PAPER

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Reduction of sulfoxides catalyzed by the commercially available manganese complex MnBr(CO)$_5$†

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A new methodology for the reduction of a wide variety of aliphatic and aromatic sulfoxides catalyzed by the air-stable, cheap and commercially available manganese catalyst MnBr(CO)$_5$ with excellent yields is reported in this work. The catalytic system MnBr(CO)$_5$/PhSiH$_3$ is highly chemoselective, allowing the effective reduction of the S=O bond in the presence of different functional groups.

Introduction

The reduction of sulfoxides to the corresponding sulfides is one of the most important chemical transformations in organic chemistry, due to the relevance of sulfides as intermediates in the synthesis of many biological, pharmaceutical and natural active molecules. Over the years, several methods have been developed to synthesize sulfides by reducing sulfoxides using a variety of catalysts containing different metals, including Mo,[1–7] Re,[8–12] Fe,[13,14] Zn,[15–17] Cu,[18] Ti,[19] Nb,[20,21] Co,[22] B,[23,24] *etc.*,[25–27] by employing silanes, boranes, phosphites and H$_2$ as reducing agents.

The development of methodologies using inexpensive, non-toxic and commercially available catalysts containing Earth-abundant metals is highly desirable. Manganese, as one of the most abundant metals in the Earth's crust, is cheap and less toxic and has been applied as a catalyst in a variety of organic reductions,[28–31] including the reduction of aldehydes and ketones,[32–38] CO$_2$,[39–47] esters,[48–56] amides,[57] and imines.[58–60]

MnBr(CO)$_5$ is also an inexpensive and commercially available air-stable manganese compound that has been used as a starting material for the preparation of several manganese catalysts containing different ligands, including triazole or N-heterocyclic carbene ligands, widely used in different organic transformations.[32–37,41,43,44,46,47,49,50,53,55–57,59]

More recently, this manganese compound has also attracted attention as an effective catalyst for the hydrogenation of N-heteroarenes,[61] reduction of CO$_2$[62] or carboxylic

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acids,[63] and the depolymerization of plastic waste.[64] The deoxygenation of sulfoxides catalyzed by manganese catalysts has been reported by Royo and coworkers using a Mn–NHC complex.[65]

With the goal of developing methodologies for the reduction of sulfoxides using simple, inexpensive and commercially available catalysts based on Earth-abundant metals, in this work, we evaluated the efficiency of the manganese catalyst MnBr(CO)$_5$ in the reduction of sulfoxides.
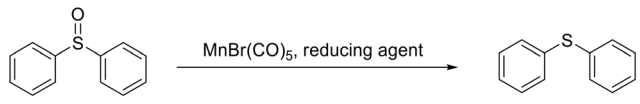
Results and discussion

Initially, we investigated the reduction of diphenyl sulfoxide using silanes and boranes catalyzed by the commercial available catalyst MnBr(CO)$_5$ under an air atmosphere (Table 1). The best yield (97%) was obtained in the presence of 5 mol% of MnBr(CO)$_5$ and an equimolar amount of PhSiH$_3$ in toluene at reflux temperature after 15 minutes (Table 1, entry 1). The reaction carried out at room temperature gave the product in 62% yield after 24 h (Table 1, entry 2). When using a lower amount of MnBr(CO)$_5$ (3 mol%), the reduction produced the sulfide in only 65% yield after 24 h (Table 1, entry 3). The reduction carried out with diphenylsilane also produced the sulfide in good yields after 30 minutes (Table 1, entry 4). In THF, the reduction did not occur, even when using 150 mol% of PhSiH$_3$ (Table 1, entry 5). Several silanes, namely (EtO)$_2$MeSiH, Pr$_3$SiH, Et$_3$SiH, Me$_2$PhSiH, Ph$_3$SiH, TMDS and PMHS, were also evaluated in the reduction of diphenyl sulfoxide in the presence of 5 mol% of MnBr(CO)$_5$ in toluene at reflux temperature. Moderate to low yields or no reactions were observed with these silanes (Table 1, entries 6–12).

The deoxygenation of diphenyl sulfoxide was also evaluated by employing boranes as the reducing agent. From the reaction with 120 mol% of pinacolborane (HBpin) in the presence of

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Table 1 Reduction of sulfoxides catalyzed by MnBr(CO)$_5$[a]

Entry	MnBr(CO)$_5$ (mol%)	Reducing agent	Reducing agent (mol%)	Solvent	Temp. (°C)	Time	Yield[b] (%)
1	5	PhSiH$_3$	100	Toluene	110	15 min	97
2	5	PhSiH$_3$	100	Toluene	r.t.	24 h	62
3	3	PhSiH$_3$	100	Toluene	110	24 h	65
4	3	Ph$_2$SiH$_2$	100	Toluene	110	30 min	90
5	5	PhSiH$_3$	150	THF	70	24 h	No reaction
6	5	(EtO)$_2$MeSiH	120	Toluene	110	24 h	29
7	5	Pr$_3$SiH	120	Toluene	110	24 h	35
8	5	Et$_3$SiH	120	Toluene	110	24 h	No reaction
9	5	Me$_2$PhSiH	120	Toluene	110	24 h	No reaction
10	5	Ph$_3$SiH	120	Toluene	110	24 h	No reaction
11	5	TMDS	120	Toluene	110	24 h	29
12	5	PMHS	120	Toluene	110	24 h	40
13	5	HBpin	120	Toluene	110	6 h	75
14	5	HBcat	120	Toluene	110	24 h	65
15	—	PhSiH$_3$	100	Toluene	110	24 h	No reaction
16	5	—	100	Toluene	110	24 h	No reaction

[a] The reactions were carried out using 0.5 mmol of sulfoxide in 3 mL of toluene. [b] Yields were determined by ^{1}H NMR spectroscopy using mesitylene as the internal standard.

5 mol% of MnBr(CO)$_5$ in toluene at reflux temperature, the corresponding sulfide was obtained in 75% yield after 6 h (Table 1, entry 13). Under the same reaction conditions, the reduction performed with catecholborane (HBcat) gave phenyl sulfide in 65% yield after 24 h (Table 1, entry 14).

Finally, no reduction of phenyl sulfoxide was observed when the reaction was performed in the absence of a catalyst or reducing agent (Table 1, entries 15 and 16).

We also evaluated the efficiency of the commercially available manganese catalysts Mn(OTf)$_2$, MeCpMn(CO)$_3$ and Mn$_2$(CO)$_{10}$ in the reduction of phenyl sulfoxide using PhSiH$_3$ as the reducing agent in toluene at reflux temperature. After 3 h, no reduction was observed in the reactions carried out with 5 mol% of Mn(OTf)$_2$ or MeCpMn(CO)$_3$ and a small amount of diphenyl sulfide (15%) was formed in the reaction with Mn$_2$(CO)$_{10}$.

The applicability of the catalytic system MnBr(CO)$_5$ (5 mol%)/PhSiH$_3$ (100 mol%) was evaluated in the deoxygenation of a wide variety of sulfoxides in toluene at reflux temperature under an air atmosphere (Table 2). Generally, this methodology proved to be very efficient, allowing the deoxygenation of sulfoxides into the corresponding sulfides with excellent yields in a few minutes, including sulfoxides bearing electron-withdrawing groups. From the analysis of Table 2, it is possible to conclude that this catalytic system is equally applicable to diaryl, aryl alkyl, and dialkyl sulfoxides.

The reduction of substituted diaryl and dibenzyl sulfoxides was successfully achieved within a few minutes (15–30 minutes) at 110 °C with excellent yields (94–97%) (Table 2, entries 1–4). The deoxygenation of furfuryl sulfoxide was also efficiently carried out, giving the corresponding sulfide in 91% yield after 1 h (Table 2, entry 5).

This methodology is very chemoselective, tolerating the presence of several functional groups. For example, halogen

atoms (Cl– and Br–) in the aromatic ring or in the aliphatic chain were not affected under these reaction conditions (Table 2, entries 2, 8, 9, 11 and 16). This method also tolerates double and triple bonds as observed in the selective reduction of phenyl vinyl sulfoxide and phenyl propargyl sulfoxide giving 89% and 92% yields, respectively (Table 2, entries 12 and 13), which is confirmed by the analysis of ^{1}H NMR spectra of the products (ESI†). The deoxygenation of methyl phenylsulfonylacetate was also possible in the presence of an ester group (Table 2, entry 14), which was confirmed by the presence of the signal at δ 170.2 ppm in the ^{13}C NMR spectrum of sulfide corresponding to the CO$_2$Me group (ESI†). The reduction of 4-nitrophenyl phenyl sulfoxide and 4-chloro-4'-nitrodiphenyl sulfoxide, containing a NO$_2$ group, was carried out, which gave good yields (Table 2, entries 15 and 16); however, the formation of a small amount of the amino products (15–18% yields) was also observed.

Finally, we decided to study the efficiency of the catalytic system PhSiH$_3$/MnBr(CO)$_5$ in the reduction of aliphatic sulfoxides. The reaction of butyl sulfoxide led to the formation of butyl sulfide in 95% yield after 35 minutes (Table 2, entry 17) and the deoxygenation of tetrahydrothiophene 1-oxide gave tetrahydrothiophene in 96% yield after 30 minutes (Table 2, entry 18).

To further evaluate the chemoselectivity of the catalytic system MnBr(CO)$_5$/PhSiH$_3$, we also investigated the reduction of phenyl sulfoxide in the presence of 4-chlorobenzonitrile, benzamide, acetophenone or furfuryl alcohol. These reactions were carried out using 0.5 mmol of the substrates, 5 mol% of MnBr(CO)$_5$ and 0.5 mmol of PhSiH$_3$ in toluene at reflux temperature. From the reaction of phenyl sulfoxide and 4-chlorobenzonitrile, we observed the formation of diphenyl sulfide with a yield of 85% after 15 minutes and a small amount of sulfoxide that did not react. No reduction products of 4-chloro-

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Table 2 Reduction of sulfoxides with the PhSiH$_3$/MnBr(CO)$_5$ system[a]
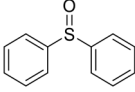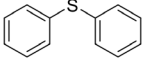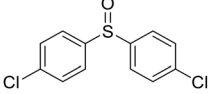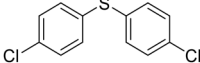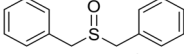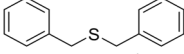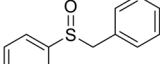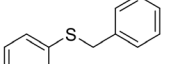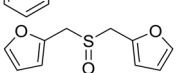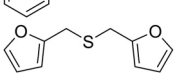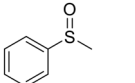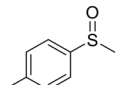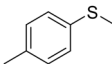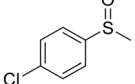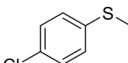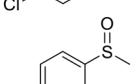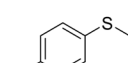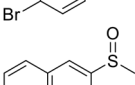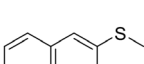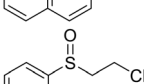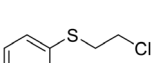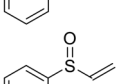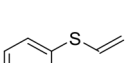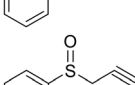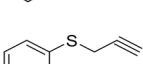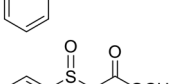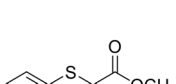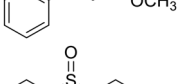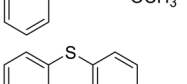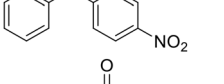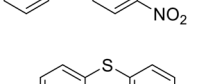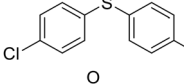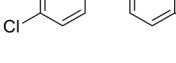
Entry	Sulfoxide	Product	Time	Yield[b] (%)
1			15 min	97
2			30 min	97
3			15 min	95
4			15 min	94
5			1 h	91
6			1 h	83
7			15 min	97
8			15–30 min	96
9			1 h 15 min	95
10			15 min	95
11			15 min	97
12			30 min	89
13			1 h	92
14			2 h 30 min	87
15			1 h	77
16			1 h	79
17			35 min	95

Table 2 *(Contd.)*

Entry	Sulfoxide	Product	Time	Yield[b] (%)
18			30 min	96

[a] The reactions were carried out using 0.5 mmol of sulfoxide, 0.5 mmol of PhSiH$_3$, and 5 mol% of MnBr(CO)$_5$ in 3 mL of toluene at reflux temperature. [b] Yields were determined by ^{1}H NMR spectroscopy using mesitylene as the internal standard.
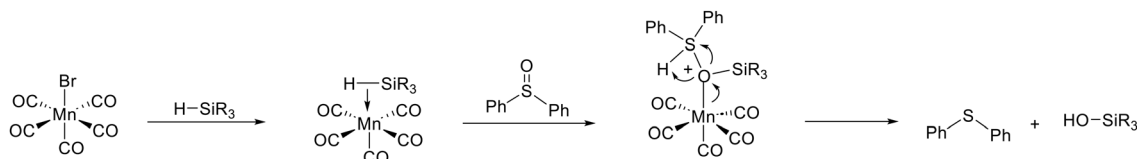
Scheme 1 Proposed mechanism for the reduction of phenyl sulfoxide with the MnBr(CO)$_5$/HSiR$_3$ system.

benzonitrile were detected. Likewise, the reaction of phenyl sulfoxide in the presence of benzamide only led to the selective reduction of sulfoxide in 95% yield after 15 minutes. In contrast, when the reduction of phenyl sulfoxide was carried out in the presence of acetophenone, the simultaneous reduction of the sulfoxide and the acetophenone occurs giving good yields after 15 minutes. A similar result was also observed in the reaction of phenyl sulfoxide in the presence of furfuryl alcohol, which led to the complete reduction of phenyl sulfoxide and the partial deoxygenation of the alcohol. These results demonstrated the chemoselectivity of this catalytic system in the reduction of sulfoxide in the presence of cyano and amide functional groups.

The catalytic system MnBr(CO)$_5$/PhSiH$_3$ was also successfully applied to the reduction of 1 g of phenyl sulfoxide in 15 minutes with a yield of 95%.

In another experiment, we evaluated the reduction of phenyl sulfone with MnBr(CO)$_5$ (5 mol%) and PhSiH$_3$ in toluene at reflux temperature, but we did not observe the reduction of this substrate even after 24 h.

The reduction of sulfoxides using the MnBr(CO)$_5$/HSiR$_3$ system should involve the activation of the Si–H bond of the silane by the catalyst, generating a hydride species. This species then promotes the hydrosilylation of the sulfur–oxygen double bond present in the sulfoxide, leading to the formation of sulfide and silanol (Scheme 1).

Conclusion

This work reports a novel methodology for the reduction of a large variety of aliphatic and aromatic sulfoxides using an air-stable, cheap and commercially available manganese catalyst. The use of a catalyst based on an Earth-abundant metal is very

relevant, making the reduction of sulfoxides more eco-friendly and economical.

Excellent yields were obtained with both aliphatic and aromatic sulfoxides, in many cases in just a few minutes, with good chemoselectivity. The method has also the advantage of using a very simple catalyst without containing complex ligands, which is beneficial from a scale-up point of view. Other advantages of this methodology include the air stability of the catalyst and easy work-up, allowing the reaction to be carried out under an air atmosphere. All these features make this method a useful and practical alternative to the conventional methods for the deoxygenation of sulfoxides to sulfides.

The high efficiency of the MnBr(CO)$_5$/PhSiH$_3$ catalytic system suggests its future application in the reduction of other functional groups.

Experimental section

General procedure for the reduction of sulfoxides with the catalytic system PhSiH$_3$/MnBr(CO)$_5$

To an open-air flask containing a sulfoxide (0.5 mmol) and MnBr(CO)$_5$ (5 mol%, 0.006 g) in toluene (3 mL), PhSiH$_3$ (0.5 mmol, 0.062 mL) was added and the reaction mixture was stirred at 110 °C. The progress of the reaction was monitored by TLC and ^{1}H NMR spectroscopy. Upon completion, the product was purified by silica gel column chromatography using an appropriate mixture of hexane/ethyl acetate, affording the corresponding pure sulfides, which are all known products.

Conflicts of interest

There are no conflicts to declare.

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