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Iron-Catalyzed Imination of Sulfoxides and Sulfides

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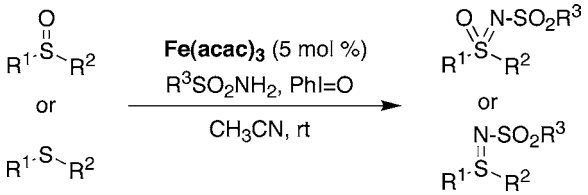
ABSTRACT



The Fe(III)-catalyzed imination of sulfoxides and sulfides with sulfonylamides in the presence of iodinanes has been investigated. The best results were obtained when $Fe(acac)_3$ was used as a catalyst in combination with iodosylbenzene, providing an effective alternative (stereospecific) access to sulfoximines and sulfilimines.

Since the discovery of sulfoximines in the early 1950s by Whitehead and Bentley,[1] sulfoximines and sulfilimines have attracted great attention among organic chemists. Due to the presence of an amphoteric nitrogen and a stereogenic sulfur atom, they have been widely used as building blocks for chiral ligands[2] and as structural units in pseudopeptides.[3] Several strategies for their preparation have been developed.[4] However most of them require the use of toxic and potentially explosive reagents such as hydrazoic acid (NaN_3/H_2SO_4)[5] or *O*-mesitylenesulfonylhydroxylamine (MSH).[6] Recently, to avoid such reagents, interest has grown in metal-catalyzed nitrene transfer reactions to sulfur compounds. In this context, copper salts[7] and manganese or ruthenium complexes[8] have been described as catalysts for this transformation. However, those methods generally lead to N-substituted products with protecting groups such as tosyl,

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(2) For examples, see: (a) Bolm, C.; Simic, O. *J. Am. Chem. Soc.* **2001**, *123*, 3830. (b) Harmata, M.; Ghosh, S. K. *Org. Lett.* **2001**, *3*, 3321. (c) Bolm, C.; Martin, M.; Simic, O.; Verrucci, M. *Org. Lett.* **2003**, *5*, 427. (d) Bolm, C.; Verrucci, M.; Simic, O.; Cozzi, P. G.; Raabe, G.; Okamura, H. *Chem. Commun.* **2003**, 2816. (e) Bolm, C.; Martin, M.; Gescheidt, G.; Palivan, C.; Neshchadin, D.; Bertagnolli, H.; Feth, M. P.; Schweiger, A.; Mitrikas, G.; Harmer, J. *J. Am. Chem. Soc.* **2003**, *125*, 6222. (g) Langner, M.; Bolm, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5984. (h) Mössner, C.; Bolm C. *Angew. Chem., Int. Ed.* **2005**, *44*, 7564. (i) Langner, M.; Rémy, P.; Bolm, C. *Synlett* **2005**, 781. (j) Langner, M.; Rémy, P.; Bolm, C. *Chem. Eur. J.* **2005**, *11*, 6254. (k) Reetz, M. T.; Bondarev, O. G.; Gais, H.-J.; Bolm, C. *Tetrahedron Lett.* **2005**, *46*, 5643. Reviews: (l) Harmata, M. *Chemtracts* **2003**, *16*, 660. (m) Okamura, H.; Bolm, C. *Chem. Lett.* **2004**, *33*, 482.

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

(4) Reviews concerning sulfoximines and sulfilimines: (a) Johnson, C. R. *Acc. Chem. Res.* **1973**, *6*, 341. (b) Pyne, S. G. *Sulfur Rep.* **1999**, *21*, 281. (c) Taylor, P. C. *Sulfur Rep.* **1999**, *21*, 241. (d) Reggelin, M.; Zur, C. *Synthesis* **2000**, 1. (e) Bentley R. *Chem. Soc. Rev.* **2005**, *34*, 609.

(5) NaN_3/H_2SO_4: (a) Fusco, R.; Tericoni, F. *Chim. Ind. (Milan)* **1965**, *47*, 61. (b) Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc.* **1973**, *95*, 7418. For an improved protocol, see: (c) Brandt, J.; Gais, H.-J. *Tetrahedron: Asymmetry* **1997**, *6*, 909. For the toxicity of NaN_3, see: (d) *Merck Index*, 12th ed.; Budavari, S., Ed.; Merck & Co., Inc.: Rahway, NJ, 1996; p 451.

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

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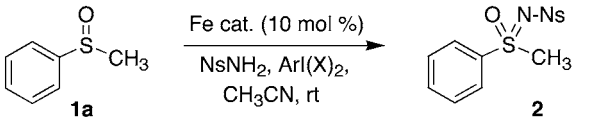
which are difficult to cleave to give the synthetically more valuable *NH*-sulfoximines.[9] Iron-catalyzed iminations of sulfides and sulfoxides affording products with more easily removable Boc and SES protecting groups appear attractive,[10,11] but since they involve the use of potentially explosive azides as nitrogen sources, their applicability in large-scale synthesis is rather limited.

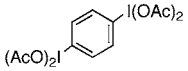
In 2004, we described that $Rh_2(OAc)_4$ is an effective catalyst for the imination of sulfur compounds at room temperature with readily available trifluoroacetamide or *p*-nosylamide as safe nitrene precursors.[12] The synthetically interesting NH-products can then be obtained by subsequent easy-to-perform cleavage reactions. A limiting feature of this protocol is the high cost of the rhodium catalyst. Further investigations have led to the discovery that less costly silver nitrate (in combination with a terpyridine ligand) is also an efficient catalyst for sulfur imination reactions.[13,14] Extending our interest in improving and simplifying such transformations, and in connection with our ongoing program showing the wide potential of sulfoximines as ligands and building blocks in organic synthesis, *we herein describe the application of simple iron catalysts for the imination of sulfoxides and sulfides with sulfonylamides under mild conditions*.

As a model reaction the imination of methyl phenyl sulfoxide (**1a**) with a combination of *N*-nosylamide ($NsNH_2$) and iodobenzene diacetate [$PhI(OAc)_2$] in the presence of an iron salt was investigated. In the first attempt, 10 mol % of $FeCl_2$ in acetonitrile was applied. In contrast to the system studied by Bach, which involved $BocN_3$ as nitrogen source,[10a−c] a low reactivity was observed here both at room temperature and at reflux (Table 1, entry 1).

Other iron salts proved more reactive (Table 1, entries 2−4), and to our delight, iron(II) or iron(III) acetylacetonate exhibited excellent reactivity, giving sulfoximine **2** in 83 or 90% yield after only 7 or 3 h, respectively (entries 3 and 4).[15,16] As expected, reaction with preformed *N*-nosylimidoiodinane (PhI═NNs) as the nitrene source proceeded faster. Thus, sulfoximine **2** was obtained in 88% yield after only 1 h (entry 5). Acetonitrile proved to be superior to other solvents such as THF or dichloromethane, which did not give **2** at all or only in low yield (20%), respectively.

Table 1. Optimization of the Iron-Catalyzed Imination with $Ns\text{-}NH_2$[a]



entry	Fe catalyst	$ArI(X)_2$	t (h)	yield (%)[b]
1	$FeCl_2$	$PhI(OAc)_2$	16 (20)[c]	20 (66)[c]
2	$Fe(ClO_4)_2$	$PhI(OAc)_2$	20	61
3[d]	$Fe(acac)_2$	$PhI(OAc)_2$	7	83
4	$Fe(acac)_3$	$PhI(OAc)_2$	3	90
5	$Fe(acac)_3$	PhI=NNs[e]	1	88
6	$Fe(acac)_3$		20	77
7	$Fe(acac)_3$	$PhI(OCOCF_3)_2$	48	20
8	$Fe(acac)_3$	PhI=O	0.5	97

[a] Reaction conditions: sulfoxide **1a** (1 equiv), Fe catalyst (10 mol %), $NsNH_2$ (1.5 equiv), and $ArI(X)_2$ (1.6 equiv) in CH_3CN (0.1 M) at room temperature. [b] Yield after columm chromatography. [c] Reaction time and yield in refluxing CH_3CN specified in parentheses. [d] See comment in ref 16. [e] Use of 1.6 equiv of PhI═NNs.

At this stage, other iodinanes were evaluated as oxidants for this process (entries 6−8). As shown in Table 1, both the aromatic and hetereoatomic substituents at iodine had a strong effect on the reactivity. The best results were obtained with iodosylbenzene (PhI═O), which provided **2** in 97% yield after 30 min (entry 8).[17]

The reduction of the catalyst loading from 10 to 5 mol % had no significant effect on the catalyst efficiency, and sulfoximine **2** was formed in similar yield (Table 2, entries 1 and 2). With 5 mol % of the catalyst a 3.5-fold increase of the reaction scale was well tolerated and the catalyst activity remained high (entry 3). Further reduction of the catalyst loading to 1 mol % led to an incomplete conversion of **1a** even after an extended reaction time and consequently, only a modest yield of **2** was obtained (54%, entry 4).

Under the optimized conditions, which involved the use of 5 mol % of $Fe(acac)_3$ and PhI═O in acetonitrile at room temperature, a variety of sulfonylamides were tested as iminating agents for sulfoxide **1a** (Table 3, entries 2−6).

Gratifyingly, albeit over longer reaction times compared to the parent *p*-nosylamide ($NsNH_2$), the iron-catalyzed iminations of **1a** with *p*-tosylamide ($TsNH_2$), 2-trimethylsilylethylsulfonylamide ($SESNH_2$), *p*-methyl-2-pyridinylsulfonylamide, and 2-benzothiazolesulfonylamide proceeded well at room temperature, affording the corresponding sulfoximines **3**−**6** in moderate to good yields (66−88%).

(8) Mn complexes: (a) Nishikori, H.; Ohta, C.; Oberlin, E.; Irie, R.; Katsuki, T. *Tetrahedron* **1999**, *55*, 13937. (b) Ohta, C.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 3885. Ru complexes: (c) Murakami, M.; Uchida, T.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 7071. (d) Tamura, Y.; Uchida, T.; Katsuki, T. *Tetrahedron Lett.* **2003**, *44*, 3301. (e) Murakami, M.; Uchida, T.; Saito, B.; Katsuki, T. *Chirality* **2003**, *15*, 116. (f) Uchida, T.; Tamura, Y.; Ohba, M.; Katsuki, T. *Tetrahedron Lett.* **2003**, *44*, 7965. See also in: (g) Katsuki, T. *Chem. Lett.* **2005**, *34*, 1304..

(9) For alternatve metal-free sulfoxide iminations, see: (a) Siu, T.; Picard, C. J.; Yudin, A. K. *J. Org. Chem.* **2005**, *70*, 932. (b) Krasnova, L. B.; Hili, R. M.; Chernoloz, O. V.; Yudin, A. K. *Arkivoc* **2005**, *iv*, 26. (c) Karabuga, S.; Kazaz, C.; Kilic, H.; Ulukanli, S.; Celik, A. *Tetrahedron Lett.* **2005**, *46*, 5225.

(10) $BocN_3$: (a) Bach, T.; Körber, C. *Tetrahedron Lett.* **1998**, *39*, 5015. (b) Bach, T.; Körber, C. *Eur. J. Org. Chem.* **1999**, *64*, 1033. (c) Bolm, C.; Muñiz, K.; Aguilar, N.; Kesselgruber, M.; Raabe, R. *Synthesis* **1999**, 1251. $SESN_3$: (d) Reggelin, M.; Weinberger, H.; Spohr, V. *Adv. Synth. Catal.* **2004**, *346*, 1295.

(11) For a general review on iron-catalyzed reactions, see: Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217.

(12) Okamura, H.; Bolm, C. *Org. Lett.* **2004**, *6*, 1305.

(13) Cho, G. Y.; Bolm, C. *Org. Lett.* **2005**, *7*, 4983.

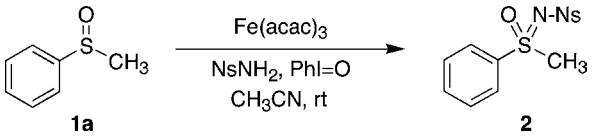
(14) For a recent contribution on metal-free iminations allowing access to NH derivatives, see: Cho, G. Y.; Bolm, C. *Tetrahedron Lett.* **2005**, *46*, 8007.

(15) The use of 1.1 equiv instead of 1.5 equiv of $NsNH_2$ hampered the conversion, providing sulfoximine **2** in a moderate yield (57%).

(16) Contaminating traces of Fe(III) salts could not be excluded from the $Fe(acac)_2$ here used. Attempts to determine the precise nature of the Fe species remained inconclusive.

(17) Iron(III) benzoylacetonate, $[Fe(bzac)_3]$, is also a good catalyst under these reaction conditions, furnishing **2** in 97% yield after 45 min.

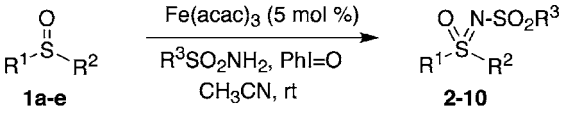
Table 2. Optimization of the Catalyst Loading[a]

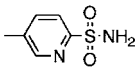
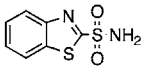
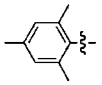


entry	$Fe(acac)_3$ (mol %)	t (h)	yield[b] (%)
1	10	0.5	97
2	5	1	96
3	5	1.5[c]	95
4	1	20	54

[a] Reaction conditions: sulfoxide **1a** (0.285 mmol, 1 equiv), $NsNH_2$ (1.5 equiv), and PhI=O (1.6 equiv) in CH_3CN (0.1 M) at room temperature. [b] Yield after columm chromatography. [c] Reaction scaled up to 1 mmol of **1a**.

Table 3. Iron-Catalyzed Imination of Sulfoxides[a]



entry	R^1	R^1	$R^3SO_2NH_2$	t (h)	product	yield (%)[b]
1	Ph	Me	$NsNH_2$	1	**2**	96
2	Ph	Me	$TsNH_2$	18	**3**	81
3	Ph	Me	$SESNH_2$	18	**4**	66
4	Ph	Me		18	**5**	87
5	Ph	Me		14	**6**	88
6	Ph	Me	$BusNH_2$	20		--
7		Me	$NsNH_2$	20		--
8	*t*-Bu	Me	$NsNH_2$	2	**7**	80
9	Ph	Ph	$NsNH_2$	6	**8**	80
10	Ph	Vinyl	$NsNH_2$	8	**9**	72
11	-(CH_2-CH_2)-		$NsNH_2$	8	**10**	86

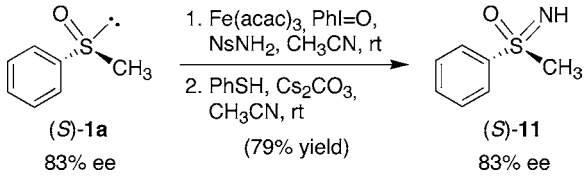
[a] Reaction conditions: sulfoxide **1** (1 equiv), $Fe(acac)_3$ (5 mol %), $NsNH_2$ (1.5 equiv), and PhI=O (1.6 equiv) in CH_3CN (0.1 M) at room temperature. [b] Yield after column chromatography.

Only the very bulky *tert*-butylsulfonyl amide ($BusNH_2$) could not iminate sulfoxide **1a** (Table 3, entry 6). These results are of particular significance, since they offer various possibilities for the deprotection of the sulfoximine nitrogen.[18]

To evaluate the scope of the imination reaction various sulfoxides were applied as substrates (Table 3, entries 7−11). In general, their conversion was smooth and the corresponding sulfoximines were formed (with ≥72% yield) after short reaction times. Even sulfoxides with a bulky *tert*-butyl group or a vinyl substituent (entries 8 and 10) reacted well affording sulfoximines in good yields. Only the imination of a substrate with a sterically demanding (2,4,6-trisubstituted) aromatic group remained unsuccessful (entry 7).

Next, the stereospecificity of both the iron-catalyzed imination process (with a combination of PhI=O and $NsNH_2$ as NNs source) and the subsequent conversion of the resulting product into the corresponding *NH*-sulfoximine were studied.[19] For this purpose, sulfoxide (*S*)-**1a** with 83% ee[20] was reacted under standard imination conditions to give *N*-nosylsulfoximine **2**, which was deprotected at room temperature by nucleophilic aromatic substitution with thiophenolate, generated in situ from Cs_2CO_3 and thiophenol (Scheme 1).[18,19] "Free" *NH*-sulfoximine (*S*)-**11** was thus obtained in good yield (79% over two steps), and the ee analysis of **11**[21] revealed that the reaction sequence had proceeded without epimerization and with retention of configuration at the stereogenic sulfur.

Scheme 1



With the goal to determine the generality of the iron-catalyzed sulfur imination, the reactions of several sulfides with combinations of PhI=O and $NsNH_2$ were examined next. Under the same reaction conditions as those employed for the sulfoxide imination, the more nucleophilic sulfides showed high reactivities providing the corresponding sulfilimines **12**−**16** in excellent yields after reaction times of 40 min to 8 h (Figure 1).

Additionally, a competition experiment using a 1:1 mixture of methyl phenyl sulfoxide (**1a**) and methyl phenyl sulfide was carried out. After 50 min, a quantitative conversion of the sulfide into sulfilimine **12** was observed, and only 15% of nitrene transfer to sulfoxide **1a** had occurred.[22] The greater reactivity of the sulfides also allowed the imination to proceed with substrates bearing bulky aromatic substituents (such as a 2,4,6-trimethylphenyl group) at sulfur, whereas the corresponding sulfoxides had failed to react in the same

(18) For example, nosyl- and benzothiazolesulfonylamides can be easily cleaved using thiolates, SES-amide react upon treatment with fluorides to give amines, and deprotection of the pyridinyl derivative could be achieved by reaction with Mg. For general methods for the deprotection of sulfonylamides, see: Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley & Sons: New York, 1999; p 603.

(19) For the pioneering work on the use of the nosyl group, see: Fukuyama, T.; Jow, C.-K.; Cheung, M. *Tetrahedron Lett.* **1995**, *36*, 6373.

(20) Sulfoxide (*S*)-**1a** was prepared by iron-catalyzed asymmetric oxidation of the corresponding sulfide with H_2O_2 as oxidant as previously described by our group. (a) Legros, J.; Bolm, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5487. (b) Legros, J.; Bolm, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 4225. (c) Legros, J.; Bolm, C. *Chem. Eur. J.* **2005**, *11*, 1086. The ee of **1a** was determined by HPLC using a chiral column: Chiralcel OD; heptane/*i*-PrOH = 90:10; 0.5 mL/min; 254 nm; t_R(*R*): 23.4 min, t_R(*S*): 29.7 min.

(21) The enantiomeric excess of **11** was determined by HPLC using a chiral column: Chiralcel OJ; heptane/*i*-PrOH = 85:15; 0.5 mL/min; 254 nm; t_R(*R*): 36.9 min, t_R(*S*): 48.9 min.

(22) Conversion ratios were determined by ^{1}H NMR on the crude mixture.

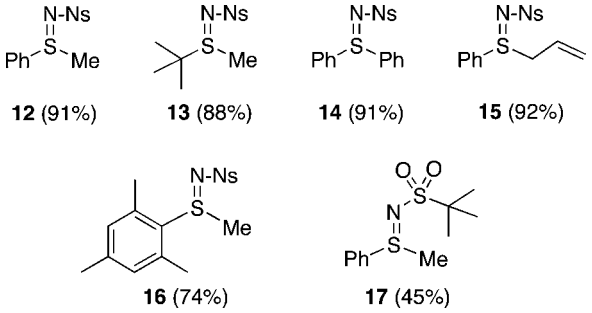
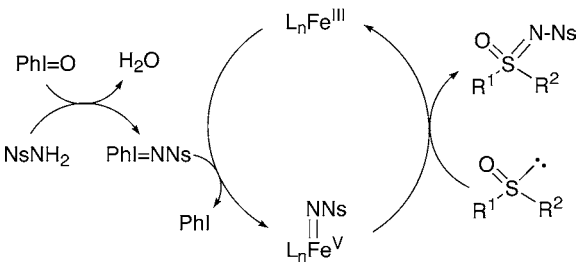


Figure 1. Protected sulfilimines obtained by Fe-catalyzed imination.

process. Likewise, methyl phenyl sulfide could be iminated with the sterically demanding $BusNH_2$ to give sulfilimine **17**, whereas the use of this sulfonamide was unsuccessful in the imination of sulfoxide **1a**.[23]

Although iron imido complexes are rare,[24] we assume that the iron-catalyzed imination of the sulfur compounds involves iron-nitrene species as intermediates. As shown in Scheme 2, the reaction of the iron catalyst with PhI═NNs,

Scheme 2



generated in situ from PhI═O and $NsNH_2$, leads to an iron nitrene complex with the concomitant formation of iodobenzene.[25] The newly generated iron intermediate is then attacked by the sulfur nucleophile to yield the corresponding sulfoximine (or sulfilimine) and to regenerate the original iron catalyst.

Noteworthy is the fact that even in the absence of sulfonyl amides neither sulfones nor sulfoxides (obtained from sulfoxides and sulfides, respectively) have been observed. This indicates that if (oxo)Fe complexes are formed by direct oxidation of the catalytically active iron salt with PhI═O, those species are less reactive oxidants than the iron−nitrene intermediates. Nevertheless, their presence might reduce the efficiency of the catalyst system as observed in an imination of **1a** performed under aerobic conditions, which led to a low conversion of the sulfoxide and the formation of **2** in only 43% yield.

In summary, the imination of a variety of sulfoxides and sulfides has been achieved under mild reaction conditions at room temperature using inexpensive $Fe(acac)_3$ as a catalyst[26] and sulfonylamides in combination with iodosylbenzene as nonhazardous nitrogen sources. The reaction proceeds in a stereospecific manner with retention of configuration at sulfur, constituting an alternative access to enantiopure sulfoximines from the corresponding sulfoxides. The deprotection of the *N*-nosyl products under standard reaction conditions gives, without epimerization, synthetically valuable ("free") *NH*-sulfoximines. Finally, an iron−nitrene complex is proposed as a reactive intermediate in this process, more readily iminating sulfides than sulfoxides.

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Supporting Information Available: Experimental procedures, full characterization of new compounds, and ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Attempts to prepare *NH*-sulfilimines from the corresponding *N*-nosyl derivatives remained unsuccessful. For example, at room temperature **14** did not react with thiophenolate, generated in situ from Cs_2CO_3 and thiophenol, and at elevated temperature decomposition occurred.

(24) (a) Verma, A. K.; Nazif, T. N.; Achim, C.; Lee, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 11013. (b) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 323. (c) Jensen, M. P.; Mehn, M. P.; Que, L., Jr. *Angew. Chem., Int. Ed.* **2003**, *42*, 4357. (d) Vyas, R.; Gao, G.-Y.; Harden, J. D.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1907 and references therein.

(25) In Scheme 2, we suggest the involvement of Fe(III) and Fe(V) species. However, it is possible that the iron intermediates have other oxidation states.

(26) It is noteworthy that $Rh_2(OAc)_4$ is about 100 times more expensive than $AgNO_3$ and that $Fe(acac)_3$ costs ca. 600 times less than $Rh_2(OAc)_4$ (Aldrich prices per gram in 2005/2006).