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PAPER

A straightforward zinc-catalysed reduction of sulfoxides to sulfides†

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In the present study, the zinc-catalysed reduction of a variety of sulfoxides with silanes as reductant to the corresponding sulfide has been examined in detail. With the straightforward and commercially available zinc(II) triflate as pre-catalyst, excellent yields and chemoselectivities were feasible. After studying the reaction conditions and the scope and limitations several attempts were undertaken to shed light on the reaction mechanism.

Introduction

The development of sustainable, efficient and selective procedures to access organic compounds with higher value is one of the fundamental research goals in modern chemistry.[1] In this regard, excellent performances have been exhibited by application of homogeneous metal-based catalysts.[2] Obviously, most of the applied metals displayed difficulties by their high price and toxicity. Hence, today's research is focusing on the replacement by cheaper and low toxic metals.[3] Here, the use of zinc is of great interest, due to abundance and biological relevance. Among the established strategies, reduction processes have been intensively investigated and are demonstrating excellent yields and remarkable selectivities (*e.g.* reduction of C=O, C=N and amides).[4] However, the reduction of sulfoxides to sulfides in the presence of homogeneous zinc-catalysts has been so far unreported.[5,6] The biological relevance of the deoxygenation of sulfoxides has been discussed with respect of avoidance of oxidative damage of cells.[7] Furthermore, the importance of sulfides for organic synthesis are evident.[8] Hence, new protocols are highly desired. Herein, we portray the successful application of an easy-to-adopt catalyst based on zinc for the homogeneous reduction of a variety of aromatic and aliphatic sulfoxides to access sulfides.

Results and discussion

Initially, the reduction of *p*-tolyl sulfoxide (**1**) with silanes in toluene was studied as a model reaction to explore appropriate conditions and to examine the influence of various reaction parameters (Table 1). As expected when applying silanes ($PhSiH_3$ or Et_3SiH) in the absence of zinc sources only marginal amounts of *p*-tolyl sulfide (**1a**) after 12 h were monitored (Table 1, entry 1). However, when performing the reduction with 5.0 mol% of commercially available $Zn(OTf)_2$ and phenylsilane as reducing reagent, an excellent yield (>99%) and chemoselectivity (>99%) was realized after 12 h under non-inert conditions (Table 1, entry 2). In addition, the effect of various silanes on the product formation was explored. Increasing the number of phenyl substituent at the silicon resulted in a decreased yield of product **1a**, while an increased number of alkyl substituent led to an excellent performance (Table 1, entry 6). Next other zinc sources, such as ZnF_2, $ZnCl_2$, $ZnBr_2$, $Zn(BF_4)_2$, $Zn(OAc)_2$, $Zn(acac)_2$, were tested in combination with triethylsilane. Best performance was still observed for zinc(II) triflate. On the other hand, good results were detected for zinc(II) halides, apart from ZnF_2 (Table 1, entries 10–12). An increased yield was monitored for heavier halides ($ZnF_2 < ZnCl_2 < ZnBr_2$). Moreover, with other zinc-based Lewis acids no product at all was attained. Besides, the loading of $Zn(OTf)_2$ was decreased to 1.0 mol%, resulting in a diminish of product **1a** (20%) even after elongation of the reaction time (20 h). Additionally, the influence of the reaction temperature was studied. Here, the amount of *p*-tolyl sulfide (**1a**) is decreased at lower temperature (80 °C: yield 20%), while the reaction in the range of (25–60 °C) is hampered. Besides toluene as solvent excellent results were obtained applying THF (Table 1, entry 18), while the reaction in PhCN and PhCOOMe proceeded smoothly (Table 1, entries 20 and 21). It is worth noting that no reduction of the solvent was observed. In addition, the zinc(II) triflate was modified by nitrogen containing ligands. However, the addition of tmeda [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine], 2,2′-bipyridine, and imidazole resulted in no improvement of the reaction outcome (yields: <5%).

Once the optimized reaction conditions were established, the scope and limitations of the zinc-catalysed deoxygenation of sulfoxides applying Et_3SiH or $PhSiH_3$ as reducing reagent were investigated. A number of sulfoxides, including aromatic and aliphatic sulfoxides were reduced to the corresponding sulfides (Table 2). In general, a better performance was detected for

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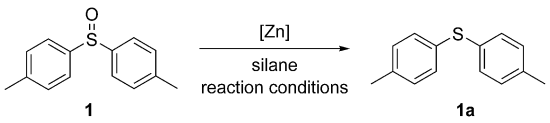
Table 1 Zinc-catalysed reduction of methyl phenyl sulfoxide **1**[a]



1 **1a**

Entry	Zn-source	Silane (equiv.)	Solvent	Yield (%)[b]
1[c]	—	$PhSiH_3$ (1.5)	Toluene	<3
2	$Zn(OTf)_2$	$PhSiH_3$ (1.5)	Toluene	>99
3	$Zn(OTf)_2$	Ph_2SiH_2 (1.5)	Toluene	50
4	$Zn(OTf)_2$	Ph_3SiH (2.0)	Toluene	25
5	$Zn(OTf)_2$	$PhMe_2SiH$ (2.0)	Toluene	42
6	$Zn(OTf)_2$	Et_3SiH (2.0)	Toluene	>99
7	$Zn(OTf)_2$	$(EtO)_3SiH$ (2.0)	Toluene	51
8	$Zn(OTf)_2$	PMHS (2.0)	Toluene	13
9	$Zn(OAc)_2$	Et_3SiH (2.0)	Toluene	<1
10	ZnF_2	Et_3SiH (2.0)	Toluene	<1
11	$ZnCl_2$	Et_3SiH (2.0)	Toluene	41
12	$ZnBr_2$	Et_3SiH (2.0)	Toluene	75
13	$Zn(BF_4)_2$	Et_3SiH (2.0)	Toluene	<1
14	$Zn(acac)_2$	Et_3SiH (2.0)	Toluene	3
15[d]	$Zn(OTf)_2$	Et_3SiH (2.0)	Toluene	20
16[e]	$Zn(OTf)_2$	Et_3SiH (2.0)	Toluene	<1
17[f]	$Zn(OTf)_2$	Et_3SiH (2.0)	Toluene	20
18[g]	$Zn(OTf)_2$	Et_3SiH (2.0)	THF-d_8	>99
19[h]	$Zn(OTf)_2$	Et_3SiH (2.0)	Toluene	>99
20	$Zn(OTf)_2$	Et_3SiH (2.0)	PhCN	63
21	$Zn(OTf)_2$	Et_3SiH (2.0)	PhCOOMe	53

[a] Reaction conditions: **1** (0.72 mmol), Zn-source (5 mol%), silane (1.5–2.0 equiv), solvent (2.0 mL), 100 °C, 12 h. [b] Determined by GC methods using biphenyl as an internal standard. [c] Run for 24 h. [d] Run for 1 h at 100 °C with 1.0 mol% $Zn(OTf)_2$. [e] Run for 24 h at r.t. [f] Run for 24 h at 60 °C. [g] Run for 12 h at 60 °C in 0.6 mL THF-d_8. [h] Up-scaling: **1** (2.4 mmol), solvent (6.0 mL).

$PhSiH_3$ compared to Et_3SiH. In most cases excellent yields and selectivities were obtained after 24 h at 100 °C. In case of **9** and **19** no product was observed probably due to low solubility of the starting materials. In order to study the selectivity of the process different substrates containing functional groups sensitive to reduction or a combination of the sulfoxide **1** with an additional substrate were reacted with phenylsilane in the presence of zinc(II) triflate (Table 2, entries 6–8, 12, 20 and Table 3). Excellent selectivity (>99%) for the reduction of S=O bond was observed in the presence of NO_2, CN, esters, and sulfonyl, while alkynyl, alkenyl, C=O and amide groups were reduced. Noteworthy, if the functional group (keto- and alkenyl group, Table 2, entries 12 and 20) is closely connected to the sulfoxide to some extend reduction took place, probably due to the neighbourhood to the active centre, while in case of separation of the two functional groups (Table 3, entries 2 and 3) resulted in selective reduction of the sulfoxide to the corresponding sulfide.

For preliminary mechanistic investigations, the reduction of **1** with $PhSiH_3$ was performed in the presence of stoichiometric amounts of the persistent radical TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) as a scavenger. However, no negative effect was observed on the yield of product **1a**, hence a radical based mechanism could be excluded.[9] Applying ^{1}H NMR spectroscopy on the reduction of **1** to **1a** with Et_3SiH in C_6D_6 and using the *para*-methyl group as probe only the decrease of **1** and the increase of **1a** were monitored, while no intermediates were observed on the NMR time scale.

In addition, with ^{29}Si NMR spectroscopy $(Et_3Si)_2O$ (δ = 9.2 ppm) was found as main product. We exclude the formation of $(Et_3Si)_2O$ *via* condensation of Et_3SiH and Et_3SiOH, which could be formed by elimination from $R_2S^+(H^-)OSiEt_3$, because no Et_3SiOH was monitored by ^{29}Si NMR during the course of reaction. Aside, the condensation reaction was separately studied in the presence and absence of catalytic amounts of $Zn(OTf)_2$.[10] Here, no formation of $R_3SiOSiR_3$ was observed. However, it was detected that two equivalents of hydride per sulfoxide are required for the reduction to the sulfide.

Afterwards, the interaction of $Zn(OTf)_2$ with the silane was studied. $Zn(OTf)_2$ was reacted with Et_3SiH (10 equiv.) in THF-d_8 for 1 h at 80 °C. The signal for Et_3SiH was unchanged in ^{1}H NMR as well as ^{29}Si NMR. Only a slight shift in the ^{19}F NMR spectra was observed, −80.7 ppm ($Zn(OTf)_2$, Et_3SiH in THF-d_8)[11] which is slightly shifted compared to $Zn(OTf)_2(THF)_4$ (δ = −79.1 ppm) probably caused by solvation or complexation.[4r,12] Based on this result, the formation of a zinc-hydride species can be probably excluded on the NMR time scale. On the other hand the interaction of zinc with sulfoxide was investigated. A solution of $Zn(OTf)_2$ in C_6D_6 was reacted first with methyl phenyl sulfoxide (**5**) for 1 h at 60 °C. The recorded ^{19}F NMR spectra showed a signal at −80.8 ppm. Indeed, after one hour at room temperature colourless crystals, which were suitable for single-crystal X-ray diffraction analysis, were collected from this solution. The obtained solid structure $Zn(\mathbf{5})_6(OTf)_2$ (**29**) showed an octahedral complexation of six sulfoxides molecules to the cationic zinc centre (Fig. 1).[13] Under same conditions the reaction of $Zn(OTf)_2$ with compound **2** (10 equiv.) led to the formation of complex $Zn(\mathbf{2})_4(OTf)_2$ (**30**) (Fig. 2). In comparison to complex **29** four sulfoxides are coordinated to the metal centre. In addition the triflate anions are attached to the metal, while in **29** the triflate anions are not fixed to the metal.

Later on, after isolation of the crystals of complex **29** $PhSiH_3$ (10 equiv.) was added at room temperature. Here, no significant change in the chemical shift was observed (^{19}F NMR δ = 80.8 ppm), while a shift to 80.3 ppm was found after heating for 1 h at 60 °C. In the ^{1}H NMR spectra the formation of the corresponding sulfide **5a** was monitored. Continuing heating for additional 23 h exhibited a shift towards −79.0 ppm, while in the ^{1}H NMR nearly full conversion of **5** was detected. The shift in the ^{19}F NMR spectra is probably caused by complexation of the corresponding sulfide **5a**. Noteworthy, the reaction of the sulfoxide with the silane in the absence of $Zn(OTf)_2$ resulted in no change of the ^{1}H NMR or ^{29}Si NMR spectra. With respect to the obtained results we excluded the formation of L_xZn=O species, while for various metals the abstraction of the oxide of the sulfoxide to yield metal oxides has been proposed.[14] Based on our findings we assumed that the zinc-catalyst acts as a Lewis acid (Scheme 1). First the sulfoxide coordinates to the zinc (intermediate **A**), thus an activation of the S=O bond occurs and increases the susceptibility of the sulfur for reduction.[6a,15] Next, the silane reacts with the intermediate **A**. An interaction of the hydride with the sulfur and an interaction of the silicon with the oxygen of the triflate group *via* a six-membered transition state are

Table 2 Zinc(II) triflate-catalysed reduction of sulfoxides[a]

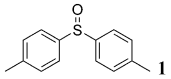
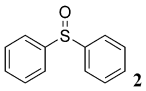
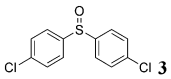
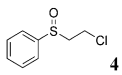
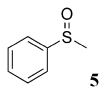
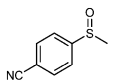
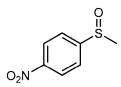
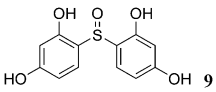
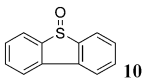
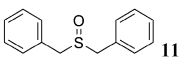
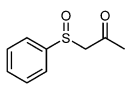
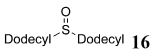
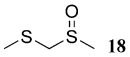
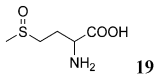
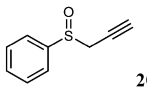
Entry	Substrate	Yield (%)[b]
1[c]	 1	**1a**: >99 (91)
2	 2	**2a**: >99 (96)
3	 3	**3a**: >99 (93)
4	 4	**4a**: 78 (69)
5	 5	**5a**: >99 (92)
6	 6	**6a**: >99 (95)
7	 7	**7a**: >99 (95)
8	 8	**8a**: >99[d]
9	 9	**9a**: <1[e]
10	 10	**10a**: >99 (95)
11	 11	**11a**: >99 (91)
12	 12	**12a**: 87[f]
13[g]	 13	**13a**: 94
14[g]	 14	**14a**: 57
15[g]	 15	**15a**: 40
16[g]	 16	**16a**: >99
17[g]	 17	**17a**: >99

Table 2 (*continued*)

Entry	Substrate	Yield (%)[b]
18[g]	 18	**18a**: >99
19	 19	**19a**: <1[e]
20	 20	**20a**: 76[h]

[a] Reaction conditions: sulfoxide (0.72 mmol), $Zn(OTf)_2$ (5 mol%), silane (1.1 mmol $PhSiH_3$), toluene (2.0 mL), 24 h, 100° C. [b] Determined by GC–MS and ^1H NMR. In parenthesis the isolated yield is stated. [c] Et_3SiH. [d] As main product PhSEt was observed. [e] Only traces of product were detected, probably due to poor solubility. Reaction was also carried out PhCN and PhCOOMe with similar results. [f] As side reaction the reduction of the carbonyl group was observed. [g] Due to the odour and the volatility the reaction was carried out in C_6D_6 and the products were not isolated. [h] Full conversion with respect to the sulfoxide was detected, while 15% are reduced to the corresponding alkene and 9% are reduced to the alkane.

assumed (intermediate **B**). Subsequently, a sulfonium salt analogue is formed (intermediate **C**), which undergoes elimination of $(R_3Si)_2O$, hydrogen and the sulfide.[16] Similar processes are assumed for the reduction of sulfoxides with boranes as reductant.[5q] However, the precise mechanism is currently uncertain and will be the subject of ongoing studies.

Conclusions

In summary, we have set up for the first time an efficient protocol for the reduction of sulfoxides to the corresponding sulfide with silanes as hydride source in the presence of straightforward zinc-salts under mild reaction conditions. Furthermore, mechanistic investigations indicated, that Zn(II) triflate acts a Lewis acid catalyst. Future studies will focus on the development of ligand modified zinc catalysts for improvement of the catalyst performance and chemoselectivity.

Experimental

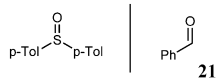
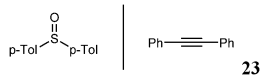
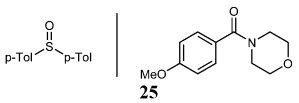
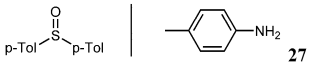
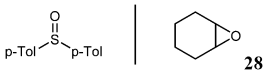
General

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

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%) and the corresponding

Table 3 Zinc(II) triflate-catalysed reduction of sulfoxide **1** in the presence of additional substrates sensitive to reduction[a]

Entry	Substrate	Conversion (%)[b]
1	 **21**	>99/>99
2	 **22**	55/<1
3	 **23**	>99/<1
4	 **24**	>99/<1
5	 **25**	>99/52
6	 **26**	>99/<1
7	 **27**	8/—
8	 **28**	>99/<1

[a] Reaction conditions: sulfoxide **1** (0.72 mmol), $Zn(OTf)_2$ (5 mol%), $PhSiH_3$ (1.1 mmol), 0.72 mmol of the second substrate, toluene (2.0 mL), 24 h. [b] Determined by GC–MS.

sulfoxide (0.72 mmol) and $PhSiH_3$ (1.1 mmol) was added. After addition of toluene (2.0 mL) the reaction mixture was stirred in a pre-heated oil bath at 100 °C for 24 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-5ms 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.[15,17]

Di(*p*-methylphenyl)sulfide (1a)[17]

Column chromatography (*n*-hexane–ethyl acetate 1 : 5). R_f 0.79. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.06–7.22 (m, 8 H), 2.30 (6 H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 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).

Diphenylsulfide (2a)[17]

Column chromatography (*n*-hexane–ethyl acetate 1 : 5). R_f 0.75. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.26–7.47 (m, 10 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 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).

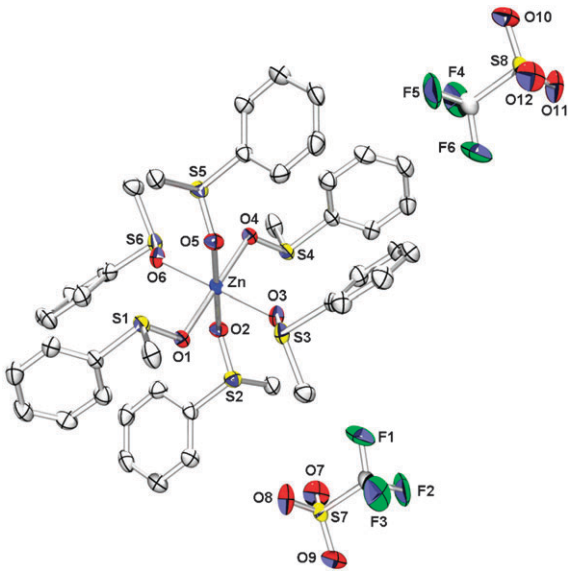


Fig. 1 Molecular structure of $Zn(\mathbf{5})_6(OTf)_2$ (**29**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å): Zn–O(1,2,3,4,5,6): 2.0817(14), O–S: 1.4265(18).

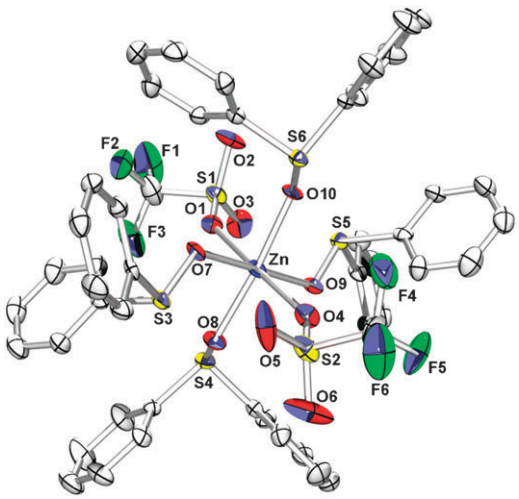


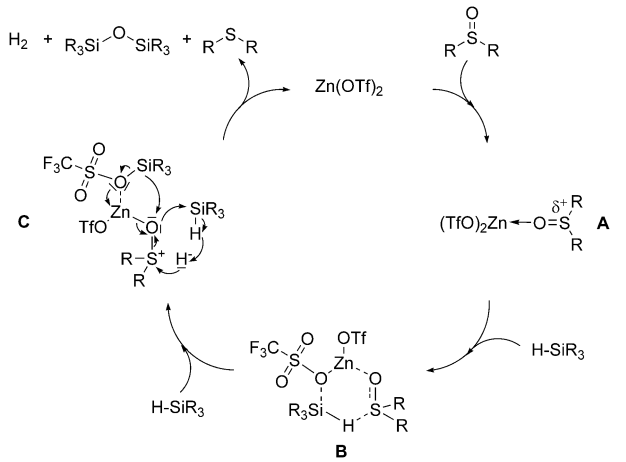
Fig. 2 Molecular structure of $Zn(\mathbf{2})_4(OTf)_2$ (**30**). Hydrogen atoms and a C_6D_6 solvent molecule are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å): Zn–O(7,8,9,10): 2.041–2.067(3), Zn–O(1,4): 2.124–2.223(3), (S(3,4,5,6)–O(3,4,5,6): 1.517–1.522(3).

Di(*p*-chlorophenyl)sulfide (3a)[15]

Column chromatography (*n*-hexane–ethyl acetate 1 : 10). R_f 0.67. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.23–7.33 (m, 8 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 133.9, 133.4, 132.3, 129.4 ppm; MS (ESI) m/z = 270 (M^+, not detected), 219 (33), 184 (100), 139 (11), 108 (29), 91 (18), 75 (24).

Phenyl 2-chloroethylsulfide (4a)[15]

Column chromatography (*n*-hexane–ethyl acetate 1 : 5). R_f 0.88. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.22–7.45 (m, 5 H), 3.59–3.68 (m, 2 H), 3.19–3.28 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz)



Scheme 1 Proposed catalytic cycle for the reduction of sulfoxides.

δ = 134.2, 130.4, 129.2, 127.1, 43.3, 36.1 ppm; MS (ESI) m/z = 172 (43, M^+), 123 (100), 109 (21), 65 (17), 45 (31).

Phenyl methylsulfide (5a)[15]

Column chromatography (*n*-hexane–ethyl acetate 1 : 5). R_f 0.88. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.19–7.35 (m, 5 H), 2.53 (s, 3 H) ppm; ^{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).

p-Cyanophenyl methylsulfide (6a)[17]

Column chromatography (acetone–CH_2Cl_2 1 : 9). R_f 0.90. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.48–7.53 (m, 2 H), 7.21–7.27 (m, 2 H), 2.49 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 146.0, 132.0, 125.3, 118.8, 107.4, 14.5 ppm; MS (ESI) m/z = 149 (100, M^+), 134 (32), 116 (60), 104 (23).

p-Nitrophenyl methylsulfide (7a)[17]

Column chromatography (acetone–CH_2Cl_2 1 : 9). R_f 0.90. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 8.07–8.12 (m, 2 H), 7.24–7.29 (m, 2 H), 2.53 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 148.8, 144.5, 124.8, 123.7, 14.8 ppm; MS (ESI) m/z = 169 (100, M^+), 139 (50), 123 (13), 111 (16), 108 (33), 82 (14), 77 (38).

Dibenzothiophene (10a)[17]

Column chromatography (*n*-hexane–ethyl acetate 1 : 5). R_f 0.78. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 8.16–8.21 (m, 2 H), 7.84–7.91 (m, 2 H), 7.44–7.53 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 139.0, 135.5, 126.8, 124.3, 122.8, 121.5 ppm; MS (ESI) m/z = 184 (100, M^+), 152 (14), 139 (21), 92 (18), 79 (12).

Dibenzylsulfide (11a)[17]

Column chromatography (*n*-hexane–ethyl acetate 1 : 5). R_f 0.74. ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.31–7.37 (m, 10 H), 3.65 (s, 4 H) ppm; ^{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).

tert-Butyl methylsulfide (13a)

^{1}H NMR ($CDCl_3$, 200 MHz) δ = 3.18 (s, 3 H, CH_3), 1.76 (s, 9 H, *t*Bu) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 47.1, 29.9, 11.0 ppm; MS (ESI) m/z = 104 (36, M^+), 57 (82), 41 (100).

tert-Dibutylsulfide (14a)

^{1}H NMR ($CDCl_3$, 200 MHz) δ = 1.42 (s, 12 H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 45.3, 33.2 ppm; MS (ESI) m/z = 146 (12, M^+), 57 (100).

Dibutylsulfide (15a)[17]

^{1}H NMR ($CDCl_3$, 200 MHz) δ = 2.28 (t, 4 H, J = 7.20 Hz, $S(CH_2CH_2CH_2CH_3)_2$), 1.14–1.49 (m, 8 H, $S(CH_2CH_2CH_2CH_3)_2$), 0.75 (t, 6 H, J = 7.20 Hz, CH_3) ppm; ^{13}C NMR (C_6D_6, 50 MHz) δ = 32.1, 32.0, 22.3, 13.8 ppm; MS (ESI) m/z = 146 (40, M^+), 103 (15), 90 (31), 61 (97), 56 (100).

Didodecylsulfide (16a)[17]

^{1}H NMR ($CDCl_3$, 200 MHz) δ = 0.47–2.80 (m, 52 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 38.0, 31.8, 29.5, 29.4, 29.3, 29.1, 28.7, 22.6, 22.4, 14.0 6.7, 6.3 ppm. MS (ESI) m/z = 370 (M^+, not detected), 216 (58), 201 (100), 111 (20), 103 (23), 97 (38), 83 (48), 75 (11), 69 (60), 61 (58), 55 (60).

Tetrahydrothiophene (17a)[17]

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

2,4-Dithiapentane (18a)[17]

^{1}H NMR ($CDCl_3$, 200 MHz) δ = 3.18 (s, 2 H), 1.76 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 40.2, 14.0 ppm; MS (ESI) m/z = 110 (14, M^+), 108 (99), 61 (100).

Procedure for the deoxygenation of sulfoxides in the presence of TEMPO

A pressure tube was charged with $Zn(OTf)_2$ (0.036 mmol, 5.0 mol%), di(*p*-methylphenyl)sulfoxide (0.72 mmol), $PhSiH_3$ (1.1 mmol) and TEMPO (0.72 mmol) in an atmosphere of nitrogen. After addition of dry toluene (2.0 mL) the reaction mixture was stirred in a preheated oil bath at 100 °C for 24 h. The mixture was cooled on an ice bath and dodecane (internal standard) was added. The solution was diluted with dichloromethane and an aliquot was taken for GC-analysis (30 m Rxi-5ms column, 40–300 °C).

Single-crystal X-ray structure determination

A NMR tube was charged with $Zn(OTf)_2$ (0.036 mmol, 5.0 mol%) and phenyl methylsulfoxide (0.72 mmol) or diphenylsulfoxide (0.72 mmol). After addition of benzene-d_6 (0.6 mL) the mixture was heated at 60 °C for 1 h. Slow cooling to room temperature yielded colourless crystals suitable for single-crystal X-ray diffraction analysis. Crystals were each mounted on a glass capillary in perfluorinated oil and measured under a flow of nitrogen. The data was collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[18] software package. The

positions of the H atoms were calculated and considered isotropically according to a riding model. **29**: crystal system: trigonal; space group: $R\bar{3}$; unit cell dimensions a = 12.5877(4) Å α = 90°, b = 12.5877(4) Å, β = 90°, c = 29.1803(11) Å, γ = 120°; volume: 4004.2(2) Å^3; Z = 3; D_{calcd}: 1.499 Mg m^{-3}; μ: 0.850 mm^{-1}; F(000): 1860; theta range for data collection: 3.24 to 24.99°; reflections collected: 5363; independent reflections: 1575 [R_{int} = 0.0315]; completeness to theta = 24.99°: 99.7%; refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2: 1.001; final R indices [$I > 2\sigma(I)$] R_1 = 0.0301, wR_2 = 0.0716; R indices (all data): R_1 = 0.0423, wR_2 = 0.0746; largest diffraction peak and hole 0.306 and −0.241 e Å^{-3}. **30**: crystal system: trigonal; space group: $P\bar{1}$; unit cell dimensions a = 10.5817(4) Å; α = 83.554(3)°, b = 13.8939(5) Å, β = 88.085(3)°, c = 19.8576(3) Å, γ = 73.177(3)°; volume: 2775.99(18) Å^3; Z = 2; D_{calcd}: 1.496 Mg m^{-3}; μ: 0.746 mm^{-1}; F(000): 1284; theta range for data collection: 3.31 to 25.00°; reflections collected: 21 815; independent reflections: 9791 [R_{int} = 0.0768]; completeness to theta = 25.00°: 99.7%; refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2: 0.826; final R indices [$I > 2\sigma(I)$] R_1 = 0.0561, R_2 = 0.1010; R indices (all data): R_1 = 0.1276, wR_2 = 0.0930; largest diffraction peak and hole 0.559 and −0.372 e Å^{-3}.

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