide, both PhI=O and PhI(OAc)$_2$ were used as oxidants (entries 3–4 and 8–9). These iodinanes led to good yields of the corresponding sulfoximines **3** and **4**, with iodosylbenzene giving complete conversions and therefore better yields than PhI(OAc)$_2$ (83 vs 78% and 88 vs 73%, respectively). As PhI=O seems to be more suitable for iron-catalyzed

Table 1. Metal-catalyzed imination of methyl phenyl sulfoxide **1**.[a]

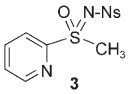
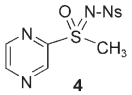
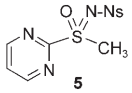
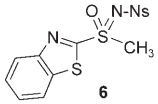
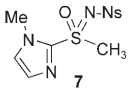
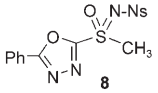


1 2

Entry	Catalyst (mol%)	Method	PhI(X)$_2$	t [h]	Yield [%][b]
1	[Rh$_2$(OAc)$_4$] (2.5)	**A**	PhI(OAc)$_2$	6	86
2	AgNO$_3$/tBu$_3$tpy (8:8)	**A**	PhI(OAc)$_2$	16	83
3	[Fe(acac)$_3$] (10)	**A**	PhI(OAc)$_2$	3	90
4	[Fe(acac)$_3$] (10)	**A**	PhI=O	0.5	97
5	Cu(OTf)$_2$ (10)	**A**	PhI(OAc)$_2$	16	28
6	Co(ClO$_4$)$_2$ (10)	**A**	PhI(OAc)$_2$	72	25
7	[Co(acac)$_3$] (10)	**A**	PhI(OAc)$_2$	24	–
8	[Mn(acac)$_3$] (10)	**A**	PhI(OAc)$_2$	24	–
9	[Rh$_2$(OAc)$_4$] (2.5)	**B**	PhI=NNs	1	93
10	AgNO$_3$/tBu$_3$tpy (8:8)	**B**	PhI=NNs	8	85
11	[Fe(acac)$_3$] (10)	**B**	PhI=NNs	1	88
12	Cu(OTf)$_2$ (10)	**B**	PhI=NNs	16	81
13	Co(ClO$_4$)$_2$ (10)	**B**	PhI=NNs	72	28
14	[Co(acac)$_3$] (10)	**B**	PhI=NNs	24	–
15	[Mn(acac)$_3$] (10)	**B**	PhI=NNs	24	–

[a] Reaction conditions: sulfoxide **1** (1 equiv) and metal catalyst in MeCN or CH_2Cl_2 at room temperature. Method **A**: $NsNH_2$ (1.2–2.0 equiv) and PhI(OAc)$_2$ or PhI=O (1.5–1.6 equiv). Method **B**: PhI=NNs (1.5 equiv). [b] Yield after column chromatography.

Table 2. Metal-catalyzed iminations for the preparation of heteroaromatic *N*-nosyl sulfoximines.[a]

Entry	Catalyst (mol %)	Sulfoximine	Method	$PhI(X)_2$	*t* [h]	Yield [%][b]	Method	*t* [h]	Yield [%][b]
1	$[Rh_2(OAc)_4]$ (2.5)		**A**	$PhI(OAc)_2$	24	52	**B**	24	57
2	$AgNO_3$/*t*Bu_3tpy (8:8)	 **3**	**A**	$PhI(OAc)_2$	24	79	**B**	18	93
3	$[Fe(acac)_3]$ (10)		**A**	$PhI(OAc)_2$	4	78	**B**	0.75	92
4	$[Fe(acac)_3]$ (10)		**A**	PhI=O	1	83	--	–	–
5	$Cu(OTf)_2$ (10)		**A**	–	–	–	**B**	5	80
6	$[Rh_2(OAc)_4]$ (2.5)		**A**	$PhI(OAc)_2$	48	15	**B**	24	24
7	$AgNO_3$/*t*Bu_3tpy (8:8)	 **4**	**A**	$PhI(OAc)_2$	24	84	**B**	18	90
8	$[Fe(acac)_3]$ (10)		**A**	$PhI(OAc)_2$	4	73	**B**	0.5	98
9	$[Fe(acac)_3]$ (10)		**A**	PhI=O	2	88	--	–	–
10	$Cu(OTf)_2$ (10)		**A**	–	–	–	**B**	48	85
11	$[Rh_2(OAc)_4]$ (2.5)		**A**	$PhI(OAc)_2$	72	29	**B**	24	35
12	$AgNO_3$/*t*Bu_3tpy (8:8)	 **5**	**A**	$PhI(OAc)_2$	48	70	**B**	18	90
13	$[Fe(acac)_3]$ (10)		**A**	PhI=O	24	70	**B**	0.7	87
14	$Cu(OTf)_2$ (10)		**A**	–	–	–	**B**	20	86
15	$[Rh_2(OAc)_4]$ (2.5)		**A**	$PhI(OAc)_2$	48	52	**B**	24	54
16	$AgNO_3$/*t*Bu_3tpy (8/:8)	 **6**	**A**	$PhI(OAc)_2$	48	53	**B**	18	88
17	$[Fe(acac)_3]$ (10)		**A**	PhI=O	24	70	**B**	1.5	86
18	$Cu(OTf)_2$ (10)		**A**	–	–	–	**B**	24	82
19	$[Rh_2(OAc)_4]$ (2.5)		**A**	$PhI(OAc)_2$	24	18	**B**	24	20
20	$AgNO_3$/*t*Bu_3tpy (8:8)	 **7**	**A**	$PhI(OAc)_2$	24	47	**B**	24	51
21	$[Fe(acac)_3]$ (10)		**A**	PhI=O	24	43	**B**	24	47
22	$Cu(OTf)_2$ (10)		**A**	–	–	–	**B**	16	68
23	$[Rh_2(OAc)_4]$ (2.5)		**A**	$PhI(OAc)_2$	24	<10	**B**	48	12
24	$AgNO_3$/*t*Bu_3tpy (8:8)	 **8**	**A**	$PhI(OAc)_2$	24	14	**B**	48	25
25	$[Fe(acac)_3]$ (10)		**A**	PhI=O	24	12	**B**	48	21
26	$Cu(OTf)_2$ (10)		**A**	–	–	–	**B**	20	39

[a] Reaction conditions: sulfoxide (1 equiv) and metal catalyst in MeCN or CH_2Cl_2 at room temperature. Method **A**: $NsNH_2$ (1.2–2.0 equiv) and $PhI(OAc)_2$ or PhI=O (1.5–1.6 equiv). Method **B**: PhI=NNs (1.5 equiv). [b] Yield after column chromatography.

iminations than $PhI(OAc)_2$, it was used for the following studies.

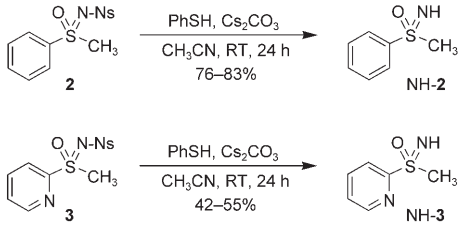
As expected, the best results were obtained when PhI=NNs was used as nitrogen source (method **B**). Unfortunately, the rhodium-catalyzed reactions using the preformed iodinane remained unsatisfactory with only a minor increase in the yields being observed. Thus, rhodium is not the metal of choice for the imination of heteroaromatic-substituted sulfoxides, probably due to a strong coordination of the catalyst with the starting sulfoxides and/or the corresponding sulfoximines. On the other hand, iron was shown to be a more effective catalyst than copper and silver (86–98% yield on **3**–**6**), except for the synthesis of **7** and **8** in which copper provided higher yields (entries 22 and 26, 68 and 39%, respectively).

The low yields observed in the formation of imidazole-sulfoximine **7** (18–68%) and oxadiazole-sulfoximine **8** (<10–39%) with all four systems can again be explained by a partial or complete poisoning of the catalyst through heteroatom coordination. Additionally, the imination of the oxadiazole-sulfoxide was attempted in the absence of metal catalyst at room temperature. Under these conditions, no conversion to sulfoximine **8** was observed, which indicated the necessity of adding a metal catalyst for this transformation to take place.

As mentioned before, it would be most interesting to be able to obtain the synthetically most attractive free NH-sulfoximines. With few exceptions, for example the use of $[Rh_2(OAc)_4]$, which permits the imination of simple sulfoxides with electron-poor amides such as trifluoroacetamide, the methods described so far still lead to *N*-sulfonyl sulfoximines, in which the sulfonamide group is often difficult to cleave in the presence of sensitive functionality.

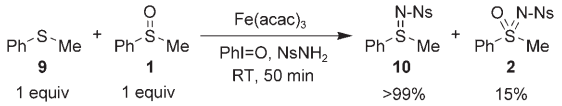
Although the deprotection of simple *N*-nosyl sulfoximines such as **2** has been reported with phenylthiolates (Scheme 2),[16,17] the same transformation was unknown for heteroaomatic sulfoximines. Therefore, we also studied the deprotection of *N*-nosyl methyl 2-pyridyl sulfoximine (**3**). Gratifyingly, it was possible to obtain the desired NH-sulfoximine NH-**3** in reasonable yields (42–55%).

On the other hand, it is worth mentioning that due to the instability of analogous NH-sulfilimines[19] it was not possible to achieve a similar deprotection of the corresponding *N*-substituted sulfilimines, which can also obtained by metal-catalyzed iminations.[14–17]



Scheme 2. Deprotection of *N*-nosyl sulfoximines.

Iminations of sulfides versus sulfoxides: In order to determine the electronic preferences of the various catalyst systems, competitive iminations of sulfoxides and their more nucleophilic sulfide counterparts were explored next. In previous studies, similar reactivities were detected in conversions of simple sulfides and sulfoxides with the $AgNO_3$ system. In contrast, we had observed that sulfides were more reactive than sulfoxides in iminations with $[Rh_2(OAc)_4]$ and $[Fe(acac)_3]$. Moreover, in the case of the iron-catalyzed reactions this observation was verified by a competition experiment with an equimolecular mixture of methyl phenyl sulfide (**9**) and methyl phenyl sulfoxide (**1**).[17] As a result, a quantitative conversion of sulfide **9** into sulfilimine **10** was observed after 50 min, whereas only 15% of nitrene transfer to sulfoxide **1** occurred (Scheme 3).



Scheme 3. Competitive iron-catalyzed imination of sulfides and sulfoxides.

With the goal of further studying the relative imination rates, we first chose thianthrene-5-oxide (**11**) for a competitive imination at both sulfur atoms. While a number of reports on oxidation of thianthrene-5-oxide to the corresponding sulfoxides or sulfones exist in the literature,[20,21] the aza version of this atom transfer process has not been systematically studied.[22]

Due to the high insolubility of the corresponding *N*-nosyl products, the study was carried out with $TsNH_2$ as nitrogen source (method **A**, entries 1–3, Table 3).

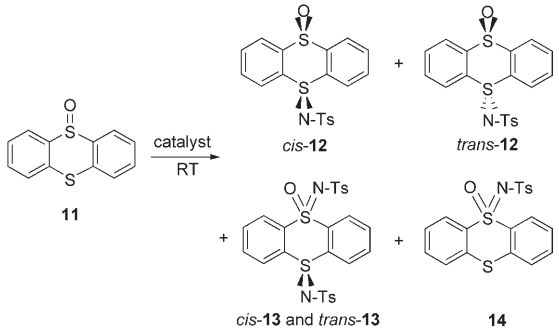
In most cases, the formation of all four possible iminated compounds *cis*-**12**, *trans*-**12**, **13** and **14** was observed.[23] When $[Rh_2(OAc)_4]$ was used, the catalyst showed complete selectivity towards sulfide imitation even when an excess of iodinane (1.5 equiv) was employed (Table 3, entry 1). In the iminations with silver and iron small amounts of sulfoximines **13** and **14** were detected, although the major products were sulfilimines **12** (entries 2–3). Moreover, formation of the *trans*-sulfilimine **12** was clearly favored, especially under silver-catalyzed conditions. This observation was not surprising, considering the reported importance of steric and electronic effects on both the rate and the site of further oxidation of thianthrene-5-oxide depending on the oxidation conditions employed.[20f,h]

In order to improve the reactivity and selectivity of this transformation, we also explored the imination of thianthrene-5-oxide (**11**) with *N*-tosyl iminoiodinane (PhI=NTs) as nitrene precursor (method **B**, Table 3, entries 4–7). Sulfilimines **12** were formed selectively under rhodium-catalyzed conditions. However, unfortunately, only low yields were obtained (entry 4). In contrast, silver-, iron- or copper-based catalysts were more reactive, but less selective with this reagent, leading to complete conversion in relatively short times (1–6 h) and varied mixtures of the corresponding reaction products **12**–**14** (entries 5–7). Due to the higher reactivity exhibited by PhI=NTs, sulfoximine **14** became a major product and was obtained together with *cis*- and *trans*-**12**. While the double imination of thianthrene-5-oxide to give **13** was not favored, a preferential formation of one of the diastereoisomers was always observed (78–90% *de*; the relative configurations of the isomers remained undetermined).

Subsequently, iminations of different, and easier to analyze, *para*-thio phenylsulfoxides **15** were carried out. Of the three possible imination products **16**–**18**, the *para*-thio phenylsulfoximines **18** were not detected, suggesting a second nitrene transfer at sulfoxide in **16** for the formation of the double iminated compound **17** (Scheme 4).

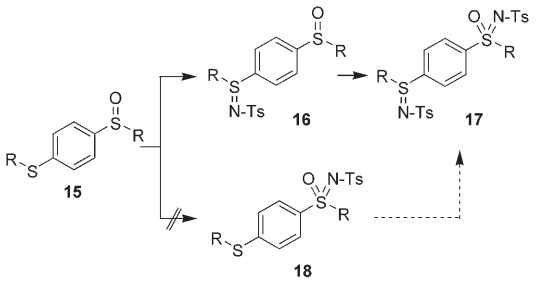
Furthermore, as shown in Table 4, a similar tendency was observed with all metal salts, in which the imination at sulfide was clearly favoured. Predictably, $[Rh_2(OAc)_4]$ acted as an excellent catalyst in this transformation, exhibiting high regioselectivities in the formation of the corresponding sulfilimines. Moreover, the relative ratio of sulfide/sulfoxide imination was almost independent of the nitrene precursor employed (Table 4, entries 1, 5 and 9).

Table 3. Imination of thianthrene-5-oxide (**11**).[a]



Entry	Catalyst	Method	*t* [h]	Yield [%][b] *cis*-**12**/*trans*-**12**/**13**/**14**	*de* of **13** [%][c]
1	$[Rh_2(OAc)_4]$	**A**	20	22:39:–:–	
2	$AgNO_3$/*t*Bu_3tpy	**A**	48	<5:31:8:13	90
3	$[Fe(acac)_3]$	**A**	48	22:26:<5:23	nd
4	$[Rh_2(OAc)_4]$	**B**	8	9:27:–:–	
5	$AgNO_3$/*t*Bu_3tpy	**B**	6	<5:30:28:34	78
6	$[Fe(acac)_3]$	**B**	4	24:29:8:21	80
7	$Cu(OTf)_2$	**B**	1	<5:32:15:36	82

[a] Reaction conditions: **11** (1 equiv) and metal catalyst in MeCN or CH_2Cl_2 at room temperature. Method **A**: $TsNH_2$ (1.2–2.0 equiv) and $PhI(OAc)_2$; for the Fe catalysis: PhI=O (1.5–1.6 equiv). Method **B**: PhI=NTs (1.5 equiv). [b] After column chromatography. [c] Determined by NMR spectroscopy.



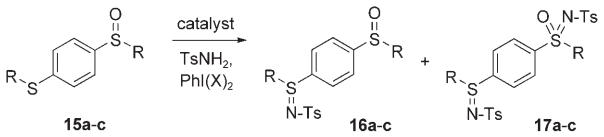
Scheme 4. Imination of *para*-thio phenylsulfoxides.

As previously observed, the silver catalyst reacted slower than the others, but its selectivity was high (entries 2, 6 and 10). Using method **A**, the imination occurred essentially exclusively at the sulfide sulfur of **15** (entries 2, 6 and 10). With method **B** the catalyst turnover improves, but the reaction is less regioselective.

The iron-catalyzed imination of **15** exhibited intermediate reactivity between the rhodium- and silver-catalyzed one (Table 4, entries 3, 7 and 11). While good selectivities in favor of the formation of sulfilimines **16** were observed when the combination of sulfonamide and PhI=O was used (approximately 4:1 ratio, method **A**), the use of PhI=NTs translated to lower selectivity towards the mono-imination (method **B**).

Finally, with the copper catalyst, we confirmed the importance of using preformed iodinanes PhI=NR to achieve good results (entries 4, 8 and 12, method **B**). In the case of the imination of **15a** (R = Ph) under in situ generation of this species (method **A**), the major oxidation product was the corresponding 1,4-disulfoxide (62% yield, entry 4).

Table 4. Imination of *para*-thiophenylsulfoxides **15**.[a]



Entry	Catalyst	R	Thiosulfoxide	Method	*t* [h]	Yield [%][b] **16/17**	Method	*t* [h]	Yield [%][b] **16/17**
1	$[Rh_2(OAc)_4]$	Ph	**15a**	**A**	3	84:<10	**B**	2	80:10
2	$AgNO_3$/*t*Bu_3tpy	Ph	**15a**	**A**	24	45:<5	**B**	2	48:47
3	$[Fe(acac)_3]$	Ph	**15a**	**A**	4	68:8	**B**	2.5	54:29
4	$Cu(OTf)_2$	Ph	**15a**	**A**	4	35:<5[c]	**B**	1	53:36
5	$[Rh_2(OAc)_4]$	*n*Bu	**15b**	**A**	1	76:19	**B**	0.4	70:13
6	$AgNO_3$/*t*Bu_3tpy	*n*Bu	**15b**	**A**	24	67:<10	**B**	3	58:26
7	$[Fe(acac)_3]$	*n*Bu	**15b**	**A**	3	74:13	**B**	3.5	56:17
8	$Cu(OTf)_2$	*n*Bu	**15b**	**A**	–	–	**B**	0.25	35:35
9	$[Rh_2(OAc)_4]$	Me	**15c**	**A**	0.75	73:16	**B**	0.25	72:20
10	$AgNO_3$/*t*Bu_3tpy	Me	**15c**	**A**	24	62:<10	**B**	4	57:14
11	$[Fe(acac)_3]$	Me	**15c**	**A**	0.75	76:17	**B**	2	68:17
12	$Cu(OTf)_2$	Me	**15c**	**A**	–	–	**B**	0.17	74:10

[a] and [b] See respective footnotes in Table 3. [c] The corresponding disulfoxide was isolated as major product (62% yield).

Conclusion

In this comparative study, we investigated the effect of various metal catalysts in oxidative iminations of sulfur compounds. Furthermore, the effect of isolated or in situ generated iminoiodinanes as nitrogen sources was evaluated. A variety of substituted sulfoxides as well as thio-sulfoxides were iminated. No rational reactivity pattern could be found in the imination of heteroaromatic sulfoxides with the different metal catalysts. In all cases, the imination with preformed iminoiodinanes was more effective. The presence of additional heteroatoms in the substrates could inhibit the imination reaction. Iron and copper catalysts showed the greatest tolerance of heteroatom-containing substrates. An important effect of the different oxidation states of sulfur on the reactivity and selectivity in the nitrogen transfer process was observed. Generally sulfilimines were formed in preference over sulfoximines, especially when the iminoiodinane was generated in situ. In this case, rhodium was the most selective catalyst, giving predominantly sulfide imination, even when the more reactive preformed iminoiodinanes were used.

Experimental Section

General: Microanalyses were obtained with a Vario EL element analyzer. Mass spectra were acquired on a Finnigan SSQ7000 (CI 100 eV) spectrometer. IR spectra were taken on a Perkin-Elmer FT/IR 1760 and were recorded as KBr pellets or in solution. ^1H and ^{13}C NMR spectra were recorded in CD_2Cl_2, $CDCl_3$ or $[D_6]$DMSO on a Varian Inova 400 or a Varian Mercury 300 spectrometer (400 and 100 MHz, and 300 and 75 MHz, respectively), see also Supporting Information. Chemical shifts are given in ppm and spin–spin coupling constants, *J*, are given in Hz. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus and are uncorrected. All catalysts were used as purchased. Starting materials: Sulfoxides **1–8** and thiosulfoxides **15a-c** were prepared by oxidation with *m*-CPBA of the corresponding sulfides. Thianthrene-5-oxide (**11**)[24] and iminoiodinanes PhI=NR[25] were synthesized according to literature procedures.

General procedures for the rhodium-catalyzed iminations

Method A: A mixture of the sulfur compound (0.20 mmol), $[Rh_2(AcO)_4]$ (2.2 mg, 0.005 mmol), sulfonyl amide (0.40 mmol) and $PhI(OAc)_2$ (96.6 mg, 0.30 mmol) in CH_2Cl_2 (2.0 mL) was stirred at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

Method B: As described in method **A** but using the corresponding preformed iminoiodinane PhI=NR (0.30 mmol) instead of the sulfonyl amide/$PhI(OAc)_2$ mixture.

General procedures for the silver-catalyzed iminations

Method A: A mixture of the sulfur compound (0.20 mmol), $AgNO_3$ (2.7 mg, 0.016 mmol), tBu$_3$tpy (6.4 mg, 0.016 mmol), sulfonyl amide (0.24 mmol) and $PhI(OAc)_2$ (96.6 mg, 0.30 mmol) in CH_3CN (2.0 mL) was stirred at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

Method B: As described in method **A** but using the corresponding preformed iminoiodinane PhI=NR (0.30 mmol) instead of the sulfonyl amide/$PhI(OAc)_2$ mixture.

General procedures for the iron-catalyzed iminations

Method A: A mixture of sulfur compound (0.20 mmol), $[Fe(acac)_3]$ (7.1 mg, 0.020 mmol), sulfonyl amide (0.30 mmol) and PhI=O (70.4 mg, 0.32 mmol) in CH_3CN (2.0 mL) was stirred at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

Method B: As described in method **A** but using the corresponding preformed iminoiodinane PhI=NR (0.30 mmol) instead of the sulfonyl amide/PhI=O mixture.

General procedure for the copper-catalyzed iminations

Method B: A mixture of sulfur compound (0.20 mmol), $Cu(OTf)_2$ (7.2 mg, 0.020 mmol) and the corresponding iminoiodinane PhI=NR (0.30 mmol) in CH_3CN (2.0 mL) was stirred at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

***N*-(4-Nitrobenzenesulfonyl) methyl phenyl sulfoximine (2)**:[12,14–17] Chromatography: gradient of ethyl acetate/pentane 1:2 to 1:1; pale yellow solid; m.p. 148–150 °C (lit.:[14] 148–151 °C); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.32$ (d, $J = 9.2$ Hz, 2H, H_{Ar}), 8.16 (d, $J = 9.2$ Hz, 2H, H_{Ar}), 8.03 (d, $J = 7.9$ Hz, 2H, H_{Ar}), 7.80–7.72 (m, 1H, H_{Ar}), 7.68–7.62 (m, 2H, H_{Ar}), 3.47 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.7$ (C), 149.0 (C), 137.8 (C), 134.9 (CH), 130.0 (2×CH), 128.1 (2×CH), 127.4 (2×CH), 124.0 (2×CH), 46.9 ppm (CH_3).

***N*-(4-Nitrobenzenesulfonyl) methyl (2-pyridyl) sulfoximine (3)**: Chromatography: gradient of ethyl acetate/pentane 1:1 to ethyl acetate; white solid; m.p. 132–134 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.63$ (d, $J = 4.7$ Hz, 1H, H_{Ar}), 8.20 (d, $J = 8.8$ Hz, 2H, H_{Ar}), 8.11 (d, $J = 7.7$ Hz, 1H, H_{Ar}), 8.01–7.94 (m, 3H, H_{Ar}), 7.57 (dd, $J = 7.7$, 4.7 Hz, 1H, H_{Ar}), 3.44 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 155.6$ (C), 150.3 (CH), 149.6 (C), 140.8 (C), 138.7 (CH), 128.3 (CH), 127.8 (2×CH), 123.9 (2×CH), 123.0 (CH), 41.8 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3104$, 3029, 2936, 1603, 1526, 1466, 1312, 1256, 1159, 1094, 961, 720 cm^{-1}; MS (CI): m/z (%): 342 (100) $[M+H^+]$, 326 (5) $[(M+H)^+-O]$; elemental analysis calcd (%) for $C_{12}H_{11}N_3O_5S_2$ (341.36): C 42.22, H 3.25, N 12.31; found: C 42.34, H 3.47, N 12.27.

***N*-(4-Nitrobenzenesulfonyl) methyl (2-pyrazinyl) sulfoximine (4)**: Chromatography: gradient of ethyl acetate/pentane 1:1 to ethyl acetate; white solid; m.p. 166–167 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 9.39$ (brs, 1H, H_{Ar}), 8.95 (brs, 1H, H_{Ar}), 8.75 (brs, 1H, H_{Ar}), 8.31 (brd, $J = 9.1$ Hz, 2H, H_{Ar}), 8.08 (brd, $J = 9.1$ Hz, 2H, H_{Ar}), 3.53 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 152.1$ (C), 149.8 (C), 149.0 (CH), 148.4 (C), 144.5 (CH), 143.8 (CH), 127.9 (2×CH), 124.0 (2×CH), 41.9 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3075$, 3027, 1730, 1603, 1522, 1312, 1158, 1073, 779, 713, 620 cm^{-1}; MS (CI): m/z (%): 343 (100) $[M+H^+]$, 327 (7) $[(M+H)^+-O]$; elemental analysis calcd (%) for $C_{11}H_{10}N_4O_5S_2$ (342.35): C 38.59, H 2.94, N 16.37; found: C 38.72, H 3.20, N 16.34.

***N*-(4-Nitrobenzenesulfonyl) methyl (2-pyrimidinyl) sulfoximine (5)**: Chromatography: gradient of ethyl acetate/pentane 1:1 to ethyl acetate and then acetone; white solid; m.p. > 205 °C (decomp); ^{1}H NMR (300 MHz, $[D_6]$DMSO): $\delta = 9.13$ (d, $J = 5.0$ Hz, 2H, H_{Ar}), 8.35 (d, $J = 9.0$ Hz, 2H, H_{Ar}), 7.99 (d, $J = 9.0$ Hz, 2H, H_{Ar}), 7.91 (t, $J = 5.0$ Hz, 1H, H_{Ar}), 3.73 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, $[D_6]$DMSO): $\delta = 164.1$ (C), 160.0 (2×CH), 149.9 (C), 148.7 (C), 128.2 (2×CH), 125.6 (CH), 124.8 (2×CH), 41.1 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3013$, 2922, 1572, 1531, 1383, 1307, 1163, 1073, 614 cm^{-1}; MS (CI): m/z (%): 343 (100) $[M+H^+]$; elemental analysis calcd (%) for $C_{11}H_{10}N_4O_5S_2$ (342.35): C 38.59, H 2.94, N 16.37; found: C 38.21, H 3.28, N 16.51.

***N*-(4-Nitrobenzenesulfonyl) (2-benzothiazolyl) methyl sulfoximine (6)**: Chromatography: gradient of CH_2Cl_2 to ethyl acetate/CH_2Cl_2 1:20; white solid; m.p. 202–204 °C; ^{1}H NMR (400 MHz, $[D_6]$DMSO): $\delta = 8.36$–8.30 (m, 1H, H_{Ar}), 8.25 (d, $J = 8.8$ Hz, 2H, H_{Ar}), 8.19–8.13 (m, 1H, H_{Ar}), 7.97 (d, $J = 8.8$ Hz, 2H, H_{Ar}), 7.72–7.66 (m, 2H, H_{Ar}), 3.91 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $[D_6]$DMSO): $\delta = 165.1$ (C), 152.2 (C), 149.9 (C), 147.9 (C), 137.5 (C), 128.9 (CH), 128.5 (CH), 128.3 (2×CH), 125.2 (CH), 124.8 (2×CH), 124.0 (CH), 40.7 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3099$, 3015, 2926, 1602, 1529, 1311, 1155, 1068, 764, 620 cm^{-1}; MS (CI): m/z (%): 398 (100) $[M+H^+]$, 136 (55); elemental analysis calcd (%) for $C_{14}H_{11}N_3O_5S_3$ (397.45): C 42.31, H 2.79, N 10.57; found: C 42.40, H 3.14, N 10.46.

***N*-(4-Nitrobenzenesulfonyl) methyl [2-(*N*-methylimidazolyl)] sulfoximine (7)**: Chromatography: gradient of ethyl acetate/pentane 2:1 to ethyl acetate; white solid; m.p. 126–129 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.20$ (d, $J = 8.8$ Hz, 2H, H_{Ar}), 7.89 (d, $J = 8.8$ Hz, 2H, H_{Ar}), 7.06 (brs, 1H, H_{Ar}), 7.03 (brs, 1H, H_{Ar}), 3.89 (s, 3H, CH_3), 3.56 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 149.7$ (C), 148.2 (C), 138.2 (C), 129.6 (CH), 127.8 (2×CH), 127.2 (CH), 123.9 (2×CH), 44.8 (CH_3), 35.8 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3119$, 3021, 2924, 1609, 1533, 1316, 1244, 1157, 1057, 745; MS (CI): m/z (%): 345 (100) $[M+H^+]$; elemental analysis calcd (%) for $C_{11}H_{12}N_4O_5S_2$ (344.37): C 38.37, H 3.51, N 16.27; found: C 38.51, H 3.60, N 16.01.

***N*-(4-Nitrobenzenesulfonyl) methyl [2-(5-phenyl-1,3,4-oxadiazolyl)] sulfoximine (8)**: Chromatography: CH_2Cl_2; white solid; m.p. 182–183 °C; ^{1}H NMR (400 MHz, $[D_6]$DMSO): $\delta = 8.33$ (d, $J = 8.8$ Hz, 2H, H_{Ar}), 8.04 (d, $J = 8.8$ Hz, 2H, H_{Ar}), 8.03 (d, $J = 7.4$ Hz, 2H, H_{Ar}), 7.73 (t, $J = 7.4$ Hz, 2H, H_{Ar}), 7.64 (t, $J = 7.4$ Hz, 2H, H_{Ar}), 4.04 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $[D_6]$DMSO): $\delta = 167.0$ (C), 160.7 (C), 150.2 (C), 147.1 (C), 134.1 (CH), 130.2 (2×CH), 128.4 (2×CH), 127.8 (2×CH), 125.1 (2×CH), 122.0 (C), 43.7 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3015$, 2922, 1778, 1607, 1533, 1344, 1279, 1088, 750; MS (CI): m/z (%): 409 (12) $[M+H^+]$, 307 (32), 163 (100); elemental analysis calcd (%) for $C_{15}H_{12}N_4O_6S_2$ (408.41): C 44.11, H 2.96, N 13.72; found: C 43.97, H 3.34, N 13.70.

***cis*-10-Monoxy-5-[*N*-(*p*-toluenesulfonyl)]imino thianthrene (*cis*-12)**:[21] Chromatography: gradient of ethyl acetate/pentane 1:2 to ethyl acetate; white solid; m.p. 211–212 °C (lit.:[21] 215–221 °C); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.99$ (d, $J = 7.7$ Hz, 2H, H_{Ar}), 7.96 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 7.90 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 7.69 (t, $J = 7.6$ Hz, 2H, H_{Ar}), 7.61 (t, $J = 7.7$ Hz, 2H, H_{Ar}), 7.26 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 2.36 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.8$ (C), 140.3 (C), 139.2 (C), 131.9 (2×CH), 131.4 (2×CH), 129.7 (2×CH), 129.2 (2×CH), 126.4 (2×CH), 124.9 (2×CH), 124.3 (2×CH), 21.7 ppm (CH_3); MS (CI): m/z (%): 402 (47) $[M+H^+]$, 233 (100) $[(M+H)^+-NTs]$, 172 (42); elemental analysis calcd (%) for $C_{19}H_{15}NO_3S_3$ (401.53): C 56.83, H 3.77, N 3.49; found: C 56.69, H 4.89, N 3.61.

***trans*-10-Monoxy-5-[*N*-(*p*-toluenesulfonyl)]imino thianthrene (*trans*-12)**:[21] Chromatography: gradient of ethyl acetate/pentane 1:2 to ethyl acetate; white solid; m.p. 210–212 °C (lit.:[21] 210–215 °C); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (dd, $J = 7.4$, 1.4 Hz, 2H, H_{Ar}), 7.97 (dd, $J = 7.4$, 1.4 Hz, 2H, H_{Ar}), 7.70 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 7.63 (td, $J = 7.4$, 1.4 Hz, 2H, H_{Ar}), 7.56 (td, $J = 7.3$, 1.4 Hz, 2H, H_{Ar}), 7.12 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 2.30 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 143.8$ (C), 142.2 (C), 140.5 (C), 133.0 (C), 132.4 (C), 131.9 (CH), 129.4 (2×CH), 129.0 (2×CH), 128.3 (2×CH), 126.3 (2×CH), 21.6 ppm (CH_3); MS (CI): m/z (%): 402 $[(M+H)^+$, 22], 233 $[(M+H)^+$-NTs, 100], 172 (35); elemental analysis calcd (%) for $C_{19}H_{15}NO_3S_3$ (401.53): C 56.83, H 3.77, N 3.49; found: C 56.89, H 3.80, N 3.65.

10-Monoxy-5,10-bis[*N*-(*p*-toluenesulfonyl)imino] thianthrene (*cis*- and *trans*-13): Chromatography: gradient of ethyl acetate/pentane 1:2 to ethyl acetate; white solid; major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.19$ (dd, $J = 7.4$, 1.7 Hz, 2H, H_{Ar}), 7.89 (dd, $J = 7.7$, 1.4 Hz, 2H, H_{Ar}), 7.82 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 7.75–7.65 (m, 4H, H_{Ar}), 7.42 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 7.27 (d, $J = 8.0$ Hz, 2H, H_{Ar}), 7.12 (d, $J = 8.0$ Hz, 2H, H_{Ar}), 2.38 (s, 3H, CH_3), 2.33 ppm (s, 3H, CH_3); major isomer: ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.1$ (C), 143.1 (C), 140.1 (C), 138.2 (C), 137.9 (C), 134.0 (2×CH), 132.4 (C), 131.9 (2×CH), 129.9 (2×CH), 129.6 (2×CH), 128.1 (2×CH), 126.7 (2×CH), 126.5 (2×CH), 126.4 (2×CH), 21.6 (CH_3), 21.5 ppm (CH_3); IR (KBr): $\tilde{\nu} = 3073$, 2956, 1594, 1444, 1329, 1273, 1152,

1072, 1002, 756 cm^{-1}; MS (CI): *m/z* (%): 571 (2) [*M*+H^+], 402 (9) [(*M*+H)$^+$−NTs], 172 (100); elemental analysis calcd (%) for $C_{26}H_{22}N_2O_5S_4 \cdot 0.5\,H_2O$ (579.74): C 53.87, H 4.00, N 4.83; found: C 53.94, H 4.01, N 5.02.

5-Monoxy-5-[*N*-(*p*-toluenesulfonyl)]imino thianthrene (14): Chromatography: gradient of ethyl acetate/pentane 1:2 to ethyl acetate; white solid; m.p. 212–213 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30–8.20 (m, 2H, H_{Ar}), 7.62–7.50 (m, 6H, H_{Ar}), 7.45 (d, *J* = 8.4 Hz, 2H, H_{Ar}), 7.09 (d, *J* = 8.0 Hz, 2H, H_{Ar}), 2.37 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.6 (C), 139.1 (C), 134.9 (C), 132.6 (2×CH), 131.7 (C), 128.9 (2×CH), 128.7 (2×CH), 128.0 (2×CH), 127.4 (2x CH), 126.6 (2×CH), 21.5 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 3069, 1573, 1444, 1311, 1239, 1148, 1073, 1028, 765 cm^{-1}; MS (CI): *m/z* (%): 402 (100) [*M*+H^+], 233 (17) [(*M*+H)$^+$−NTs], 172 (15); elemental analysis calcd (%) for $C_{19}H_{15}NO_3S_3$ (401.53): C 56.83, H 3.77, N 3.49; found: C 56.60, H 4.03, N 3.31.

***N*-(*p*-Toluenesulfonyl) phenyl 4-(phenylsulfinyl)phenyl sulfilimine (16a)**: Chromatography: ethyl acetate/pentane 1:1 to elution of the starting material and $TsNH_2$, then ethyl acetate/CH_2Cl_2 1:10; white solid; m.p. 58–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.61 (m, 6H, H_{Ar}), 7.57–7.51 (m, 4H, H_{Ar}), 7.48–7.36 (m, 6H, H_{Ar}), 7.06 (d, *J* = 8.3 Hz, 2H, H_{Ar}), 2.26 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5 (C), 144.3 (C), 141.9 (C), 141.0 (C), 139.7 (C), 135.6 (C), 132.7 (CH), 131.8 (CH), 130.1 (2×CH), 129.7 (2×CH), 129.2 (2×CH), 127.9 (CH), 127.8 (CH), 127.3 (2×CH), 126.2 (2×CH), 125.8 (2×CH), 124.8 (2×CH), 21.6 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 3013, 1597, 1474, 1445, 1292, 1144, 963, 755 cm^{-1}; MS (CI): *m/z* (%): 480 (2) [*M*+H^+], 233 (36) [(*M*+H)$^+$−NTs], 295 (57) [(*M*+H)$^+$−NTs−O], 172 (68), 69 (100); elemental analysis calcd (%) for $C_{25}H_{21}NO_3S_3$ (479.64): C 62.60, H 4.41, N 2.92; found: C 62.45, H 4.77, N 2.79.

***N*-(*p*-Toluenesulfonyl) phenyl 4-[*N*-(*p*-toluenesulfonyl)imino phenylthio] phenyl sulfoximine (17a)**: Chromatography: ethyl acetate/pentane 1:1 to elution of the starting material and $TsNH_2$, then ethyl acetate/CH_2Cl_2 1:10; white solid; m.p. 82–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–8.00 (m, 2H, H_{Ar}), 7.93 (d, *J* = 7.7 Hz, 2H, H_{Ar}), 7.84–7.68 (m, 5H, H_{Ar}), 7.67–7.42 (m, 9H, H_{Ar}), 7.22 (d, *J* = 7.9 Hz, 2H, H_{Ar}), 7.14 (d, *J* = 7.9 Hz, 2H, H_{Ar}), 2.38 (s, 3H, CH_3), 2.33 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1 (C), 143.2 (2×C), 142.2 (C), 140.9 (C), 140.4 (C), 138.4 (C), 135.1 (C), 134.5 (CH), 133.2 (CH), 130.4 (2×CH), 129.9 (2×CH), 129.3 (4×CH), 127.9 (2×CH), 127.5 (2×CH), 127.5 (2×CH), 127.4 (2×CH), 126.7 (2×CH), 126.2 (2×CH), 21.5 (CH_3), 21.4 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 2926, 1727, 1619, 1302, 1148, 1091, 757 cm^{-1}; MS (ESI+): *m/z* (%): 687 (15) [*M*+K^+], 671 (100) [*M*+Na^+], 649 (37) [*M*+H^+]; elemental analysis calcd (%) for $C_{32}H_{28}N_2O_5S_4$ (648.84): C 59.24, H 4.35, N 4.32; found: C 59.19, H 4.66, N 3.93.

***N*-(*p*-Toluenesulfonyl) butyl 4-(butylsulfinyl)phenyl sulfilimine (16b)**: Chromatography: gradient of ethyl acetate/pentane 1:1 to ethyl acetate; pale yellow syrup; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84–7.77 (m, 2H, H_{Ar}), 7.74–7.66 (m, 4H, H_{Ar}), 7.14 (d, *J* = 7.9 Hz, 2H, H_{Ar}), 3.10–2.97 (m, 1H, butyl), 2.92–2.65 (m, 3H, butyl), 2.31 (s, 3H, CH_3), 1.80–1.64 (m, 1H, butyl), 1.64–1.18 (m, 7H, butyl), 0.82 (t, *J* = 7.3 Hz, 3H, CH_3), 0.75 ppm (t, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4 (C), 141.9 (C), 141.0 (C), 138.2 (C), 129.2 (2×CH), 126.9 (2×CH), 126.3 (2×CH), 125.5 (2×CH), 57.0 (CH_2), 53.8 (CH_2), 24.8 (CH_2), 24.0 (CH_2), 23.9 (CH_2), 21.8 (CH_2), 21.4 (CH_3), 21.3 (CH_2), 13.6 (CH_3), 13.4 ppm (CH_3); IR ($CHCl_3$): $\tilde{\nu}$ = 2960, 1464, 1386, 1285, 1144, 1089, 968, 755 cm^{-1}; MS (CI): *m/z* (%): 440 (1) [*M*+H^+], 271 (6) [(*M*+H)$^+$−NTs], 172 (100); elemental analysis calcd (%) for $C_{21}H_{29}NO_3S_3$ (439.66): C 57.37, H 6.65, N 3.19; found: C 57.61, H 6.75, N 3.59.

***N*-(*p*-Toluenesulfonyl) butyl 4-[*N*-(*p*-toluenesulfonyl)imino butylthio]-phenyl sulfoximine (17b)**: Chromatography: gradient of ethyl acetate/pentane 1:1 to ethyl acetate; pale yellow solid; m.p. 52–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.02 (m, 2H, H_{Ar}), 7.95–7.86 (m, 2H, H_{Ar}), 7.80–7.68 (m, 4H, H_{Ar}), 7.24–7.13 (m, 4H, H_{Ar}), 3.47–3.22 (m, 2H, butyl), 3.10–2.96 (m, 1H, butyl), 2.92–2.75 (m, 1H, butyl), 2.34 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 1.65–1.39 (m, 4H, butyl), 1.39–1.15 (m, 4H, butyl), 0.82 (t, *J* = 7.4 Hz, 3H, CH_3), 0.75 ppm (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2 (C), 142.7 (C), 142.2 (C), 141.3 (C), 140.8 (C), 140.4 (C), 129.8 (CH), 129.7 (CH), 129.4 (4×CH), 127.3 (CH), 127.2 (CH), 126.6 (2×CH), 126.3 (2×CH), 57.8 (CH_2), 57.7 (CH_2), 53.7 (CH_2), 24.9 (CH_2), 24.1 (CH_2), 21.6 (CH_3), 21.4 (CH_3), 21.2 (2×CH_2), 13.4 ppm (2×CH_3); IR (KBr): $\tilde{\nu}$ = 2961, 1598, 1462, 1392, 1314, 1150, 1090 cm^{-1}; MS (ESI+): *m/z* (%): 647 (80) [*M*+K^+], 631 (100) [*M*+Na^+], 609 (3) [*M*+H^+]; elemental analysis calcd (%) for $C_{28}H_{36}N_2O_5S_4$ (608.86): C 55.23, H 5.96, N 4.60; found: C 55.03, H 5.62, N 4.33.

***N*-(*p*-Toluenesulfonyl) methyl 4-(methylsulfinyl)phenyl sulfilimine (16c)**: Chromatography: ethyl acetate and then acetone; white solid; m.p. 143–145 °C; ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 7.96 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 7.85 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 7.57 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 7.23 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 3.00 (s, 3H, CH_3), 2.77 (s, 3H, CH_3), 2.30 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 151.4 (C), 141.8 (C), 141.7 (C), 139.3 (C), 129.7 (2×CH), 127.5 (2×CH), 126.2 (2×CH), 125.4 (2×CH), 43.5 (CH_3), 37.5 (CH_3), 21.3 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 3005, 2918, 1595, 1388, 1273, 1140, 1089, 954 cm^{-1}; MS (CI): *m/z* (%): 356 (6) [*M*+H^+], 164 (51) [(*M*+H)$^+$−Ns], 172 (100), 155 (83); elemental analysis calcd (%) for $C_{15}H_{17}NO_3S_3$ (355.50): C 50.68, H 4.82, N 3.94; found: C 50.29, H 4.87, N 3.95.

***N*-(*p*-Toluenesulfonyl) methyl 4-[*N*-(*p*-toluenesulfonyl)imino methylthio] phenyl sulfoximine (17c)**: Chromatography: ethyl acetate and then acetone; white solid; m.p. 233–235 °C; ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 8.14–8.01 (m, 4H, H_{Ar}), 7.62 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 7.55 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 7.32–7.22 (m, 4H, H_{Ar}), 3.64 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.31 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 143.3 (C), 143.1 (C), 142.0 (C), 141.8 (C), 141.7 (C), 140.7 (C), 129.8 (2×CH), 129.7 (2×CH), 129.1 (2×CH), 127.6 (2×CH), 126.5 (2×CH), 126.2 (2×CH), 44.7 (CH_3), 37.6 (CH_3), 21.4 (CH_3), 21.3 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 3008, 2921, 1594, 1389, 1280, 1235, 1145, 1093, 963 cm^{-1}; MS (CI): *m/z* (%): 563 (100) [*M*+K^+], 547 (25) [*M*+Na^+], 525 (2) [*M*+H^+]; elemental analysis calcd (%) for $C_{22}H_{24}N_2O_5S_4$ (524.70): C 50.36, H 4.61, N 5.34; found C, 49.98, H 4.78, N 4.99.

General procedure for the deprotection of *N*-nosyl sulfoximines: To a solution of sulfoximine (0.80 mmol) in acetonitrile (13 mL) was added Cs_2CO_3 (469.2 mg, 1.44 mmol) and thiophenol (130 μL, 1.28 mmol) at room temperature and the reaction mixture was stirred overnight. Water was added to the reaction mixture and the product was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and concentrated and the residue was purified by flash column chromatography.

Methyl phenyl sulfoximine (NH-2):[4c,14–17] Chromatography: gradient of ethyl acetate to ethyl acetate/20% EtOH; colorless oil; H NMR (300 MHz, $CDCl_3$): δ = 8.05–8.00 (m, 2H, H_{Ar}), 7.69–7.52 (m, 3H, H_{Ar}), 3.11 (s, 3H, CH_3), 2.47 ppm (br s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.5 (C), 133.1 (CH), 129.3 (2×CH), 127.7 (2×CH), 46.2 ppm (CH_3).

Methyl (2-pyridyl) sulfoximine (NH-3):[26] Chromatography: gradient of ethyl acetate to acetone; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 4.0 Hz, 1H, H_{Ar}), 8.15 (d, *J* = 7.7 Hz, 1H, H_{Ar}), 7.97 (t, *J* = 7.7 Hz, 1H, H_{Ar}), 7.54 (dd, *J* = 7.7, 4.1 Hz, 1H, H_{Ar}), 3.28 (s, 3H, CH_3), 2.74 ppm (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (C), 150.0 (CH), 138.2 (CH), 126.7 (CH), 121.1 (CH), 42.4 ppm (CH_3); IR ($CHCl_3$): $\tilde{\nu}$ = 3267, 3009, 2929, 1651, 1576, 1425, 1227, 1011 cm^{-1}; MS (CI): *m/z* (%): 157 (100) [*M*+H^+]; elemental analysis calcd (%) for $C_6H_8N_2OS$ (156.21): C 46.13, H 5.16, N 17.93; found: C 45.73, H 5.31, N 17.62.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie. O.G.M. thanks the Spanish Ministerio de Educación y Ciencia (M.E.C.) for a postdoctoral fellowship.

[1] For selected examples, see: a) C. Bolm, O. Simic, *J. Am. Chem. Soc.* **2001**, *123*, 3830–3831; b) M. Harmata, S. K. Ghosh, *Org. Lett.* **2001**, *3*, 3321–3323; c) C. Bolm, M. Martin, O. Simic, M. Verrucci, *Org.*

Lett. **2003**, *5*, 427–429; d) C. Bolm, M. Verrucci, O. Simic, P. G. Cozzi, G. Raabe, H. Okamura, *Chem. Commun.* **2003**, 2826–2827; e) C. Bolm, M. Martin, G. Gescheidt, C. Palivan, D. Neshchadin, H. Bertagnolli, M. P. Feth, A. Schweiger, G. Mitrikas, J. Harmer, *J. Am. Chem. Soc.* **2003**, *125*, 6222–6227; f) M. Langner, C. Bolm, *Angew. Chem.* **2004**, *116*, 6110–6113; *Angew. Chem. Int. Ed.* **2004**, *43*, 5984–5987; g) C. Mössner, C. Bolm, *Angew. Chem.* **2005**, *117*, 7736–7739; *Angew. Chem. Int. Ed.* **2005**, *44*, 7564–7567; h) M. Langner, P. Rémy, C. Bolm, *Synlett* **2005**, 781–784; i) M. Langner, P. Rémy, C. Bolm, *Chem. Eur. J.* **2005**, *11*, 6254–6265; j) M. T. Reetz, O. G. Bondarev, H.-J. Gais, C. Bolm, *Tetrahedron Lett.* **2005**, *46*, 5643–5646; reviews: k) M. Harmata, *Chemtracts* **2003**, *16*, 660–666; l) H. Okamura, C. Bolm, *Chem. Lett.* **2004**, *33*, 482–487.

[2] a) C. Bolm, J. D. Kahmann, G. Moll, *Tetrahedron Lett.* **1997**, *38*, 1169–1172; b) C. Bolm, G. Moll, J. D. Kahmann, *Chem. Eur. J.* **2001**, *7*, 1118–1128; c) H. Tye, C. L. Skinner, *Helv. Chim. Acta* **2002**, *85*, 3272–3282; d) C. Bolm, D. Müller, C. P. R. Hackenberger, *Org. Lett.* **2002**, *4*, 893–896; e) C. Bolm, D. Müller, C. Dalhoff, C. P. R. Hackenberger, E. Weinhold, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3207–3211.

[3] a) C. R. Johnson, *Acc. Chem. Res.* **1973**, *6*, 341–347; b) *Methoden Org. Chem. (Houben-Weyl), Vol. E11* (Ed.: D. Klamann), Thieme, Stuttgart, **1985**, Parts 1–2; c) S. Pyne, *Sulfur Rep.* **1992**, *12*, 57–89; d) M. Mikolajczk, J. Drabowicz, P. Kielbasinski in *Chiral Sulfur Reagents*, CRC Press, **1997**; e) P. C. Taylor, *Sulfur Rep.* **1999**, *21*, 241–280; f) M. Reggelin, C. Zur, *Synthesis* **2000**, 1–64; g) R. Bentley, *Chem. Soc. Rev.* **2005**, *34*, 609–624.

[4] a) R. Fusco, F. Tenconi, *Chim. Ind.* (Milan) **1965**, *47*, 61–62; b) C. R. Johnson, C. W. Schroeck, *J. Am. Chem. Soc.* **1973**, *95*, 7418–7423; c) for an improved protocol, see: J. Brandt, H.-J. Gais, *Tetrahedron: Asymmetry* **1997**, *8*, 909–912.

[5] a) Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii, M. Ikeda, *J. Org. Chem.* **1973**, *38*, 1239–1241, b) C. R. Johnson, R. A. Kirchhoff, H. G. Corkins, *J. Org. Chem.* **1974**, *39*, 2458–2459, c) Y. Tamura, H. Matushima, J. Minamikawa, M. Ikeda, K. Sumoto, *Tetrahedron* **1975**, *31*, 3035–3040, d) M. Fieser, L. F. Fieser, *Reagents for Organic Synthesis, Vol. 5*, Wiley, New York, **1975**, p. 430; see also: e) S. Allenmark, S. Claeson, C. Lowendahl, *Tetrahedron: Asymmetry* **1996**, *7*, 361–364.

[6] For alternative metal-free sulfoxide iminations, see: a) G. Y. Cho, C. Bolm, *Tetrahedron Lett.* **2005**, *46*, 8007–8008, b) T. Siu, C. J. Picard, A. K. Yudin, *J. Org. Chem.* **2005**, *70*, 932–937, c) S. Karabuga, C. Kazaz, H. Kilic, S. Ulukanli, A. Celik, *Tetrahedron Lett.* **2005**, *46*, 5225–5227, d) L. B. Krasnova, R. M. Hili, O. V. Chernoloz, A. K. Yudin, *Arkivoc* **2005**, *Part iv*, 26–38.

[7] For the first reported copper-catalyzed imination of sulfoxides, see: H. Kwart, A. A. Kahn, *J. Am. Chem. Soc.* **1967**, *89*, 1950–1951.

[8] a) T. Bach, C. Körber, *Tetrahedron Lett.* **1998**, *39*, 5015–5016, b) T. Bach, C. Körber, *Eur. J. Org. Chem.* **1999**, *64*, 1033–1039.

[9] J. F. K. Müller, P. Vogt, *Tetrahedron Lett.* **1998**, *39*, 4805–4806.

[10] C. Bolm, K. Muñiz, N. Aguilar, M. Kesselgruber, R. Raabe, *Synthesis* **1999**, 1251–1260.

[11] J. Nakayama, T. Otani, Y. Sugihara, Y. Sano, A. Ishii, A. Sakamoto, *Heteroat. Chem.* **2001**, *12*, 333–348.

[12] S. Cren, T. C. Kinahan, C. L. Skinner, H. Tye, *Tetrahedron Lett.* **2002**, *43*, 2749–2751.

[13] a) E. Lacôte, M. Amatore, L. Fensterbank, M. Malacria, *Synlett* **2002**, 116–118, b) for other example of Cu-catalyzed iminations, see: H. Takada, K. Ohe, S. Uemura, *Angew. Chem.* **1999**, *111*, 1367–1369; *Angew. Chem. Int. Ed.* **1999**, *38*, 1288–1289.

[14] H. Okamura, C. Bolm, *Org. Lett.* **2004**, *6*, 1305–1308.

[15] Despite the high reagent cost, the rhodium-catalyzed sulfoxide imination protocol has already been mentioned in the patent literature; a) A. Jeanguenat, A. C. O'Sullivan, WO 032462 A1, 2006 (Syngenta); b) A. Jeanguenat, A. C. O'Sullivan, WO 061200 A1, **2006** (Syngenta); c) U. Lücking, G. Siemeister, R. Jautelat, WO 099974 A1, **2006** (Schering); d) U. Lücking, EP 1710246 A1, **2006** (Schering).

[16] G. Y. Cho, C. Bolm, *Org. Lett.* **2005**, *7*, 4983–4985.

[17] O. García Mancheño, C. Bolm, *Org. Lett.* **2006**, *8*, 2349–2352.

[18] For the use of Mn–porphyrin complexes, see: a) H. Nishikori, C. Ohta, E. Oberlin, R. Irie, T. Katsuki, *Tetrahedron* **1999**, *55*, 13937–13946; b) C. Ohta, T. Katsuki, *Tetrahedron Lett.* **2001**, *42*, 3885–3888; for the use of a nitrido–Mn^{V} catalyst, see: c) C. S. Tomooka, E. M. Carreira, *Helv. Chim. Acta* **2002**, *85*, 3773–3784; for Ru complexes, see: d) M. Murakami, T. Uchida, T. Katsuki, *Tetrahedron Lett.* **2001**, *42*, 7071–7074; e) Y. Tamura, T. Uchida, T. Katsuki, *Tetrahedron Lett.* **2003**, *44*, 3301–3303; f) M. Murakami, T. Uchida, B. Saito, T. Katsuki, *Chirality* **2003**, *15*, 116–123; g) T. Uchida, Y. Tamura, M. Ohba, T. Katsuki, *Tetrahedron Lett.* **2003**, *44*, 7965–7968; see also: h) T. Katsuki, *Chem. Lett.* **2005**, *34*, 1304–1309.

[19] For the use of the lability of sulfilimines to generate alkenes, see: J. Matsuo, T. Kozai, H. Ishibashi, *Org. Lett.* **2006**, *8*, 6095–6098.

[20] For oxygen-transfer reactions to thianthrene 5-oxide, see: a) W. Adam, W. Haas, G. Seiker, *J. Am. Chem. Soc.* **1984**, *106*, 5020–5022; b) W. Adam, Y. Y. Chan, D. Cremer, J. Gauss, D. Scheutzow, M. Schindler, *J. Org. Chem.* **1987**, *52*, 2800–2803; c) W. Adam, W. Haas, B. B. Lohray, *J. Am. Chem. Soc.* **1991**, *113*, 6202–6208; d) F. P. Batllistreti, G. A. Tomaselli, R. M. Toscano, V. Conte, F. D. Furia, *J. Am. Chem. Soc.* **1991**, *113*, 6209–6212; e) E. L. Clennan, K. Yang, *J. Org. Chem.* **1993**, *58*, 4504–4505; f) W. Adam, D. Golsch, *Chem. Ber.* **1994**, *127*, 1111–1113; g) M. Bonchio, V. Conte, M. A. De Conciliis, F. D. Furia, F. P. Batllistreti, G. A. Tomaselli, R. M. Toscano, *J. Org. Chem.* **1995**, *60*, 4475–4480; h) W. Adam, D. Golsch, F. C. Görth, *Chem. Eur. J.* **1996**, *2*, 255–258; i) W. Adam, D. Golsch, *J. Org. Chem.* **1997**, *62*, 115–119; j) D. V. Deubel, *J. Org. Chem.* **2001**, *66*, 2686–2691.

[21] For oxidation studies of 5-*N*-imininothianthrene derivatives, see: H. Morita, H. Kawaguchi, T. Yoshimura, E. Tsukurimichi, C. Shimasaki, E. Horn, *Chem. Eur. J.* **2000**, *6*, 3976–3983.

[22] For iminations of thianthrene and derivatives, see: a) H. J. Shine, J. J. Silber, *J. Am. Chem. Soc.* **1972**, *94*, 1026–1027; b) P. Stoss, G. Satzinger, *Tetrahedron Lett.* **1974**, *15*, 1973–1976; c) H. J. Shine, K. Kim, *Tetrahedron Lett.* **1974**, *15*, 99–101; d) S. R. Mani, H. J. Shine, *J. Org. Chem.* **1975**, *40*, 2756–2758.

[23] The relative *cis* or *trans* configuration of sulfilimines **12** was determined by comparison with the literature data, see ref. [21].

[24] H. Gilman, D. R. Swayampati, *J. Am. Chem. Soc.* **1955**, *77*, 3387–3389.

[25] S. Taylor, J. Gullick, P. McMorn, D. Bethell, P. C. Bulman Page, F. E. Hancock, F. King, G. J. Hutchings, *Top. Catal.* **2003**, *24*, 43–50.

[26] N. Furukawa, F. Takahashi, K. Kishimoto, H. Morita, S. Oae, *Heterocycles* **1980**, *14*, 1273–1278.

Received: March 2, 2007
Published online: May 30, 2007

