



## Reduction of sulfoxides catalyzed by oxo-complexes

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### ABSTRACT

This work reports the catalytic activity of the oxo-complexes  $\text{HReO}_4$ ,  $\text{MoO}_2(\text{acac})_2$ ,  $\text{WO}_2\text{Cl}_2$ , and  $\text{VO}(\text{acac})_2$  in the reduction of sulfoxides with  $\text{PhSiH}_3$  or  $\text{HBcat}$ . The results obtained showed that the catalyst systems  $\text{PhSiH}_3/\text{HReO}_4$  (5 mol %) and  $\text{HBcat}/\text{HReO}_4$  (5 mol %) are highly efficient for the deoxygenation of sulfoxides. The complex  $\text{MoO}_2(\text{acac})_2$  was also efficient, but the reactions required more time and heating. Finally, the complexes  $\text{WO}_2\text{Cl}_2$  and  $\text{VO}(\text{acac})_2$  showed a moderate activity.

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High valent oxo-molybdenum and -rhenium complexes were known for their abilities to catalyze oxygen-transfer reactions to sulfides, phosphines, and olefins.<sup>1,2</sup> Recently, we have demonstrated the reversal role of oxo-molybdenum and -rhenium complexes by showing their abilities to catalyze the hydrosilylation of aldehydes and ketones<sup>3,4</sup> and organic reductions, such as the reduction of imines,<sup>5</sup> amides,<sup>6</sup> aromatic nitro compounds,<sup>7</sup> esters,<sup>8</sup> sulfoxides,<sup>9–12</sup> pyridine *N*-oxides,<sup>9</sup> and alkenes.<sup>13</sup>

As the deoxygenation of sulfoxides to the corresponding sulfides is an important reaction that has found utility in organic synthesis and in biochemical reactions, over the years, several methods have been developed to reduce sulfoxides.<sup>14–36</sup> However, many of these are limited by side reactions, low yields, lack of chemoselectivity or harsh conditions. For these reasons, the search for alternative efficient and highly chemoselective methods for the reduction of sulfoxides remains an important target in organic synthesis.

Recently, we have demonstrated that high valent oxo-molybdenum and -rhenium complexes are excellent catalysts for the deoxygenation of sulfoxides.<sup>9–12</sup> In the literature there are some other examples of the reduction of sulfoxides catalyzed by rhenium complexes, but these methods are less efficient.<sup>37–42</sup> In continuation of our studies on the use of high valent oxo-complexes in the deoxygenation of sulfoxides, in this work we explored the catalytic activity of other oxo-rhenium, -molybdenum, -tungsten, and -vanadium complexes in this reduction using silanes or boranes as reducing agents.

The reaction of phenyl sulfoxide was chosen as the model reaction for studying the influence of catalysts, silanes, boranes, and critical parameters such as solvent and temperature (Tables 1–3). The progress of the reactions was monitored by thin layer chromatography and by <sup>1</sup>H NMR.

In order to compare the catalytic activity of several oxo-complexes, the reduction of phenyl sulfoxide was carried out with  $\text{PhSiH}_3$  or catecholborane ( $\text{HBcat}$ ) in the presence of the catalysts  $\text{HReO}_4$ ,  $\text{MoO}_2(\text{acac})_2$ ,  $\text{WO}_2\text{Cl}_2$ , and  $\text{VO}(\text{acac})_2$ <sup>43</sup> as summarized in Table 1.

Among the oxo-complexes tested,  $\text{HReO}_4$  (5 mol %) was the most effective catalyst, reducing completely the phenyl sulfoxide in 30 min at room temperature with  $\text{PhSiH}_3$  (120 mol %) (Table 1, entry 1). Similar reduction using  $\text{HBcat}$  (200 mol %) instead of  $\text{PhSiH}_3$  was much faster, and required only 5 min (Table 1, entry 2).

The dioxo-molybdenum complex  $\text{MoO}_2(\text{acac})_2$  (10 mol %) was also very efficient in the reduction of phenyl sulfoxide with  $\text{PhSiH}_3$  (120 mol %) or  $\text{HBcat}$  (200 mol %) under nitrogen atmosphere. However, these reactions required more time and heating (120 °C) (Table 1, entries 3 and 4).

The catalytic activity of  $\text{WO}_2\text{Cl}_2$  was also explored in the reduction of phenyl sulfoxide with  $\text{PhSiH}_3$  or  $\text{HBcat}$ . These reactions were carried out with 10 mol % of catalyst in refluxing toluene under nitrogen atmosphere. The reduction with  $\text{PhSiH}_3$  (120 mol %) afforded the corresponding sulfide in 30% conversion after 22 h (Table 1, entry 5). Similar reduction using  $\text{HBcat}$  gave the sulfide in 50% conversion after 6 h (Table 1, entry 6).

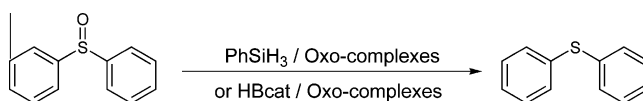
Finally, the oxo-vanadium complex  $\text{VO}(\text{acac})_2$  showed a moderate activity in the reduction of phenyl sulfoxide using  $\text{PhSiH}_3$  or  $\text{HBcat}$  in refluxing toluene (Table 1, entries 7 and 8).

In the absence of catalyst, no reduction was observed with  $\text{PhSiH}_3$  (Table 1, entry 9) and only a small amount of sulfide was

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**Table 1**  
Reduction of phenyl sulfoxide with PhSiH<sub>3</sub> or HBcat catalyzed by high valent oxo-complexes<sup>a</sup>

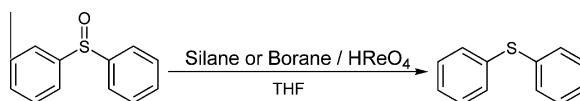


Entry	Catalyst	Reducing agent	Solvent /Temp (°C)	Time	Conversion <sup>b</sup> (%)
1	HReO <sub>4</sub> (5 mol %)	PhSiH <sub>3</sub>	THF/rt	30 min	100
2	HReO <sub>4</sub> (5 mol %)	HBcat	THF/rt	5 min	100
3	MoO <sub>2</sub> (acac) <sub>2</sub> (10 mol %)	PhSiH <sub>3</sub>	Toluene/reflux	7 h	100
4	MoO <sub>2</sub> (acac) <sub>2</sub> (10 mol %)	HBcat	Toluene/reflux	5 h	100
5	WO <sub>2</sub> Cl <sub>2</sub> (10 mol %)	PhSiH <sub>3</sub>	Toluene/reflux	22 h	30
6	WO <sub>2</sub> Cl <sub>2</sub> (10 mol %)	HBcat	Toluene/reflux	6 h	50
7	VO(acac) <sub>2</sub> (10 mol %)	PhSiH <sub>3</sub>	Toluene/reflux	30 h	40
8	VO(acac) <sub>2</sub> (10 mol %)	HBcat	Toluene/reflux	2 h 30 min	55
9	Without catalyst	PhSiH <sub>3</sub>	THF/rt	24 h	No reaction
10	Without catalyst	HBcat	THF/rt	24 h	20

<sup>a</sup> The reactions were carried out with 1.0 mmol of sulfoxide, PhSiH<sub>3</sub> (120 mol %) or HBcat (200 mol %).

<sup>b</sup> Conversion was determined by <sup>1</sup>H NMR.

**Table 2**  
Reduction of phenyl sulfoxide with different silanes or boranes catalyzed by HReO<sub>4</sub><sup>a</sup>

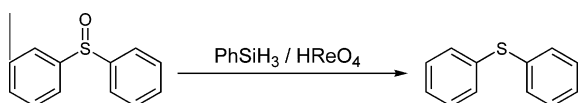


Entry	Reducing agent	Silane (mol %)	Temperature	Time	Conversion <sup>b</sup> (%)
1	PhSiH <sub>3</sub>	120	rt	30 min	100
2	PhSiH <sub>3</sub>	100	rt	40 min	100
3	PMHS	0.30	rt	7 h 30 min	100
4	PhMe <sub>2</sub> SiH	100	rt	48 h	50
5	PhMe <sub>2</sub> SiH	200	Reflux	3 h 30 min	100
6	Et <sub>3</sub> SiH	100	rt	48 h	60
7	Et <sub>3</sub> SiH	200	Reflux	2 h 30 min	100
8	Ph <sub>3</sub> SiH	200	Reflux	24 h	49
9	Without silane	—	rt	24 h	No reaction
10	HBcat	200	rt	5 min	100
11	HBcat	100	rt	6 h 30 min	55
12	HBpin	200	rt	5 min	100

<sup>a</sup> All reactions were carried out with 1.0 mmol of sulfoxide and 5 mol % of HReO<sub>4</sub>.

<sup>b</sup> Conversion was determined by <sup>1</sup>H NMR.

**Table 3**  
Reduction of phenyl sulfoxide in different solvents<sup>a</sup>



Entry	Solvent	Time	Conversion <sup>b</sup> (%)
1	THF	30 min	100
2	CHCl <sub>3</sub>	6 h 30 min	100
3	Benzene	19 h 30 min	100
4	Toluene	24 h	100
5	CH <sub>2</sub> Cl <sub>2</sub>	48 h	70
6	CH <sub>3</sub> CN	24 h	55

<sup>a</sup> All reactions were carried out with 1.0 mmol of sulfoxide, 120 mol % of PhSiH<sub>3</sub>, 5 mol % of HReO<sub>4</sub> at room temperature.

<sup>b</sup> Conversion was determined by <sup>1</sup>H NMR.

formed with HBcat, after 24 h at room temperature (Table 1, entry 10), demonstrating the catalytic role of the oxo-complexes.

The reduction of phenyl sulfoxide was also studied with several silanes, namely, phenylsilane, dimethylphenylsilane, triethylsilane, triphenylsilane, and polymethylhydrosiloxane (PMHS). Of these silanes, phenylsilane (120 mol %) was the most efficient reducing agent, giving the sulfide in 100% conversion after 30 min at room temperature (Table 2, entry 1). Using only 100 mol % of phenylsi-

lane, the reaction required more time (40 min) (Table 2, entry 2). PMHS also afforded the complete reduction of phenyl sulfoxide, but the reaction needed 7 h 30 min (Table 2, entry 3). In contrast, moderate conversions were obtained, after 48 h, using 1 equiv of PhMe<sub>2</sub>SiH or Et<sub>3</sub>SiH at room temperature (Table 2, entries 4 and 6). Adding 2 equiv of these silanes at refluxing THF, the sulfide was obtained in 100% conversion in few hours (Table 2, entries 5 and 7). Triphenylsilane was less efficient, affording the sulfide in 49% conversion, after 24 h in refluxing THF, using 2 equiv of this silane (Table 2, entry 8). Finally, no reaction was observed in the absence of silane (Table 2, entry 9).

We have also studied the reduction of phenyl sulfoxide with HBcat and pinacolborane (HBpin). The reaction with HBcat (200 mol %) was very fast (5 min), giving the sulfide in 100% conversion at room temperature (Table 2, entry 10). Adding only 100 mol % of HBcat, this reduction was not complete, affording the sulfide in 55% conversion after 6 h 30 m (Table 2, entry 11). The reduction of phenyl sulfoxide with HBpin was also successfully accomplished, giving the sulfide in 100% conversion after 5 min (Table 2, entry 12).

The influence of the solvent on the reduction of sulfoxides was also explored with the system PhSiH<sub>3</sub>/HReO<sub>4</sub> (5 mol %) (Table 3). Among the solvents tested, THF proved to be the best at room temperature, affording the sulfide in 100% conversion after 30 min (Table 3, entry 1). Chloroform, benzene, and toluene also

gave the sulfide in 100% conversion, but the reactions required more time (Table 3, entries 2–4). In contrast, dichloromethane and acetonitrile only afforded the sulfide in moderate conversions (Table 3, entries 5 and 6).

To evaluate the general applicability of the catalytic system  $\text{PhSiH}_3/\text{HReO}_4$  (5 mol %), we carried out the reduction of several sulfoxides bearing other potentially labile functional groups (Table 4, method A). These reactions were performed with 1.0 mmol of substrate in THF at room temperature under air atmosphere.<sup>44</sup> Generally, good to excellent yields of sulfides were obtained, including sulfides bearing electron-withdrawing or electron-donating groups. As shown in Table 4, this methodology is equally applicable to diaryl, aryl alkyl, and dialkyl sulfoxides. The reduction of sulfoxides containing several functional groups such as -Cl, -CO<sub>2</sub>R, -NO<sub>2</sub>, and double or triple bond was successfully accomplished with the catalytic system  $\text{PhSiH}_3/\text{HReO}_4$  (5 mol %) (Table 4, entries 3, 11, 13, 15, 17), showing the high chemoselectivity of this novel methodology.

We have also explored the reduction of sulfoxides with the catalytic system  $\text{HBcat}/\text{HReO}_4$  (5 mol %) at room temperature under air atmosphere (Table 4, method B).<sup>44</sup> The reactions were very fast

(5–10 min), affording the sulfides in good to excellent yields. The functional-group tolerance of this catalytic system was evident from entries 4, 12, 14, 16, 18 of Table 4, which showed that -Cl, -CO<sub>2</sub>R, -NO<sub>2</sub>, and double or triple bonds were unaffected under these experimental conditions.

In conclusion, we have demonstrated that the catalyst  $\text{HReO}_4$  is highly efficient for the reduction of a large variety of aryl, aryl alkyl, and alkyl sulfoxides with  $\text{PhSiH}_3$  or  $\text{HBcat}$  at room temperature under air atmosphere. Both the systems  $\text{PhSiH}_3/\text{HReO}_4$  and  $\text{HBcat}/\text{HReO}_4$  were also highly chemoselective, tolerating several functional groups such as -Cl, -NO<sub>2</sub>, -CO<sub>2</sub>R, and double or triple bonds. Comparing the catalytic systems  $\text{PhSiH}_3/\text{HReO}_4$  and  $\text{HBcat}/\text{HReO}_4$ , we concluded that the reactions with the second system were much faster.

This novel methodology has other advantages such as high yields, mild reaction conditions, fast reaction times, simple experimental operation, use of the cheap commercially available and air stable catalyst  $\text{HReO}_4$ . We believe that this novel procedure represents a practical, useful, highly efficient and chemoselective alternative to the traditional methods for the deoxygenation of sulfoxides.

**Table 4**  
Reduction of sulfoxides with  $\text{PhSiH}_3$  or  $\text{HBcat}$  catalyzed by  $\text{HReO}_4$ <sup>a</sup>

Entry	Substrate	Product	Method	Time	Yield <sup>b</sup> (%)
1			A	30 min	95
2			B	5 min	85
3			A	1 h 30 min	86
4			B	5 min	89
5			A	1 h 30 min	94
6			B	5 min	90
7			A	1 h 30 min	92
8			B	5 min	90
9			A	2 h	91
10			B	10 min	89
11			A	2 h 45 min	98
12			B	5 min	98
13			A	3 h 10 min	85
14			B	10 min	98
15			A	2 h	92
16			B	5 min	89
17			A	50	55
18			B	5 min	66
19			A	55 min	100 <sup>c</sup>
20			B	5 min	100 <sup>c</sup>

<sup>a</sup> All reactions were carried out with 1.0 mmol of sulfoxide, 5 mol % of  $\text{HReO}_4$ , 120 mol % of  $\text{PhSiH}_3$  or 200 mol % of  $\text{HBcat}$ .

<sup>b</sup> Isolated yields.

<sup>c</sup> Conversion was determined by <sup>1</sup>H NMR.

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43. Oxo-complexes HReO<sub>4</sub>, MoO<sub>2</sub>(acac)<sub>2</sub>, WO<sub>2</sub>Cl<sub>2</sub>, and VO(acac)<sub>2</sub> are commercially available compounds.
44. In a typical experiment for the reduction of sulfoxides with PhSiH<sub>3</sub> or HBcat catalyzed by HReO<sub>4</sub>, to a solution of catalyst (5 mol %) and sulfoxide (1.0 mmol) in THF (3 ml) was added PhSiH<sub>3</sub> (1.2 mmol) or HBcat (2.0 mmol). The reaction mixture was stirred at room temperature under air atmosphere and the progress of the reaction was monitored by TLC and <sup>1</sup>H NMR. Upon completion, the reaction mixture was evaporated and purified by silica gel column chromatography with the appropriate mixture of *n*-hexane and ethyl acetate to afford the sulfides, which are all known compounds.