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Deoxygenation of Sulfoxides to Sulfides in the Presence of Zinc Catalysts and Boranes as Reducing Reagents

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Abstract In the present study, the zinc-catalyzed deoxygenation of aliphatic and aromatic sulfoxides in the presence of boranes as reducing reagent has been explored. After investigation of different reaction parameters the abilities of catalytic amounts of $Zn(OTf)_2$ has been demonstrated in the deoxygenation of various sulfoxides. Moreover, various experiments have been performed to shed light on the underlying reaction mechanism.

Keywords Catalysis · Zinc · Deoxygenation · Sulfoxide · Sulfide

1 Introduction

During the last decades a remarkable number of protocols and improvements have been reported for transition metal-catalyzed reductions; hence nowadays the methodology is applicable in the synthesis of fine chemicals, pharmaceuticals, agricultural chemicals and natural products [1, 2]. In recent times attention was drawn to the replacement of expensive and toxic catalyst metals, which have been dominated the field, by cheaper and low toxic metals [3, 4]. In this regard, the application of zinc catalysts in combination with hydrosilanes has been demonstrated to succeed in the reduction of various functional groups with excellent yields and selectivities (e.g., C=O, C=N, amides, esters) [5–31]. An attractive model reaction to study the abilities of catalysts is the deoxygenation of sulfoxides to obtain the corresponding sulfides. In more detail, the deoxygenation of sulfur-based compounds is an essential method in biological processes (dimethylsulfoxide-, biotin-, and methionine sulfoxide reductase) and has some significance in organic chemistry [32–70]. Recently, we have studied the deoxygenation of sulfoxides and amides with silanes and different metal catalysts (e.g., Mo, Fe, Cu, Zn) [71–74]. In case of zinc excellent yields and chemoselectivities have been realized under mild reaction conditions. Aside hydrosilanes the reduction properties of hydroboranes in the presence of catalytic amounts of transition metals has been used in organic chemistry [75–80]. Herein, we report our investigations on the zinc-catalyzed deoxygenation of sulfoxides to generate the corresponding sulfides with hydroboranes as reductant.

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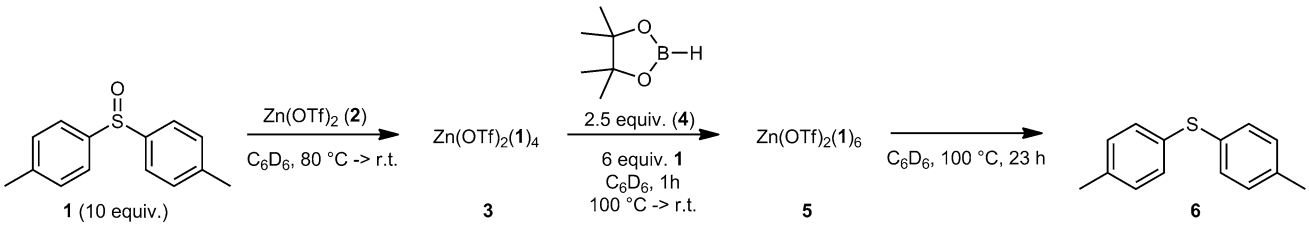
2 Results and Discussion

At first the interaction of the zinc source with the sulfoxide functionality was investigated (Scheme 1). As model substrate *p*-tolyl sulfoxide (**1**) was chosen. To a solution of **1** (10 equiv.) in C_6D_6 was added $Zn(OTf)_2$ (**2**, 1.0 equiv.). The suspension was heated to 80 °C for 1 h, while at 80 °C a clear solution was obtained. The mixture was slowly cooled to room temperature, while colorless crystals were obtained, which were suitable for X-ray measurements. The solid-state structure of complex **3** has been characterized by single-crystal X-ray diffraction analysis. Thermal ellipsoid plots, selected bond lengths and angles are shown in Fig. 1. The obtained solid structure of $Zn(OTf)_2(\mathbf{1})_4$ (**3**) showed an octahedral structure with four sulfoxides which are equatorially coordinated to the zinc via the oxygen of the sulfoxide functionality, while the triflate groups are axially coordinated. Recently, we have



Scheme 1 Investigation of the deoxygenation of sulfoxide **1** with borane **4** in the presence of $Zn(OTf)_2$

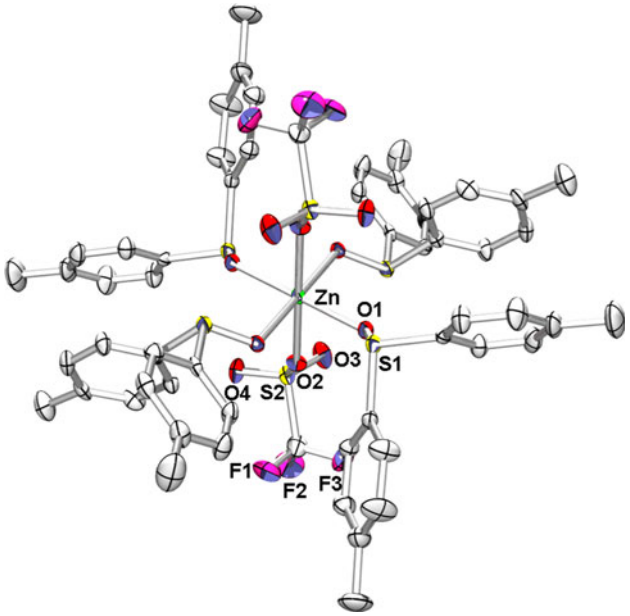


Fig. 1 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å): Zn–O1: 2.0552(19), Zn–O2: 2.256 (2), O1–S1: 1.520(2), O2–S2: 1.459(2)

reported a similar motif by using diphenyl sulfoxide as substrate [72]. In contrast, decreasing the sterical demand of the sulfoxide, e.g., dimethyl sulfoxide or methyl phenyl sulfoxide, a different coordination mode was observed [80, 81]. In more detail, the obtained solid structures $Zn(sulfoxide)_6(OTf)_2$ showed an octahedral complexation of six sulfoxides molecules to the cationic zinc center, while the triflate anions are not coordinated to the metal.

A comparison of the S=O bond length in complex **3** [1.520(2) Å] with the free sulfoxide **1** [1.492 (2) Å] showed an elongation of the bond by complexation [82]. Based on that, the obtained structure **3** can be interpreted as an intermediate for the activation of sulfoxides and probably it initiates the subsequent reduction process to obtain the corresponding sulfide. Moreover, to prove this assumption theoretical investigations were carried out. DFT calculations of the model compound $Zn(dmso)_4(OTf)_2$ (the tolyl groups at the sulfur were replaced by methyl groups, because of simplicity) were performed at the 6-31G(d) basis set for C, F, H, O, and S atoms and the LANL2DZ for the Zn atom [83–86]. The computed geometry is in good agreement with the experimental values. While the HOMO of $Zn(dmso)_4(OTf)_2$ shows mainly the lone pair orbitals of oxygen and sulfur atoms, it represents somewhat interaction between the *d*-orbital of the zinc atom and the lone pair orbitals of the oxygen atoms. The S–O bond lengths (1.5442–1.5480 Å) of dimethylsulfoxide moieties in $Zn(dmso)_4(OTf)_2$ are obviously longer than that of "free" dimethylsulfoxide (1.5114 Å). Likewise, the WBI values of the S–O bonds in dimethylsulfoxide (1.2780) are significantly higher than those of dimethylsulfoxide moieties in $Zn(dmso)_4(OTf)_2$ (1.0876–1.0947). These results indicates that the S=O bond of dimethylsulfoxide is activated by coordination to the zinc center (Fig. 2).

To study the effect of activation of the sulfoxide by complexation IR-measurements were performed with the free sulfoxide **1** and the isolated complex **3** (Fig. 3). As pointed out in Fig. 2 a shift of the S–O stretching vibration was observed. The observed behavior is in agreement with earlier reported systems and furthermore proves the coordination of the sulfoxide via the oxygen atom to the zinc center [87].

After investigation of the complexation of the sulfoxide **1** to $Zn(OTf)_2$, pinacolborane (**4**, 2.5 equiv. with respect to **1**) was added to the mixture in C_6D_6 (Scheme 1). Subsequently, the reaction mixture was heated for 1 hour to 100 °C and afterwards slowly cooled to room temperature, while colorless crystals were obtained. The solid-state structure of complex **5** has been characterized by single-crystal X-ray diffraction analysis. Unfortunately, due to disordering the structure was not fully solved. However, the preliminary solid structure of $Zn(OTf)_2(\mathbf{1})_6$ (**5**) showed an octahedral structure with four sulfoxides equatorially coordinated to the zinc via the oxygen of the sulfoxide functionality and two sulfoxides in the axial position, while the triflate groups are not coordinated to the metal. In addition, IR measurements revealed a band at 993 cm^{-1}, which is comparable to the value for complex **3**.

Moreover, the proceeding of the reaction was investigated by NMR techniques (Fig. 3, 4). In case of ^1H NMR measurements characteristic signals for the methyl groups

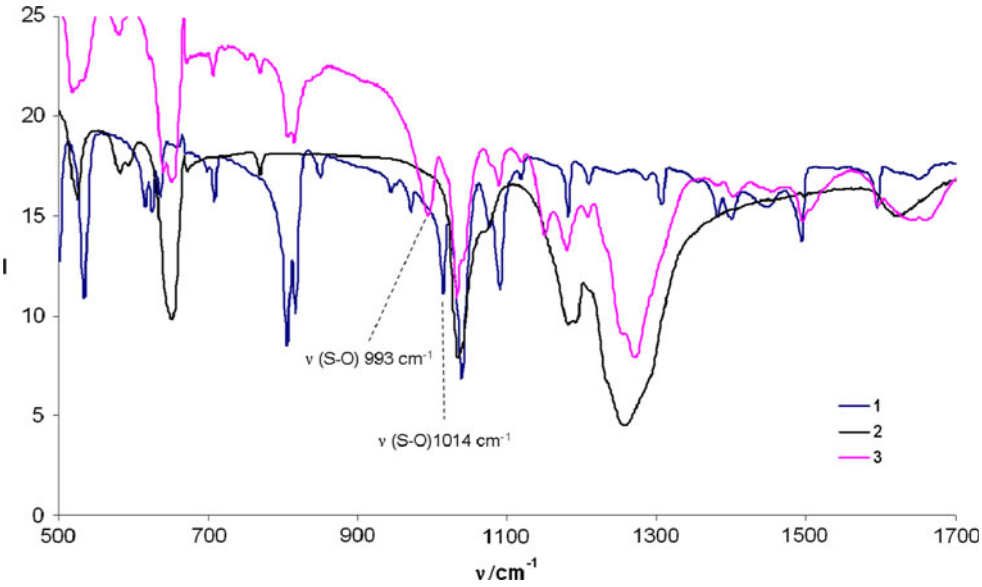


Fig. 2 IR-investigations of the free sulfoxide **1** and the complex **3**

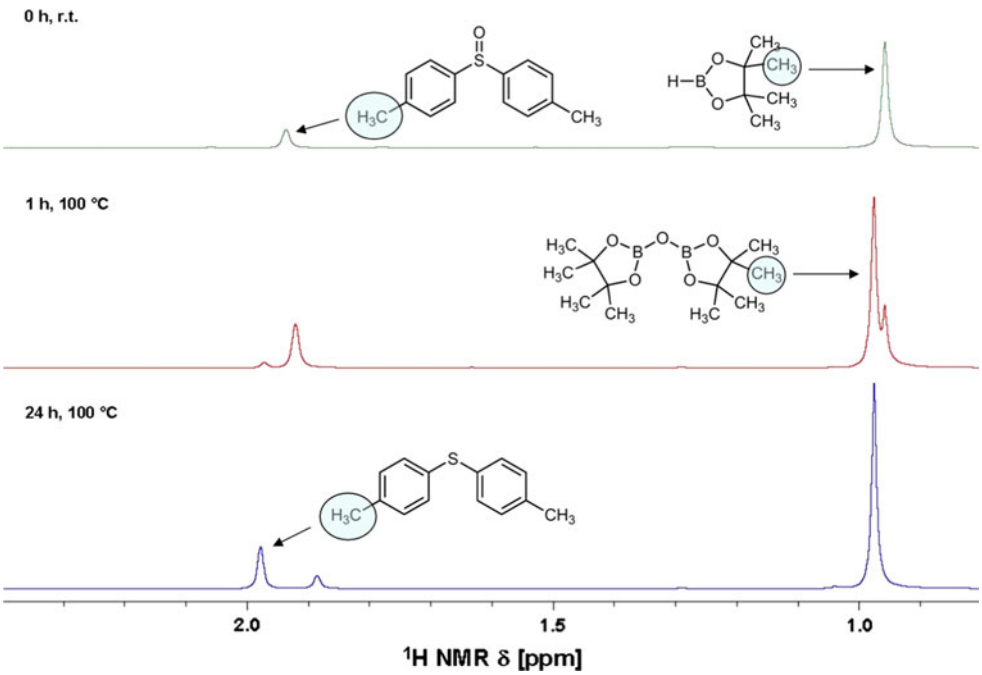


Fig. 3 ^{1}H NMR investigation of the deoxygenation of sulfoxide **1** (1.0 equiv., 0.72 mmol) with borane **4** (2.5 equiv., 1.8 mmol) in the presence of $Zn(OTf)_2$ (5.0 mol %, 0.036 mmol) in C_6D_6 (0.5 mL)

of the sulfoxide **1** (1.93 ppm) and the borane **4** (0.95 ppm) were found after mixing the compounds at room temperature. After heating for 1 h at 100 °C the formation of the sulfide **5** (1.95 ppm) and the bis-boryloxide $O(Bpin)_2$ (0.97 ppm) was observed [88]. The bis-boryloxide $O(Bpin)_2$ was furthermore characterized by ^{11}B NMR and GC–MS. Afterwards the heating was continued for 23 h (Fig. 4). The measured ^{1}H NMR spectrum showed an increase of the product. On the other hand the reaction was followed by ^{19}F NMR to investigate the role of zinc(II) triflate during catalysis. However, no significant change was observed on the NMR time scale. Afterwards, the interaction of $Zn(OTf)_2$ with the borane **4** was studied. $Zn(OTf)_2$ was reacted with **4** (10 equiv.) for 1 h at 80 °C. The signals for **2** and **4** were unchanged in ^{1}H NMR, ^{19}F NMR as well as ^{11}B NMR. Based on this result, the formation of a zinc-hydride species can be excluded on the NMR time scale. Noteworthy, the reaction of the sulfoxide with the borane in the absence of $Zn(OTf)_2$ resulted in no change of the ^{1}H NMR or ^{19}F NMR spectra and product formation. With regard to the obtained results we excluded the formation of a $L_xZn{=}O$ species, which was proposed for different metals via the abstraction of the oxygen of the sulfoxide to yield metal oxides [78].

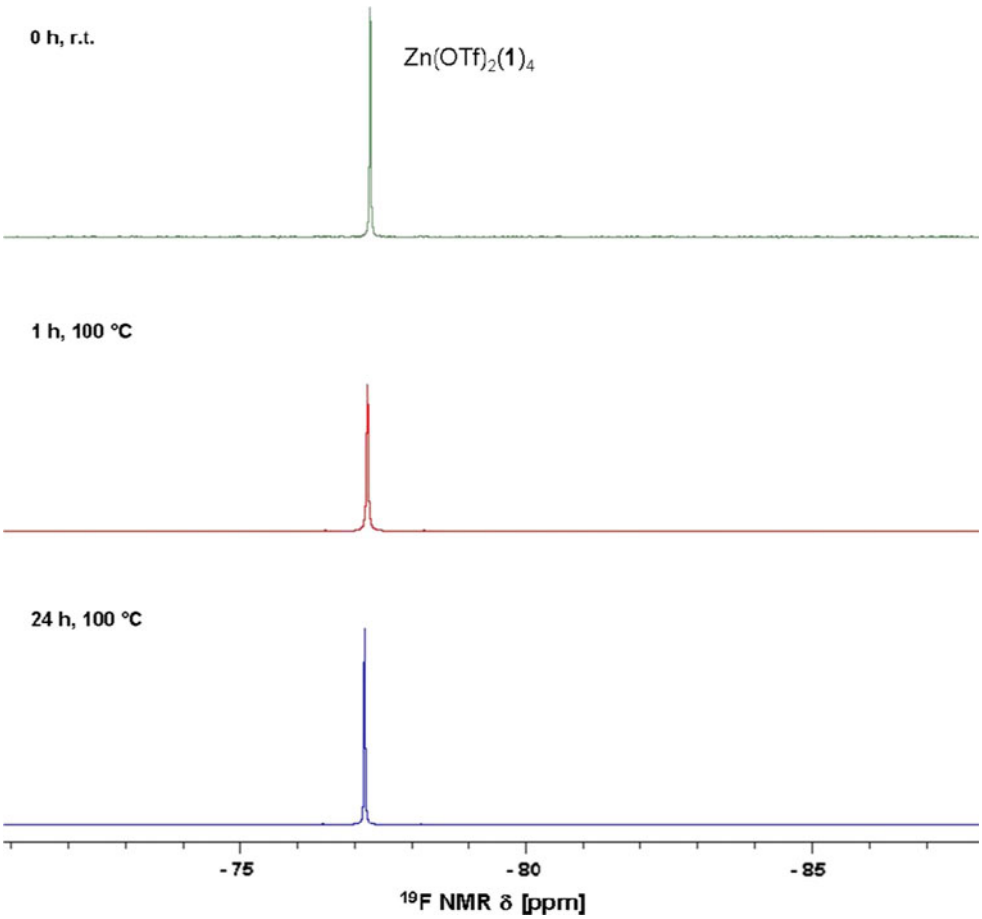


Fig. 4 ^{19}F NMR investigation of the deoxygenation of sulfoxide **1** (1.0 equiv., 0.72 mmol) with borane **4** (2.5 equiv., 1.8 mmol) in the presence of $Zn(OTf)_2$ (5.0 mol %, 0.036 mmol) in C_6D_6 (0.5 mL)

The produced sulfide is a potential ligand and can influence significantly the catalyst activity; hence attempts were undertaken to synthesize complexes with sulfide ligands as well as mixed complexes with sulfoxide and sulfide ligands (Scheme 2). Unfortunately, no suitable complexes were accessible and crystal structures were only obtained of the starting material (**7**) and the complex $Zn(OTf)_2(thf)_2(H_2O)_4$ (**8**) (Fig. 5). The solid-state structure of complex **8** has been characterized by single-crystal X-ray diffraction analysis. Unfortunately, due to disordering the structure was not fully refined.

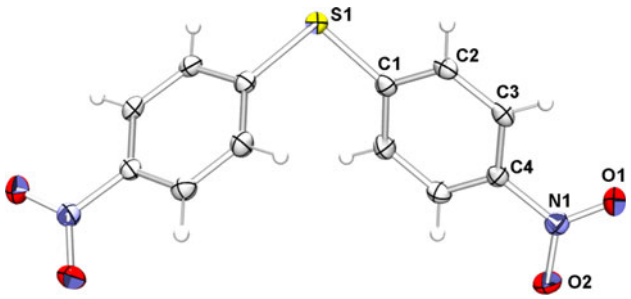
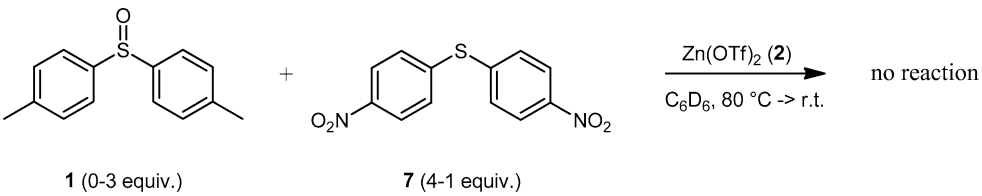
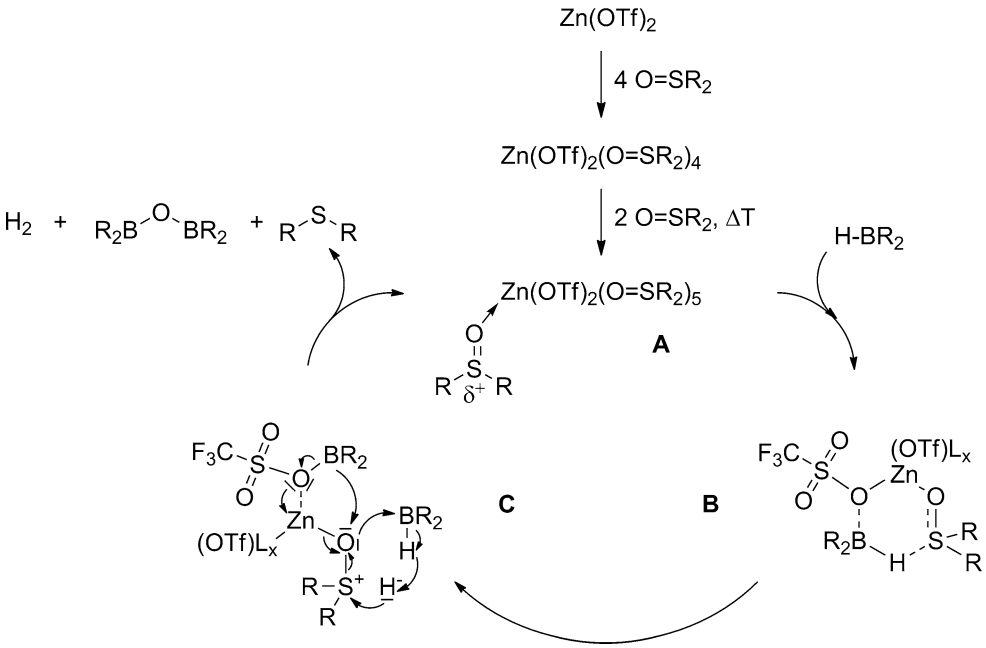


Fig. 5 Molecular structure of **7**. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å): S1–C1: 1.7769(14), N1–O(1,2): 1.2294(15), N1–C4: 1.4630(17)

Based on the obtained results we assume that the zinc-catalyst acts as a Lewis-acid (Scheme 3). First, the sulfoxide coordinates to the zinc center (intermediate **A**) thus an activation of the S=O bond occurs and enhances the susceptibility of the sulfur for reduction [62, 89]. Subsequently, the borane reacts with the intermediate **A**. An interaction of the hydride with the sulfur and an interaction of the boron with the oxygen of the triflate group via a six-membered transition state is proposed (intermediate **B**). Next a sulfonium salt analog is created (intermediate **C**),

Scheme 2 Investigation of mixed sulfoxide–sulfide zinc complexes





Scheme 3 Proposed catalytic cycle for the reduction of sulfoxides with boranes in the presence of $Zn(OTf)_2$

which undergoes elimination of bis-boryloxide $O(Bpin)_2$, hydrogen, and the desired sulfide [80].[1]

After investigation of the reaction mechanism the scope and limitations of the zinc-catalyzed deoxygenation of various sulfoxides, including aromatic and aliphatic sulfoxides, using boranes as reducing reagent were examined (Table 1). At first different boranes were tested in the deoxygenation of **1**. Excellent yields were observed for the boranes **4** and **9**, while with BH_3 only moderate yields of **6** were obtained (Table 1, entries 1–3). Moreover, excellent yields (>99 %) accompanied by excellent chemoselectivities were achieved for alkyl substituted sulfoxides after 18 h at 100 °C with a catalyst loading of 5.0 mol % using borane **9** (Table 1, entries 6–10). To some extent lower yields were noticed for aryl based sulfoxides (Table 1, entries 4 and 5).

3 Experimental Section

3.1 General

All compounds were used as received without further purification. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker AFM 200 spectrometer (^{1}H: 200.13 MHz; ^{19}F: 188.31 MHz; ^{13}C: 50.32 MHz) using the proton signals of the deuterated solvents as reference. GC–MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5 ms column) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer.

[1] Hydrogen was not detectable during the 1H NMR studies

*3.1.1 Synthesis of Zn(OTf)$_2$(**1**)$_4$*

A mixture of $Zn(OTf)_2$ (0.036 mmol) and sulfoxide **1** (0.36 mmol) in C_6D_6 (0.5 mL) was heated to 80 °C until all compounds were dissolved. Afterwards the temperature was slowly decreased to room temperature. Colorless crystal were obtained, which were suitable for X-ray measurements. Mp: 162 °C; IR (KBr): ν = 1,660 w, 1,595 w, 1,452 w, 1,404 w, 1,271 s, 1,207 w, 1,179 m, 1,150 m, 1,119 w, 1,088 w, 1,032 m, 994 m, 814 w, 806 w, 769 w, 706 w, 650 m, 640 m, 580 w, 518 cm^{-1-}.

3.2 Single-Crystal X-Ray Structure Determination

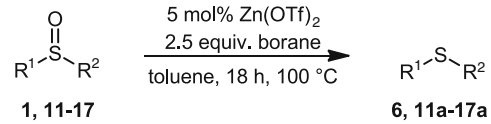
Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data were collected using an Oxford Diffraction Xcalibur S Sapphire at 150(2) K (Mo_{Ka} radiation, l = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package [90]. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model.

CCDC-882111 (for **7**) and 882112 (for **3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

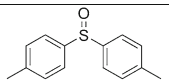
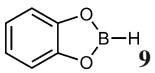
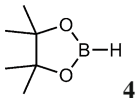
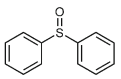
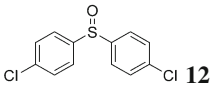
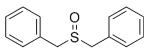
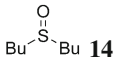
3.3 General Procedure for the Deoxygenation of Sulfoxides

A pressure tube was charged with an appropriate amount of $Zn(OTf)_2$ (0.036 mmol, 5.0 mol %), the corresponding sulfoxide (0.72 mmol) and the borane (2.5 equiv.,

Table 1 Scope and limitations of the zinc-catalyzed deoxygenation of sulfoxides



1, 11-17 **6, 11a-17a**

Entry	Substrate	Borane	Product	Yield [%][b]
1	 **1**	 **9**	**6**	>99 (93)
2	**1**	 **4**	**6**	>99 (94)
3[c]	**1**	BH_3•THF **10**	**6**	57
4	 **11**	**9**	**11a**	85 (81)
5	 **12**	**9**	**12a**	89 (83)
6	 **13**	**9**	**13a**	>99 (91)
7	 **14**	**9**	**14a**	>99 (89)
8	 **15**	**9**	**15a**	>99 (93)
9[d]	 **16**	**9**	**16a**	>99
10	 **17**	**9**	**17a**	>99 (95)

[a] Determined by GC methods and ^{1}H NMR. In *brackets* the isolated yield is stated

[b] Reaction was performed in THF at 60 °C for 24 h. BH_3•THF stock solution (~1.0 M in THF)

[c] The product **16a** has been characterized only by GC–MS

Reaction conditions: Substrate (0.72 mmol), $Zn(OTf)_2$ (5 mol %), borane (2.5 equiv. 1.80 mmol), toluene (2.0 mL), 18 h, 100 °C

1.80 mmol). After addition of toluene (2.0 mL) the reaction mixture was stirred in a preheated oil bath at 100 °C for 18 h. The mixture was cooled on an ice bath and biphenyl (internal standard) was added. The solution was diluted with dichloromethane and an aliquot was taken for GC-analysis (30 m Rxi-5 ms column, 40–300 °C). The solvent was removed and the residue was purified by column chromatography. The analytical properties of the corresponding sulfides are in agreement with literature data.

3.3.1 Di(p-Methylphenyl)sulfide (*6*)

$R_f = 0.79$ (*n*-hexane:ethyl acetate 1:5); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.06$–7.22 ppm (*m*, 8H), 2.30 (*s*, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 137.1$, 132.8, 131.3, 130.1, 21.3 ppm; MS (ESI) m/z = 214 (100, M^+), 199 (34), 184 (20), 105 (18), 91 (33), 65 (19); IR (KBr): ν = 1,662 w, 1,594 w, 1,493 m, 1,448 w, 1,400 w, 1,381 w, 1,307 w, 1,286 w, 1,118 w, 1,090 m, 1,076 w, 1,039 s, 1,014 m, 970 w, 944 w, 849 w, 816 s, 805 s, 708 w, 635 w, 625 w, 615 w, 534 m, 501 m.

3.3.2 Diphenylsulfide (*11a*)

$R_f = 0.75$ (*n*-hexane:ethyl acetate 1:5); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.26$–7.47 ppm (*m*, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 135.8$, 131.0, 129.2, 127.0 ppm;

MS (ESI) m/z = 186 (100, M^+), 152 (11), 92 (19), 77 (27), 65 (20), 51 (43).

3.3.3 Di(p-Chlorophenyl)sulfide (**12a**)

R_f = 0.67 (*n*-hexane:ethyl acetate 1:10); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.23–7.33 ppm (*m*, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 133.9, 133.4, 132.3, 129.4 ppm; MS (ESI) m/z = 254 (M^+, not detected), 219 (33), 184 (100), 139 (11), 108 (29), 91 (18), 75 (24).

3.3.4 Dibenzylsulfide (**13a**)

R_f = 0.74 (*n*-hexane:ethyl acetate 1:5); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.31–7.37 (*m*, 10H), 3.65 ppm (*s*, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 138.0, 128.9, 128.4, 126.9, 35.5 ppm; MS (ESI) m/z = 214 (59, M^+), 123 (31), 91 (100), 65 (17).

3.3.5 Dibutylsulfide (**14a**)

^{1}H NMR ($CDCl_3$, 200 MHz) δ = 2.28 (*t*, 4H, *J* = 7.20 Hz, $S(CH_2CH_2CH_2CH_3)_2$), 1.14–1,49 (*m*, 8H, $S(CH_2CH_2CH_2CH_3)_2$), 0.75 ppm (*t*, 6H, *J* = 7.20 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 32.1, 32.0, 22.3, 13.8 ppm; MS (ESI) m/z = 146 (M^+, 40), 103 (15), 90 (31), 61 (97), 56 (100).

3.3.6 Tetrahydrothiophene (**15a**)

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.42–2.55 (*m*, 4H), 1.36–1.48 ppm (*m*, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 32.1, 32.0 ppm; MS (ESI) m/z = 87 (13, M^+), 59(49), 43 (100).

3.3.7 2,4-Dithiapentane (**16a**)

MS (ESI) m/z = 110 (14, M^+), 108 (99), 61 (100).

3.3.8 Phenyl Methylsulfide (**17a**)

R_f = 0.88 (*n*-hexane:ethyl acetate 1:5); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.19–7.35 (*m*, 5H), 2.53 ppm (*s*, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 138.3, 128.7, 126.5, 124.9, 15.7 ppm; MS (ESI) m/z = 124 (100, M^+), 109 (51), 91 (49), 78 (51), 85 (21).

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