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REVIEW ARTICLE

Reduction of oxygenated organosulfur compounds

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A comprehensive review on deoxygenation of sulfoxides to thioethers and reductive coupling of sulfonyl, sulfinyl and sulfenyl halides, sulfinates and thiosulfonates to their corresponding disulfides are discussed with different reagents and catalysts. The reported mechanisms for these transformations are also addressed.

Keywords: reduction; deoxygenation; reductive coupling; sulfoxides; sulfides; thioethers; sulfonyl halides; sulfonyl derivatives; sulfenyl halides; sulfinyl halides; sulfonic acids; thiosulfonates; disulfides, oxidative coupling

Part I. Reduction of sulfoxides to their corresponding thioethers

1. Introduction

Reduction of sulfoxides to their corresponding sulfides is an important reaction that has found considerable utility in biochemical reactions (*1*) and organic synthesis (*2–5*), especially for asymmetric transformations in which after stereoselective induction the chiral sulfinyl group is eliminated by reduction to thioethers followed by the removal of the sulfur atom (*3–6*). Due to the importance of this transformation, several reviews and monographs have been published (*7–9*). This part of the review (Part I), deals with advances in the reduction of sulfoxides to their corresponding thioethers with more emphasis on the development of the methods in the last 20 years (*10–25*). In second part of this review, we have paid attention to the reduction of sulfonic, sulfinic, and sulfenic acid derivatives by different methods.

Sulfonyl chlorides are easily and efficiently prepared by the chlorosulfonation reaction of arenes and alkanes (*26*) and are precursors for the preparation of other organic sulfur compounds such as disulfides. Therefore, we have focused on the methods which are available for the reduction of sulfonyl chlorides to their disulfides in Part II. Organic disulfides are valuable starting materials for the synthesis of a variety of organosulfur compounds such as sulfenyl (*27*) and sulfinyl

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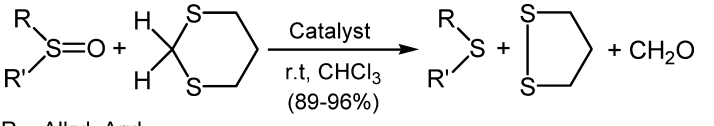
(*28, 29*) derivatives. Reductive coupling of other sulfonyl derivatives to their disulfides, which is an important transformation in organic synthesis, has been covered in Part II of this article.

2. Reduction of sulfoxides with 1,3-dithiane and electrophilic bromine (*30*)

Sulfur-containing compounds such as thiols (*31*), hydrogen sulfide (*32*), carbodithionic acids (*33*), thiophosphinic, thiophosphonic, and thiophosphoric acid (*34*), sulfides (*35, 36*), sulfenyl, sulfinyl, and sulfonyl chlorides (*37*), disulfides (*38*), elemental sulfur (S_8) (*39*), and thionyl chloride (*40*) have been applied for the reduction of sulfoxides to their sulfides. However, these methods have some disadvantages, and developing new methods using sulfur compounds is of importance.

A mild method for deoxygenation of sulfoxides has been developed in the presence of 1,3-dithiane using a catalytic amount of *N*-bromosuccinimide (NBS), 2,4,4,6-tetrabromo-2, 5-cyclohexadienone (TABCO), or Br_2 as the source of electrophilic bromine at room temperature (Scheme 1).

Among the catalysts used for this reduction, NBS or TABCO was found to be more efficient than those having electrophilic chlorine such as *N*-chlorosuccinimide (NCS) and tetrachlorocyanuric acid (TCCA). The reduction in the presence of catalytic amounts of molecular bromine was found to be as fast as using NBS and TABCO (Table 1). However, the reactions using molecular iodine as a catalyst were found to be a very slow process and incomplete, even when the excess amounts of iodine were used.



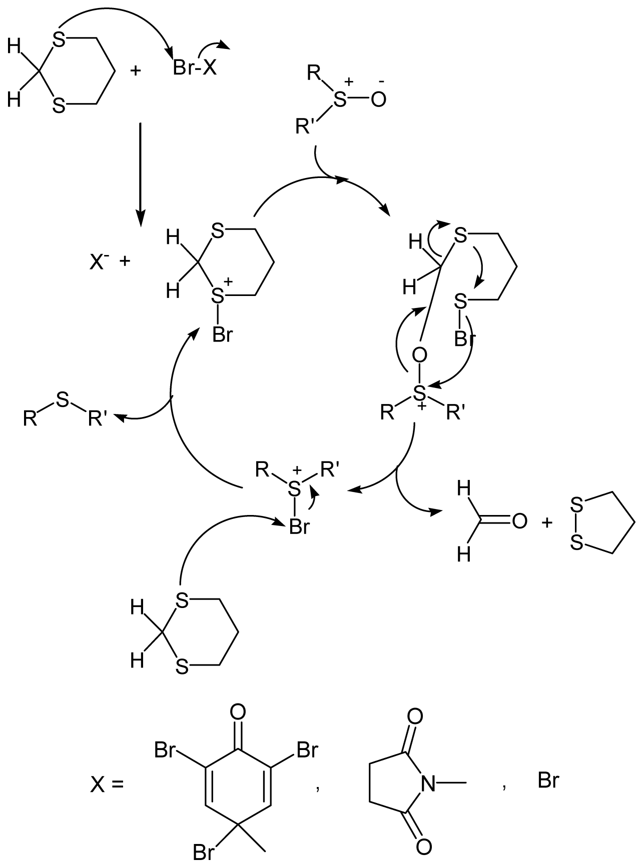
R = Alkyl, Aryl
Catalyst = NBS, TABCO, Br_2 (20-30 mol%)

Scheme 1.

Table 1. Reduction of sulfoxides to sulfides with 1,3-dithiane in the presence of TABCO (A), NBS (B), or Br_2 (C) in $CHCl_3$ at room temperature.

Entry	R	R′	Catalyst[a]	Time (min)	Yield[b]
1	Ph	CH_3	A	15	94
			B	12	94
			C	10	95
2	Ph	$PhCH_2-$	A	40	90
			B[c]	20	91
			C	25	90
3	Ph	Ph	A[c]	55	93
			B[c]	40	94
			C[c]	35	95
4	$PhCH_2-$	$PhCH_2-$	A	35	92
			B	30	94
			C	20	95
5	$PhCH_2-$	$CH_3CH_2CH_2-$	A	45	89
			B	35	91
			C	25	94
6	$CH_3\ (CH_2)_2CH_2-$	$CH_3(CH_2)_2CH_2-$	A	12	94
			B	10	96
			C	8	96

[a]The ratio of sulfoxides/1,3-dithiane/catalyst is 1/1.1/0.2, unless otherwise stated.
[b]Isolated yield.
[c]The ratio of sulfoxides/1,3-dithiane/catalyst is 1/1.2/0.3.



Scheme 2.

The reduction of dibenzyl sulfoxide in the presence of urea, thiourea, benzamide, ethylcarbamate, and carbonyl groups performs well with a slight decrease in the rate of the reaction. This decrease in the rate of the reaction in the presence of −NH-containing compounds could be due to the possibility of bromine exchange between NBS and the −NH functionality. However, reduction in the presence of the −SH functional group does not occur, due to the ready coupling of thiol group to its corresponding disulfide.

Scheme 2 illustrates the proposed mechanism for the deoxygenation of sulfoxides in the presence of 1,3-dithiane and electrophilic bromine.

1,2-Dithiacyclopentane, which is produced as a byproduct of the reaction as indicated in Scheme 2, can be easily removed from the reaction mixture due to its ease of polymerization to an unidentified polymer upon concentrating the reaction mixture (*41*).

3. Reduction of sulfoxides with phosphorus compounds

Due to the nature of the S=O and P=O bonds, the oxo-transfer reaction from sulfoxides to phosphines and phosphites is expected to be, in general, a thermodynamically favorable process. Phosphorus derivatives are widely used to cleave the S−O bond of sulfoxides for their high affinity for oxygen (*10*). The rate of the reduction of sulfoxides by phosphines is closely linked to the nature of the phosphorus substituents (*42–44*).

3.1. *Reduction of sulfoxides with homogeneous phosphine compounds*

Phosphines (*41–50*), phosphates (*43, 51, 52*) cyclic phospholanes (*53, 54*), phosphorus (III or V) halides (*45, 55–73*), hypophosphorus acid (*74*), and phosphorus sulfur compounds (*75–82*) are trivalent and pentavalent phosphorus compounds that are applied for the successful reduction of sulfoxides to their corresponding thioethers under homogeneous conditions.

3.1.1. *Reduction of sulfoxides in the presence of phosphites catalyzed by dichlorodioxomolybdenum (VI)* (22)

Phosphites are usually preferred over phosphines because of their greater reactivity and ease of removal in the oxidized form (*51*). However, in most of the cases, the reaction requires rather high temperatures and long reaction times, limiting their use in organic reactions.

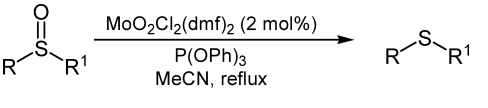
Chemoselective reduction of sulfoxides to sulfides has been carried out by $P(OPh)_3$ in the presence of $MoO_2Cl_2(dmf)_2$ as a catalyst (Scheme 3) with complete conversion at reflux condition in MeCN in a short reaction time (Table 2). For this reduction, $P(OEt)_3$ and $P(OMe)_3$ could also be used. However, when these phosphites were heated with sulfoxides at 110 °C, deoxygenation of the sulfoxide moiety does not occur. Rather, the rearrangement of the trialkylphosphite to dialkyl alkylphosphonate has been observed (*51*).

By this method, dialkyl sulfoxides are deoxygenated faster than diaryl sulfoxides, and sulfoxides possessing β-keto or β-ethoxycarbonyl functionalities could be chemoselectively reduced without affecting the carbonyl functionalities.

The catalytic function of $MoO_2Cl_2(dmf)_2$ for the reduction of sulfoxides with phosphites is presented in Scheme 4.

3.1.2. *Reduction of sulfoxides with $PPh_3/TiCl_4$* (83)

It was found that the combination of $PPh_3/TiCl_4$ was an effective promoter for the deoxygenation of sulfoxides and gave the corresponding sulfides in good yields (up to 97%) under mild conditions (Table 3, Scheme 5). This method has been used in the reaction between racemic phosphines and (*R*)-methyl *p*-tolyl sulfoxide which was accompanied by kinetic resolution in moderate selectivities.

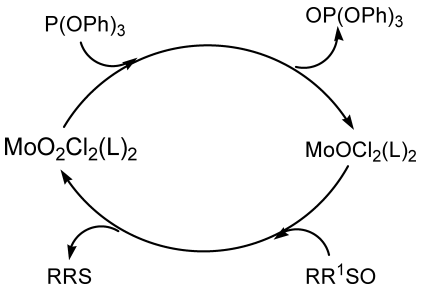


Scheme 3.

Table 2. Deoxygenation of sulfoxides in the presence of $P(OPh)_3$ and $MoO_2Cl_2(dmf)_2$.

Entry	R	R^1	Time	Yield[a]
1	4-MeC_6H_4	4-MeC_6H_4	1 h	98
2	4-ClC_6H_4	4-ClC_6H_4	2 h	93
3	Ph	CH_2CH	45 min	52
4	$PhCH_2-$	$PhCH_2-$	4 h	89
5	$-CH_2-CH_2-CH_2-CH_2-$		10 min	70

[a]Isolated yields based on the starting sulfoxides.

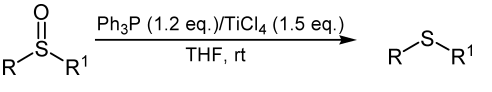


Scheme 4.

Table 3. Reduction of sulfoxides using $PPh_3/TiCl_4$ system.

Entry	R	R^1	Time (h)	Yield[a]
1	$PhCH_2-$	$PhCH_2-$	2	96
2	$PhCH_2CH_2-$	$PhCH_2CH_2-$	1	92
3	$PhCH(CH_3)$	$PhCH(CH_3)$	24	78
4	Ph	Me	2	67
5	Cyclohexyl	Cyclohexyl	14	96
6	$4\text{-}MeC_6H_4$	$PhCH_2CH_2-$	2	97
7[b]	$4\text{-}MeC_6H_4$	*t*-Bu	14	90

[a]Isolated yields.
[b]Reaction was carried out at 60 °C.



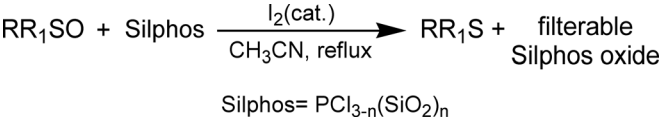
Scheme 5.

3.2. *Reduction of sulfoxides with heterogeneous phosphine compounds*

A common drawback of all the homogeneous phosphine systems used for reduction of sulfoxides is the formation of a stoichiometric amount of phosphine oxide as a byproduct. Its separation from the reaction mixture is usually a difficult task and requires time-consuming column chromatography or more frequently plate chromatography techniques. As a solution to this problem, a heterogeneous phosphine called Silphos $[PCl_{3-n}(SiO_2)_n]$ has been introduced.

3.2.1. *Reduction of sulfoxides with Silphos* $[PCl_{3-n}(SiO_2)_n]$ (84)

Deoxygenation of sulfoxides to thioethers was carried out using a heterogeneous phosphine reagent Silphos $[PCl_{3-n}(SiO_2)_n]$ and molecular iodine under reflux in dry MeCN in high yields (Scheme 6, Table 4). This method is readily applicable to the reduction of different sulfoxides to their thioethers.

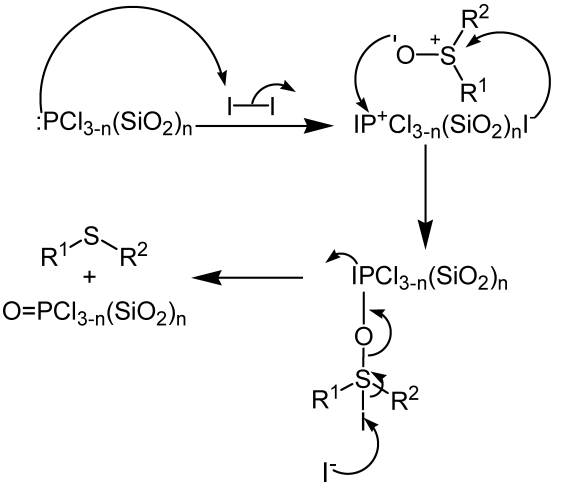


Scheme 6.

Table 4. Deoxygenation of structurally different sulfoxides to thioethers in the presence of Silphos [$PCl_{3-n}(SiO_2)_n$] and catalytic amounts of molecular iodine.

Entry	R	R^1	Yield[a]
1	$PhCH_2$	$PhCH_2$	96
2	$PhCH_2$	Ph	94
3	Ph	Me	91
4	$PhCH_2$	Me	95
5	Ph	Ph	95
6	CH_2CHCH_2	CH_2CHCH_2	89
7	Ph	i-C_3H_7	90
8	4-ClC_6H_4	4-ClC_6H_4	96
9	Dibenzothiophene		97

[a]The molar ratio of substrate/I_2 applied for the oxo-transfer process was 1:0.3 using 1.0 g of Silphos in refluxing MeCN for 15 min.



Scheme 7.

In agreement with the behavior of the reaction and the catalytic requirement of molecular iodine, there is a proposed mechanism for the deoxygenation of sulfoxides in the presence of Silphos (Scheme 7).

4. Reduction of sulfoxides with boron compounds

Boron derivatives have been frequently used to reduce sulfoxides to sulfides. Haloborane reagents such as BCl_3/CH_2Cl_2 (*85*), $HBCl_2$/THF (*86*), $BF_3{\cdot}Et_2O$/NaI (*87, 88*), $(CH_3)_2BBr$, BBr_3, 9-BBN-Br (*89*), $[(CH_3)_2CHC(CH_3)_2BHCl{\cdot}(CH_3)_2S]$ (ThxBHCl−DMS) (*90*), and other boron reagents: $[BH_3{\cdot}$THF, $BH_3{\cdot}(C_6H_5O)_3B$, $BH_3/BF_3{\cdot}(C_2H_5)_2O]$ (*91, 92*), 1,3,2-benzodioxaborole (*93, 94*), B_2S_3/CS_2 (*79, 95*), $(C_6H_5Se)_3B$, $(CH_3Se)_3B/(C_4H_9)_2B_2Se_3$ (*96*), diborane-THF (*97, 98*), disiamylborane-THF (*99*), thexylborane-DMS (*98, 100*), 9-BBN-THF (*101*), thexylchloroborane-DMS (*98*) are the classical reagents which have been applied successfully for the deoxygenation of aliphatic, aromatic, and, in some cases, heterocyclic sulfoxides. The following section will focus on newer boron reagents for sulfoxide to sulfide transformation.

4.1. *Deoxygenation of sulfoxides with sodium borohydride and additives*

Metal hydrides are valuable reagents in organic chemistry (*102–118*). The most frequently used hydride is $NaBH_4$ reagent which has been used in a wide range of reduction processes (*119*). The reactivity of $NaBH_4$ can be enhanced by carrying out the reaction in the presence of certain additives.

4.1.1. *Deoxygenation of sulfoxides with sodium borohydride/$NiCl_2$* (120)

Deoxygenation of diaryl, dibenzyl, benzyl aryl, benzyl alkyl, aryl alkyl and dialkyl (including fatty) sulfoxides, and selenoxides (Table 5) have been achieved successfully with anhydrous nickel chloride and sodium borohydride in tetrahydrofuran at 0–5 °C (Scheme 8). In this reaction, nickel boride is formed *in situ* which is believed to be the active moiety in the reaction.

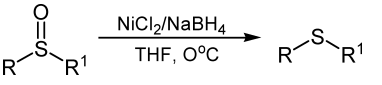
Earlier studies conducted by Okamoto *et al.* (*121–123*) and Maybury and coworkers (*124*) have shown that surface contamination by spectator ions such as Na^+ and Cl^- as well as the percentage of BO_2^- have a marked effect on the reactivity of this catalyst. The lower the ion solubility in boride-forming solvents, the higher is its concentration as a surface contaminant and thus lower reactivity. Although the contamination of Na^+ and Cl^- was high because of the use of THF, anhydrous nickel chloride and THF reduced (if not completely eliminated) the contamination of BO_2^- which is produced by the reaction of $NaBH_4$ with water (*125*). This presumably gives the catalyst the ideal selectivity for deoxygenation without desulfurization and deselenization.

The probable mechanism in these reactions is an oxidative addition of sulfoxide followed by hydrogenolysis (Scheme 9).

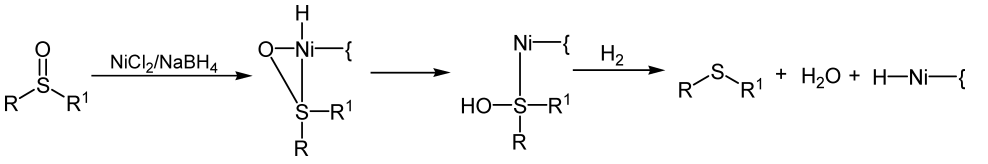
Table 5. Deoxygenation of sulfoxides with anhydrous $NaBH_4/NiCl_2$ in THF at 0–5 °C.

Entry	R	R^1	Molar ratio of substrate:$NiCl_2$:$NaBH_4$	Time (h)	Yield (%)[a]	Method
1	$PhCH_2-$	$PhCH_2-$	1:3:9	2	81	A
2	$PhCH_2-$	Ph	1:3:9[b]	1.5	72	A
3	$PhCH_2-$	*n*-Pr	1:5:15	2	62	A
4	$PhCH_2-$	*n*-Pr	1:5:15	2.5	74	B
5	Ph	Ph	1:5:15	4	75	A
6	Ph	Ph	1:20:60[c]	1.5	80	B
7	Ph	*n*-Pr	1:3:9	1	65	A
8	Ph	*n*-Pr	1:15:45[c]	1.5	87	B
9	Ph	Me	1:3:96[b]	1.5	69	A
10	*n*-Dodecyl	*n*-Dodecyl	1:10:30[c]	1.5	96	B
11	*n*-Octadecyl	Ph	1:11:33[c]	3	96	B

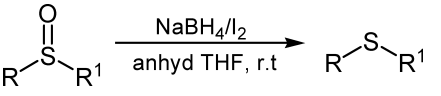
[a]The yield reported corresponds to the mercuric chloride adduct.
[b]The initial molar ratio was 1:2:6. Subsequently small lots of 1:3 molar ratio of anhydrous $NiCI_2$:$NaBH_4$ were added.
[c]Reactions carried out in dry THF.
Method A: After complete disappearance of the sulfoxide, the reaction was quenched with conc. nitric acid till the complete disappearance of the black precipitate of nickel boride.
Method B: After complete disappearance of the sulfoxide, the reaction was quenched by filtration through a Celite® pad.



Scheme 8.



Scheme 9.



Scheme 10.

Table 6. Deoxygenation of sulfoxides to thioethers using $NaBH_4/I_2$ system.

Entry	R	R^1	I_2 (equiv.)	Time (min)	Yield
1	Ph	Et	1.2	4	91
2	Ph	$PhCH_2CH_2$	1.2	9	92
3	Ph	*n*-Pr	2	10	93
4	Ph	*c*-C_5H_9	1.2	6	88
5	Ph	*c*-C_6H_{11}	1.2	6	92
6	Ph	Ph	2	18	93
7	4-MeC_6H_4	4-MeC_6H_4	2	15	95
8	*n*−Bu	*n*−Bu	1.2	3	95
9	Ph	$PhCH_2$	2	12	93
10	$PhCH_2$	$PhCH_2$	1.2	5	98
11	4-$NO_2C_6H_4$	Ph	2	15	57

[a]Yields of isolated pure products.

4.1.2. *Deoxygenation of sulfoxides with sodium borohydride/I_2 system* (18)

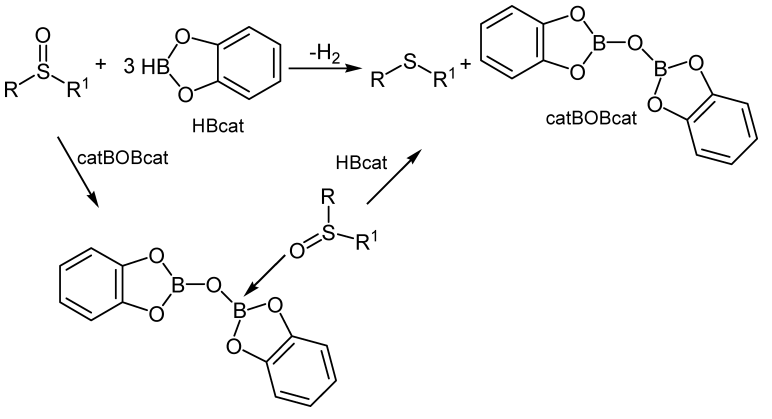
Efficient deoxygenation of sulfoxides with sodium borohydride/I_2 system has been achieved and is a valuable addition to the methodologies available for this transformation (Scheme 10).

By this method, highly chemoselective deoxygenation of sulfoxides is achieved in the presence of an olefin moiety without the formation of any detectable hydroboration products. Moreover, efficient deoxygenation of dibenzyl and benzyl phenyl sulfoxides to thioethers without cleavage of C−S bond shows the usefulness of the presented protocol (Table 6). This method can be selectively applied for the chemoselective reduction of sulfoxides in the presence of −CN and RCO_2−functional groups.

4.1.3. *Deoxygenation of sulfoxides with cathecholborane* (23)

The addition of cathecholborane (HBcat; cat = 1,2-$O_2C_6H_4$) to a wide range of sulfoxides affords the corresponding sulfides, dihydrogen, and catBOBcat (Scheme 11, Table 7).

The diboron compound catBOBcat acts like a Lewis acid and will coordinate one molecule of the starting sulfoxides. The formation of two B−O bonds provides an enormous enthalpic driving force ($\Delta H = 180$ kcal/mol) for these deoxygenations (*126*). Although deoxygenations with bulky or electron-withdrawing sulfoxides are slow, these reactions can be greatly accelerated with the use of excess HBcat or by employing a rhodium catalyst (usually $RhCl(PPh_3)$ or Rh(acac)(dppe) where acac = acetylacetonato and dppe = 1,2-bis(diphenylphosphino)ethane) (Scheme 12).

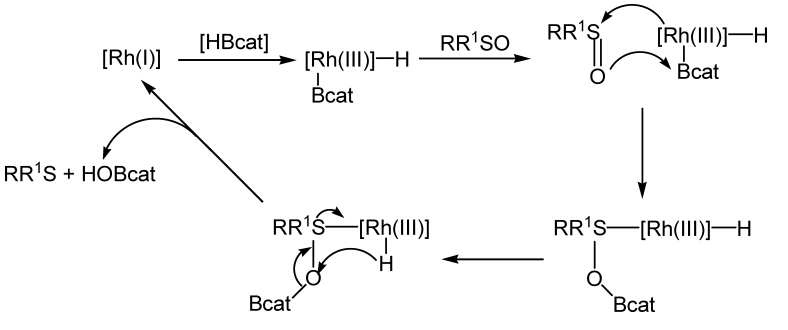


Scheme 11.

Table 7. Deoxygenation of sulfoxides using HBcat.

Entry	R	R^1	Time (h)	^{11}B NMR[a]
1	Me	Me	48	14.8
2	$-CH_2CH_2CH_2CH_2-$		0.25	14.8
3	$PhCH_2$	Me	0.5	16.2
4	4-MeC_6H_4	Me	150	17.9
5	Ph	Ph	>500	18.4
6	Ph	$CHCH_2$	–	18.9
7	4-$NO_2C_6H_4$	4-$CH_3C_6H_4$	>500	21.3
8	4-CF_3CH_2	$PhCH_2$	>500	21.4

[a] ^{11}B NMR of catBOBcat OSRR′ adduct in ppm, which could also be obtained by independent 1:1 reaction of catBOBcat with sulfoxide.



Scheme 12.

Reactions proceeded cleanly at room temperature to give the desired product and are usually complete within 1 h. Reactions with phenyl vinyl sulfoxides are complicated by the competing catalyzed hydroboration of the vinyl group.

5. Reduction of sulfoxides with metal-containing systems

The applications to organic synthesis of systems containing metals are a rapidly developing field especially in reductive transformations.

Table 8. Deoxygenation of sulfoxides with magnesium powder in ethanol.

Entry	R	R^1	Method (108)	Isolated yield (%)
1	(*Z*)-2-(4-(phenylsulfinyl) but-3-enyl)cyclopentanone		A	98
2	(*E*)-2-(4-(phenylsulfinyl) but-3-enyl)cyclopentanone		A	97
3	(*Z*)-1-(4-phenylbut-1-enylsulfinyl) benzene		A	99 (1:1)[a]
4	(*E*)-1-(4-phenylbut-1-enylsulfinyl) benzene		A	99 (1:1)[a]
5	2-(Phenylsulfinylmethylene)-7-oxa-bicyclo[4.1.0]heptane		A	83
6	(*Z*)-4-(*tert*-butylsulfinyl)-2-methylbut-3-en-2-ol		D	21
7	(*Z*)-1-((4-(*tert*-butylsulfinyl)-2-methylbut-3-en-2-yloxy)methyl) benzene		D	16
8	Ph	Me	C or E	98
9	Ph	$BnCO_2CH_2$	C	99
10	Ph	$PhCOCH_2$	C	No reaction
11	Ph	Ph	B	99
12	$-C_6H_4COC_6H_4-$		B	98
13	*t*-Bu	n-C_8H_{17}	D or E	No reaction

[a]Ratio in parentheses is Z/E as determined by ^{1}H NMR.
Method A: 3 equiv. Mg/cat. $HgCl_2$, MeOH (8 mL), −43 °C, 3 h; Method B: 3 equiv. Mg/cat. $HgCl_2$, MeOH/THF (3/1, 8 mL), −43 °C, 3 h; Method C: 6 equiv. Mg/cat. $HgCl_2$, MeOH (12 mL), −43 °C, 5 h; Method D: 6 equiv. Mg/cat. $HgCl_2$, MeOH (12 mL), rt, 4 h; Method E: 4 equiv. Mg/cat. $HgCl_2$, EtOH (12 mL), rt, 3 h.

5.1. *Reduction of sulfoxides with magnesium in alcohol* (127)

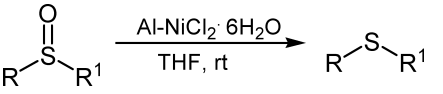
An extremely convenient deoxygenation of 1-alkenyl, alkyl, and aryl phenyl sulfoxides with magnesium powder in absolute methanol (or ethanol) afforded the corresponding sulfides in excellent yields (Table 8).

The deoxygenation reaction of keto sulfoxides proceeds without isomerization of the double bond (Table 8, entries 1 and 2). When an epoxide-containing sulfoxide was subjected to the same reaction conditions, hydroxyl sulfoxides were obtained as a major product instead of the simple deoxygenated adducts (Table 8, entry 5). The sterically compressed *cis*-configuration of the substrates was retained in the product to provide *cis*-sulfides. In contrast, the reduction of alkyl phenyl sulfoxides was so slow at low temperatures that excess amounts of magnesium and prolonged reaction times were required to complete the reaction. Dialkyl sulfoxides were inert even after the complete consumption of magnesium. In the case of the substrates containing protons acidic enough to react with magnesium metal, enolate formation took place first before deoxygenation. Thus, in contrast to α-phenylsulfinyl ester (Table 8, entry 10), the acidic proton of α-phenylsulfinyl ketone (Table 8, entry 11) reacted with magnesium metal to form the corresponding enolate which was inert toward further deoxygenation.

5.2. *Reduction of sulfoxides with Al-$NiCl_2{\cdot}6H_2O$* (21)

It has been observed that alkyl aryl and dialkyl sulfoxides can be conveniently and rapidly converted to the corresponding sulfides with an Al-$NiCl_2{\cdot}6H_2O$ system in high yields. Ketones are not affected under these reaction conditions (Scheme 13, Table 9).

The probable mechanism of the reaction can be rationalized by taking into account the mechanism proposed for this type of binary system (*128–130*) as shown in Scheme 14.

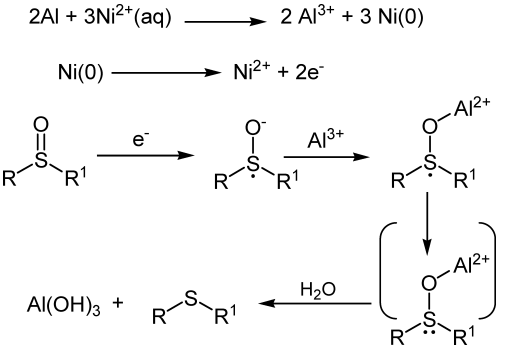


Scheme 13.

Table 9. Reduction of sulfoxides with Al-$NiCl_2 \cdot 6H_2O$.

Entry	R	R^1	Time (min)	Yield (%)[a]
1	Ph	$(CH_2)_4CH_3$	50	94
2	$PhCH_2$	Ph	45	84
3	$PhCH_2$	$(CH_2)_2OH$	40	90
4	$PhCH_2$	$(CH_2)_2OAc$	50	84
5	Et	$(CH_2)_2OAc$	50	87
6	$CH_3(CH_2)_4$	$(CH_2)_2OH$	45	93
7	Ph	CH_2COCH_2	40	86
8	$CH_3(CH_2)_{15}$	Et	45	94

[a]Isolated yields.



Scheme 14.

5.3. *Reduction of sulfoxides with high-valent molybdenum metal complexes*

Among the variety of metal complexes that have been used as catalysts for the deoxygenation of sulfoxides, molybdenum complexes have attracted considerable interest. This metal is found in a class of enzymes that are commonly referred to as mononuclear molybdoenzymes or oxotransferases, such as dimethyl sulfoxide reductases, that catalyze oxygen atom transfer to or from a physiological donor/acceptor (*131, 132*).

Several studies have shown that $Mo(VI)O_2$ complexes catalyze the oxygen atom transfer reaction from the sulfoxides to a phosphine, yielding the corresponding sulfides and the oxidized phosphine (*22, 133–136*).

5.4. *Reduction of sulfoxides with low-valent metal compounds*

Low-valent oxophilic d-block metals have become important in deoxygenation of different types of organic substrates (*137*). The successful utilization of the lower valent complexes of Ti, Mo, and W in effecting the deoxygenation of certain organic molecules is the result of the usually thermodynamic stability of Ti−, Mo−, and W−oxo bonds (*138, 139*). Some examples of these complexes are $TiCl_4/LiAlH_4$ (*140*), $TiCl_4$/Zn (*141*), $TiCl_4$/NaI (*142*), $MoOCl_3$/Zn (*143*), $TiCl_4$/Sm (*144*), Cp_2TiCl_2/Sm (*145*), WCl_6/NaI and WCl_6/Zn (*146*), and $MoCl_5$/NaI and $MoCl_5$/Zn (*147*).

5.5. *Reduction of sulfoxides with tungsten hexachloride (WCl_6)/NaI or (WCl_6)/Zn systems* (146)

Sulfoxides are reduced completely to their corresponding sulfides by WCl_6/NaI system in anhydrous CH_3CN or by WCl_6/Zn powder in anhydrous THF (Scheme 15).

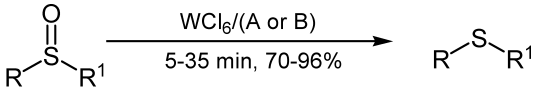
By this method, efficient deoxygenation of dibenzyl, benzyl phenyl, and allyl phenyl sulfoxides to their sulfides has been achieved in excellent yields, demonstrating the general applicability of the method for such a useful transformation (Table 10).

4-Nitrophenyl phenyl sulfoxides gave somewhat lower yield together with unidentified side products. This is presumably due to the reaction of the low-valent tungsten with the nitro group to produce the corresponding amine and azo compounds (*148*).

5.6. *Reduction of sulfoxides with molybdenum pentachloride ($MoCl_5$)/NaI or ($MoCl_5$)/Zn systems* (147)

Among the low-valent oxophilic d-block metal systems, $MoCl_5$/NaI or $MoCl_5$/Zn is also an effective system for the deoxygenation of sulfoxides to their sulfides in CH_3CN (Scheme 16).

The data summarized in Table 11 reveal that this method is applicable to the reduction of a variety of structurally different sulfoxides.



Scheme 15.

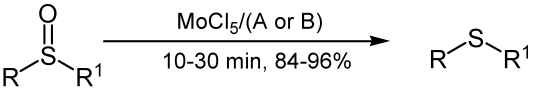
Table 10. Reduction of sulfoxides to sulfides with WCl_6 in the presence of NaI or Zn powder.

Entry	R	R^1	(A or B)[a]/ time (min)	Subst./WCl_6/ reducing agent	Yield (%)[b]
1	*p*-Me−C_6H_4	*p*-Me−C_6H_4	A (30)	1:0.8:4	91
			B (10)	1:0.8:3	95
2	*p*-NO_2−C_6H_4	Ph	A (15)	1:0.8:4	70
			B (5)	1:0.8:3	60
3	Ph	*n*-Bu	A (5)	1:0.5:3	94
			B (10)	1:0.8:1.5	89
4	Ph	*i*-C_3H_7	A (25)	1:0.5:3	89
			B (10)	1:0.8:3	85
5	Ph	$PhCH_2CH_2$	A (5)	1:0.5:3	90
			B (10)	1:0.8:1.5	87
6	Me	Me	A (5)	1:0.5:3	>98[c]
			B (5)	1:0.8:1.5	>98[c]
7	$PhCH_2$	$PhCH_2$	A (10)	1:0.5:3	92
			B (5)	1:0.8:1.5	85
8	Ph	CH_2CHCH_2	A (10)	1:0.5:3	80
			B (10)	1:0.8:1.5	82

[a]A = WCl_6/NaI/MeCN, B = WCl_6/Zn/THF.
[b]Isolated yield.
[c]GC yields.

5.7. *Reduction of sulfoxides with titanium tetrachloride/sodium iodide system* (149)

Dialkyl, diaryl, and alkyl aryl sulfoxides were rapidly deoxygenated to the corresponding sulfides in excellent yields with titanium (IV) chloride/sodium iodide at room temperature (Scheme 17, Table 12).



R, R^1= aryl or alkyl
A= Na I5 equiv., CH_3CN, rt
B=Zn, 3 equiv., THF, rt

Scheme 16.

Table 11. Reduction of sulfoxides to sulfides with $MoCl_5$ in the presence of NaI or Zn powder.

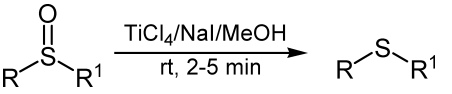
Entry	R	R^1	(A or B)[a]/time (min)	Yield (%)[b]
1	Ph	Ph	A (30)	95
			B (15)	95
2	*p*-Me−C_6H_4	*i*-C_3H_7	A (15)	84
			B (10)	85
3	Ph	CH_2CHCH_2	A (10)	85
			B (15)	85
4	Ph	*n*-Bu	A (12)	92
			B (10)	92
5	Ph	Me	A (10)	92
			B (10)	95
6	$PhCH_2$	Me	A (10)	94
			B (10)	90
7	$PhCH_2$	$PhCH_2$	A (10)	95
			B (10)	90
8	Ph	$PhCH_2$	A (20)	96
			B (10)	90
9	*n*-Bu	*n*-Bu	A (10)	85
			B (20)	89
10	Me	Me	A (10)	>98[c]
			B (15)	>98[c]

[a]A = $MoCl_5$/NaI/MeCN at rt and the molar ratio of subst./$MoCl_5$/reducing agent is 1:0.7:5; B = $MoCl_5$/Zn/THF at rt and the molar ratio of subst./$MoCl_5$/reducing agent is 1:1:3.
[b]Isolated yield.
[c]GC yields.

Table 12. Reduction of sulfoxides with titanium tetrachloride/NaI system in CH_3CN at room temperature.

Entry	R	R^1	Yield (%)[a]
1	*n*-Bu	*n*-Bu	92
2	$PhCH_2$	Me	90
3	$PhCH_2$	$PhCH_2$	95
4	Ph	$PhCH_2$	95
5	Ph	Me	94
6	Ph	Et	90
7	Ph	Ph	98

[a]Isolated yield.



Scheme 17.

Acetone is an acceptable solvent in some cases, but deoxygenation is slower in this medium due to the higher temperatures. Among the alkali halides tested, anhydrous sodium iodide appeared to be the most effective, although the use of potassium iodide also gave good results. In the first system, titanium (IV) chloride is probably reduced by the iodide anion to form a low-valent titanium complex. This, in the subsequent step, would deoxygenate the sulfoxide to form the sulfide.

5.8. *Reduction of sulfoxides with titanium tetrachloride/Sm system* (144)

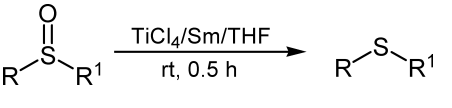
The $TiCl_4$/Sm system reduces sulfoxides rapidly to the corresponding sulfides in good yields in THF at room temperature. The reaction can be envisaged to proceed in two stages. First, $TiCl_4$ is reduced by samarium metal to form a low-valent titanium species, which in the subsequent step would deoxygenate the sulfoxide to form the corresponding sulfide (Scheme 18, Table 13).

5.9. *Reduction of sulfoxides with titanium tetrachloride/In system* (24)

The chemical reactivity of $TiCl_4$/M system (M=Te, Mg, Zn, Sm) has been the subject of considerable interest and the reducing ability of these systems has been extensively studied (*144, 150–154*). $TiCl_4$/In is an alternative to such systems which is generated by the addition of indium powder to a stirred solution of titanium tetrachloride in THF under nitrogen. $TiCl_4$/In can also be an efficient reducing agent for the conversion of sulfoxides to sulfides (Scheme 19).

This methodology is applicable to aromatic, aliphatic, and aralkyl sulfoxides (Table 14). The functional group tolerance of this method is evident in that bromo, methoxy, aldehyde, and vinyl are unaffected under the reaction conditions.

Although the role of $TiCl_4$ is still not clear, it is assumed that the reduction of titanium (IV) with indium provides a low-valent titanium species (*155*), which may act as a reducing system for the conversion of sulfoxides to their corresponding sulfides. The utility of this system is also

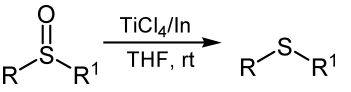


Scheme 18.

Table 13. Reduction of sulfoxides to sulfides with $TiCl_4$/Sm.

Entry	R	R^1	Yield (%)[a]
1	Ph	Ph	75
2	4-Cl−C_6H_4	4-Cl−C_6H_4	81
3	Ph	$PhCH_2$	80
4	$PhCH_2$	$PhCH_2$	78
5	Ph	Me	87
6	Ph	*n*-Bu	84

[a]Isolated yield.



Scheme 19.

Table 14. Reduction of sulfoxides to sulfides with $TiCl_4/In$[a].

Entry	R	R^1	Yield (%)[b]
1	Ph	Ph	91
2	Ph	Me	93
3	4-Br−C_6H_4	Me	93
4	4-MeO−C_6H_4	4-MeO−C_6H_4	95
5	4-MeO−C_6H_4	Me	91
6	Ph	$CHCH_2$	84
7	4-Me−C_6H_4	Me	95
8	Ph	CH_2CH_3	87
9	$PhCH_2$	$PhCH_2$	89
10	$PhCH_2$	Ph	93
11	*n*-Bu	*n*-Bu	85

[a]Molar ratio of sulfoxide:$TiCl_4$:In is 1:1:0.5; the reaction time is 10 min.
[b]Isolated yield.

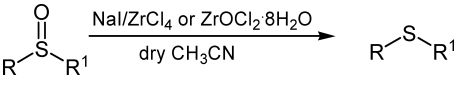
demonstrated by the high yields of dibenzyl sulfide and phenyl benzyl sulfide obtained after the reduction of the corresponding sulfoxides. Usually the reduction of sulfoxides which contain a benzyl group is a difficult task as evident by the use of other methods (*156, 157*).

5.10. *Reduction of sulfoxides with $ZrCl_4$/NaI or $ZrOCl_2 \cdot 8H_2O$/NaI systems* (158)

Zirconium tetrachloride and $ZrOCl_2 \cdot 8H_2O$ are the two convenient compounds for the sulfoxide to sulfide transformation. The only reservation about the use of $ZrCl_4$ is its mild hygroscopicity requiring it to be kept under inert atmosphere, whereas $ZrOCl_2 \cdot 8H_2O$ is a highly stable compound and does not require special precautions. Zirconium tetrachloride/sodium iodide ($ZrCl_4$/NaI) and $ZrOCl_2 \cdot 8H_2O$/NaI promote chemoselective reduction of sulfoxides to their thioethers in high yields (Scheme 20, Tables 15 and 16).

The novel feature of the $ZrCl_4$ systemis its excellent chemoselectivity. Selective reduction of sulfoxide group in the presence of $-NO_2$, −CHO, and −CN functional groups is worthy of mention. Inspection of the previously reported procedures such as WCl_6/NaI (*146*) and $NaBH_4/I_2$ (*18*) shows that in addition to the reduction of sulfoxide, the nitro group has also been effectively reduced to a mixture of amino and nitroso compounds.

A mechanism is proposed in which the plausible role of Zr (IV) compounds in the reaction mixture has been clarified (Scheme 21).



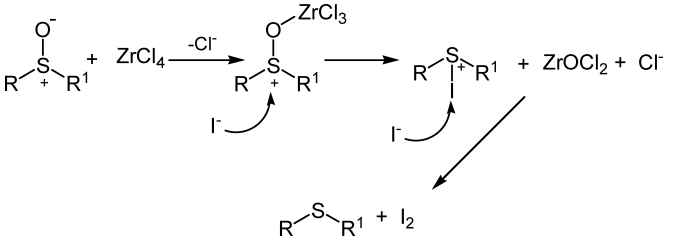
Scheme 20.

Table 15. Reduction of sulfoxides to sulfides with $ZrCl_4$/NaI systems in anhydrous CH_3CN.

Entry	R	R^1	Molar ratio of subst./$ZrCl_4$/NaI	Temperature (°C)	Time (min)	Isolated yield (%)
1	*n*-Bu	*n*-Bu	1:0.5:2	rt	<1	96
2	Ph	CH_2CHCH_2	1:0.5:2	rt	<1	96
3	Ph	*n*-Pr	1:0.5:2	rt	<1	96
4	$PhCH_2$	*n*-Pr	1:0.5:2	rt	<1	95
5	$PhCH_2$	$PhCH_2$	1:0.5:3	45	3	95
6	$PhCH_2$	Ph	1:0.5:4	45	15	95
7	Ph	$CH(CH_3)_2$	1:0.5:4	45	10	95
8	4-$MeOC_6H_4$	4-$MeOC_6H_4$	1:0.5:4	45	20	94
9	4-$O_2NC_6H_4$	4-MeC_6H_4	1:0.5:4	45	60	70
10	4-$OHCC_6H_4$	4-MeC_6H_4	1:0.5:4	45	40	84
11	3- NCC_6H_4	4-MeC_6H_4	1:0.5:4	45	60	80
12	2,4-$(NO_2)_2C_6H_3$	4-MeC_6H_4	1:0.5:4	45	24 h	Trace

Table 16. Reduction of sulfoxides to sulfides with $ZrOCl_2{\cdot}8H_2O$/NaI system in anhydrous CH_3CN.

Entry	R	R^1	Molar ratio of subst./$ZrCl_4$/NaI	Temperature (°C)	Time (min)	Isolated yield (%)
1	Ph	Me	1:1:2	rt	6	95
2	$PhCH_2$	$PhCH_2$	1:1:3	45	10	95
3	Ph	$CH(CH_3)_2$	1:1:4	45	55	84
4	4-$MeOC_6H_4$	4-$MeOC_6H_4$	1:1:4	45	100	86
5	4-$O_2NC_6H_4$	4-MeC_6H_4	1:1:4	45	120	44



Scheme 21.

5.11. *Deoxygenation of sulfoxides with SmI_2–THF–HMPA* (159)

A variety of sulfoxides were rapidly deoxygenated at room temperature using a stoichiometric amount of SmI_2 in tetrahydrofuran–hexamethylphosphoric triamide (Table 17).

Table 17. Reduction of Sulfoxides by SmI_2-THF-HMPA.

Entry	R	R^1	Temperature (°C)	Time (min)	Yield (%)[a]
1	Ph	Ph	20	1	94
2	Ph	Me	20	1	93
3	*n*-Bu	*n*-Bu	20	1	99
4	$Ph_2S(=O)_2$		20	1	93
5	$PhS(=O)_2Me$		20	10	99
6	$Bu_2S(=O)_2$		65	65	26

[a]Isolated yield.

The addition of HMPA markedly accelerates the electron transfer reaction of SmI_2 (*160–163*).

It is noteworthy that aromatic sulfides can be protected in the form of sulfones, because deoxygenation of the latter rapidly regenerated the original sulfides under extremely mild conditions. Esters remained intact under the present conditions and, in some cases, sulfoxides were selectively reduced in the presence of ketones.

5.12. *Reduction of sulfoxides with titanium tetraiodide* (15)

Chemoselective deoxygenation of sulfoxides was carried out using TiI_4 as a reducing reagent to give sulfides in good-to-excellent yields (Scheme 22, Table 18).

The sulfoxides possessing β-keto and β-methoxycarbonyl units were chemoselectively reduced to the corresponding sulfides in excellent yields without affecting the carbonyl functionalities. Amide, hydroxyl, and acetylene functionalities remained intact under the reduction conditions, and the sulfides were obtained in excellent yields.

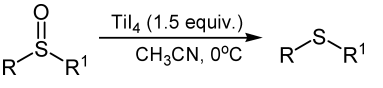
The pathway of the reaction is presented in Scheme 23 in which TiI_4 is coordinated to the oxygen atom of sulfoxides.

The coordination of TiI_4 facilitates the attack in one of the iodine ligands. The resultant iodinated species is in turn attacked by another iodide anion to give the oxygenated sulfide and concomitantly I_2.

5.13. *Reduction of sulfoxides with Cp_2TiCl_2/Al system* (164)

Sulfoxides can be deoxygenated by a low-valent Cp_2TiCl_2/Al system and form the corresponding sulfoxides under neutral and mild conditions (Scheme 24).

When the sulfoxide is added to the THF solution containing Cp_2TiCl_2 and Al powder, the reaction mixture becomes red immediately and the red solid is precipitated. In this reaction, the

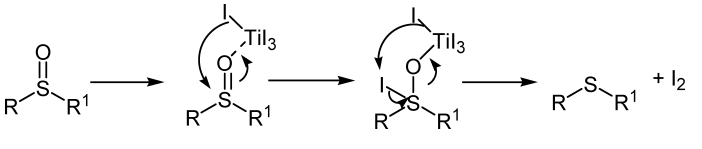


Scheme 22.

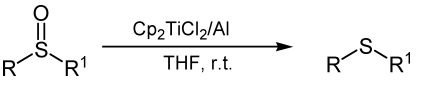
Table 18. Reduction of sulfoxides to sulfides with TiI_4.

Entry	R	R^1	Yield (%)[a]
1	*p*-Tol	*p*-Tol	93
2	$PhCH_2$	$PhCH_2$	85
3	*n*-$CH_3(CH_2)_5$	*n*-$CH_3(CH_2)_5$	85
4	Ph	*n*-$CH_3(CH_2)_7$	91
5	Ph	$PhCH_2$	94
6	*p*-Tol	Me	93
7	*n*-$CH_3(CH_2)_7$	*i*-Pr	86

[a]Isolated yield.



Scheme 23.



Scheme 24.

S−O bond in sulfoxide is cleaved and the oxygen atom is transferred to Cp_2TiCl_2 to generate the stable +4 valent titanium complex, accompanied by the formation of sulfide. Compared with the Cp_2TiCl_2/*i*-PrMgBr system, the Cp_2TiCl_2/Al system reduces sulfoxides more smoothly and the yields are much higher. This may be due to the supression of sulfonium salt formation arising from the side reaction of *i*-PrMgBr with sulfoxide.

5.14. *Reduction of sulfoxides with Cp_2TiCl_2/Sm system* (145)

Cp_2TiCl_2/Sm is an effective reducing system for deoxygenation of sulfoxides in THF at 70 °C (Scheme 25). As the reaction proceeds, Sm powder disappears and the red color of the solution of Cp_2TiCl_2–THF changes to a blue color. This is believed to be a new kind of samarium–titanium multi-nuclear complex formed $[(Cp_2TiCl)_2SmCl_2]$ in the reaction medium. This complex then acts as an effective reducing agent.

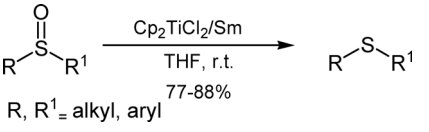
In comparison with the Cp_2TiCl_2/Al system, the Cp_2TiCl_2/Sm system reduces sulfoxides more smoothly with higher yields. This may be due to the synergistic action of divalent samarium from the complex. Both Cp_2TiCl_2 and SmI_2 can activate organic substrates via electron transfer to afford free radicals.

5.15. *Reduction of sulfoxides with titanium (II) porphyrin complexes* (165)

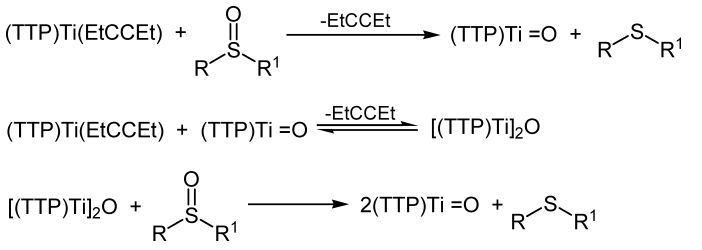
Oxygen atom transfer occurs when the Ti (II) porphyrins are treated with several different sulfoxides, resulting in two-electron redox products: (TTP)Ti=O, the sulfide, and EtCCEt or THF. The electronic properties of the substituents on the sulfoxides have a direct effect on the yield and the rate of the deoxygenation reactions.

For the deoxygenating reagents derived from low-valent transition metal compounds, the exact nature of the active reductants is poorly understood and the reaction is usually conducted under heterogeneous conditions, giving intractable metal oxo species. This observation, based on electronic effects, was corroborated by the reactions of (TTP)Ti(hapto2-EtCCEt) with various sulfoxides (R_2S=O), where R=Me, benzyl, and 4-tolyl which generate the corresponding sulfide and (TTP)Ti=O (Scheme 26). As the electron-withdrawing effect of R increases in the order of Me, benzyl, and 4-tolyl, the deoxygenation reaction of R_2S=O with (TTP)Ti(hapto2-EtCCEt) becomes faster and gives higher yields.

A mechanism is proposed for the oxygen-transfer reactions as presented in Scheme 26. The first two steps are rapid, but the third step involves oxidizing a Ti(III) complex and is slow.



Scheme 25.



Scheme 26.

5.16. *Reduction of sulfoxides with rhenium complex and triphenylphosphine* (166)

A mild and efficient method for the catalytic reduction of sulfoxides to sulfides with triphenylphosphine and $ReOCl_3(PPh_3)_2$ has been achieved. Aryl sulfoxides are reduced faster than alkylsulfoxide and the reaction is successful for sterically hindered sulfoxides as well as those with common organic functional groups (Table 19).

Increasing the phosphine concentration reduced the percent conversion of the reaction after 1 h reflux by a factor of 2. However, the percent conversion was increased by slowly adding a solution of PPh_3 to the refluxing reaction mixture of the sulfoxides and rhenium catalyst. The functional group tolerance of this method is evident in the table. Vinyl groups, primary alcohols, esters, and amides are unaffected by the reaction conditions. The facile reduction of the methionine-S-oxide derivative demonstrates the potential of this method for accomplishing this important deprotection step in peptide synthesis (*11*).

The half-lives for entries 1–5 at room temperature were measured by NMR in $CDCl_2$ and found to follow the order of reactivity shown in Scheme 27.

This order of reactivity is opposite to that observed for the high-temperature reduction of sulfoxides with PPh_3 (*42, 45*), or when activated by other reagent combinations (*46*).

A mechanism is proposed for this conversion as shown in Scheme 28.

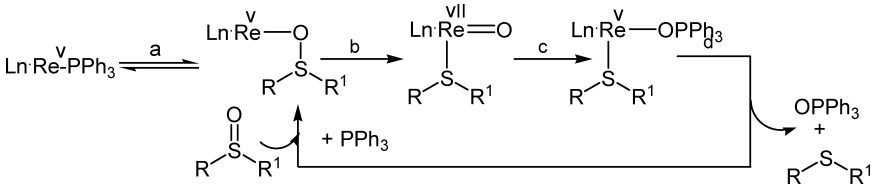
Table 19. Reduction of sulfoxides with rhenium complex and triphenylphosphine.

Entry	R	R^1	Reaction conditions[a]	Time (h)	Yield (%)[b]
1	Ph	Me	c	1	93
2	Ph	$CHCH_2$	c	1	96
3	Ph	Ph	c	1	95
4	Me	Me	c	22	95[d]
5	*t*-Bu	*t*-Bu	e	5	92[f]
			e	1	46[f]
			e,g	1	24[f]
			e,h	1	78[f]
6	Et	CH_2CH_2OH	e	5	84
7	Me	$CH_2CH_2CH(NHCOCH_3)CO_2Et$	e	5	96[i]

[a]Molar ratio of substrate:triphenylphosphine:Re complex = 1.0:0.9:0.05 unless noted otherwise.
[b]All yields are based on isolated sulfide purified by vacuum distillation (bulb to bulb) or silica gel chromatography using CH_2Cl_2 eluent.
[c]Reaction at ambient temperature.
[d]Isolated as the mercury (II) complex $[(CH_3)_2S]_2{\cdot}3HgCl_2$.
[e]Reaction mixture was heated to reflux.
[f]Percent conversion determined by ^1H NMR integration of the $[-C(CH_3)_3]$ singlets.
[g]Molar ratio of substrate:triphenylphosphine:Re complex = 1.0:1.9:0.05.
[h]Slow addition of a 0.12 M triphenylphosphine solution in CH_2Cl_2.
[i]Isolated as the carboxylic acid after saponification, aqueous extraction, and neutralization with 2 M HCl.

PhSOMe	$PhSOCHCH_2$	PhSOPh	CH_3SOCH_3	(t-Bu)SO(t-Bu)
$t_{1/2}$= 0.22 h	0.25 h	0.25 h	4 h	8 h

Scheme 27.



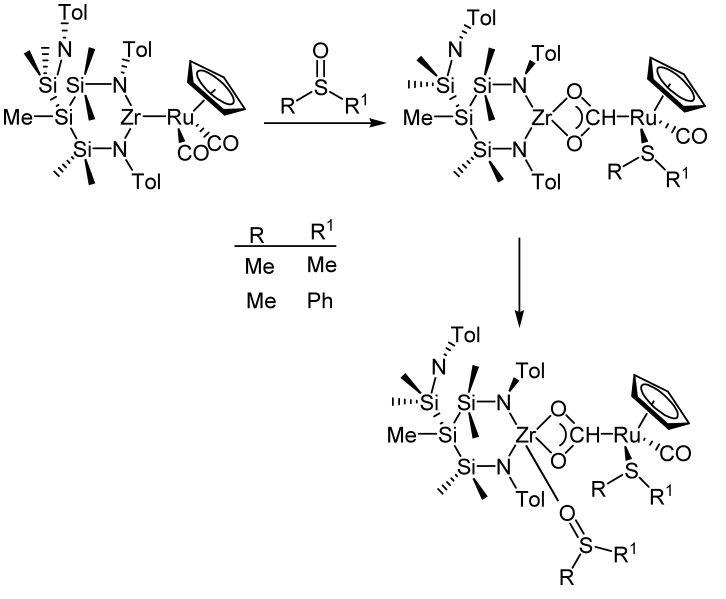
Scheme 28.

5.17. *Reduction of sulfoxides with Zr–Ru heterodimetallic complexes* (167)

Extremely rapid oxygen transfer from sulfoxides to a carbonyl ligand to give the corresponding thioether and coordinated CO_2 is observed in the reactions of Zr–Ru heterodimetallic complexes with sulfoxides. This is interpreted to arise from the cooperative reactivity of the two complementary metal complex fragments bound to each other through a highly polar metal–metal bond (Scheme 29).

6. Reduction of sulfoxides with $PhSiH_3$ or polymethylhydrosiloxane (PMHS)/molybdenum dioxo complex system (*168*)

MoO_2Cl_2, as a high-valent molybdenum-dioxo complex, is an effective catalyst for organic reductions (*169–171*). Deoxygenation of sulfoxides occurs in the presence of MoO_2Cl_2 and $MoO_2Cl_2(H_2O)_2$ in the presence of silane in organic and aqueous solvents. Methyl phenyl



R	R^1
Me	Me
Me	Ph

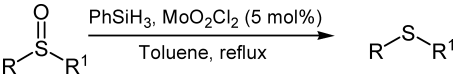
Scheme 29.

sulfoxide is completely reduced with phenylsilane ($PhSiH_3$) in the presence of 5 mol% of MoO_2Cl_2 in refluxing THF after 2 h (Scheme 30, Table 20).

This catalytic reaction is suitable for the deoxygenation of aromatic and aliphatic sulfoxides, in particular, for the reduction of benzyl sulfoxide. The catalytic activity of $MoO_2Cl_2(H_2O)_2$ was studied with the silanes $PhSiH_3$ and PMHS (polymethylhydrosiloxane) (Table 21).

The reaction of sulfoxides with polymethylhydrosiloxane (PMHS) in the presence of 5 mol% of $MoO_2Cl_2(H_2O)_2$, in refluxing methanol or at 80 °C in water, was carried out in air and produced the sulfides in excellent yields.

The system $PMHS/MoO_2Cl_2(H_2O)_2$ proved to be very efficient for the reduction of sulfoxides in organic solvents. The use of PMHS is more attractive than $PhSiH_3$ because it is easily handled, stable to air and water, inexpensive, and non-toxic. However, the reductions with PMHS required longer reaction times.



Scheme 30.

Table 20. Reduction of sulfoxide with the $PhSiH_3/MoO_2Cl_2$[a] system.

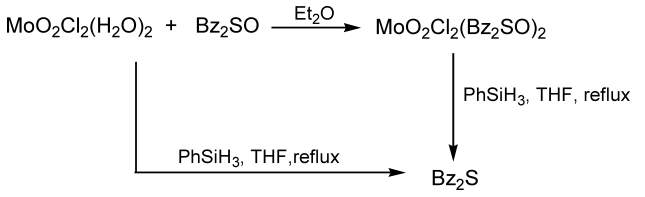
Entry	R	R^1	Time (h)	Yield (%)[b]
1	Ph	Me	2	97
2	Ph	Ph	2	97
3	$PhCH_2$	$PhCH_2$	20	96
4	*n*-Bu	*n*-Bu	7	92
5	4-ClC_6H_4	4-ClC_6H_4	2	96
6	Ph	CH_2COOCH_3	2.5	96
7	Ph	$CHCH_2$	2	92

[a]All reactions were carried out in refluxing THF with 1.0 mmol of sulfoxide, 1.0 mmol of $PhSiH_3$, using 5 mol% of MoO_2Cl_2.
[b]Isolated Yield.

Table 21. Reduction of sulfoxides by $PhSiH_3$ catalyzed with $MoO_2Cl_2(H_2O)_2$[a].

Entry	R	R^1	Silane	Solvent[b]	Time (h)	Yield (%)[c]
1	Ph	Me	$PhSiH_3$	THF	1.5	95
2			PMHS	Methanol	2	95
3			PMHS	H_2O[d]	20	52
4	Ph	Ph	$PhSiH_3$	THF	2	96
5			PMHS	Methanol	20	96
6			PMHS	H_2O[d]	20	92
7	$PhCH_2$	$PhCH_2$	$PhSiH_3$	THF	20	95
8			PMHS	Methanol	20	95
9	4-ClC_6H_4	4-ClC_6H_4	PHMS	Methanol	20	95
10			PHMS	H_2O[d]	20	50
11	Ph	CH_2COOCH_3	PHMS	Methanol	20	90

[a]All reactions were carried out with 1.0 mmol of sulfoxide, 100 mol% of $PhSiH_3$, or 0.3 mol% of PMHS, using 5 mol% of $MoO_2Cl_2(H_2O)_2$.
[b]Reflux temperature.
[c]Isolated yield.
[d]The reaction was carried out at 80 °C.



Scheme 31.

In the reaction of the complex $MoO_2Cl_2(Bz_2SO)_2$, prepared by the addition of benzyl sulfoxide to the ether solution of $MoO_2Cl_2(H_2O)_2$ (*136*) with 1 equiv. of the phenylsilane in refluxing THF, was observed the reduction of the sulfoxide, giving the corresponding benzyl sulfide (Scheme 31). A similar result was obtained when the benzyl sulfoxide was reduced with the system $PhSiH_3/MoO_2Cl_2(H_2O)_2$. This result suggests the initial activation of the sulfoxide by the oxygen coordination to the molybdenum, yielding the complex $MoO_2Cl_2(sulfoxide)_2$. This complex weakens the S−O bond and renders the sulfur atom more susceptible to the reduction. After the addition of the silane, the complex $MoO_2Cl_2(sulfoxide)_2$is reduced with the elimination of the sulfide and a siloxane.

7. Reduction of sulfoxides with other reagents

7.1. *Reduction of sulfoxides with silica chloride* (172)

Deoxygenation of sulfoxides to sulfides has been achieved in a simple procedure using silica chloride. Silica chloride is obtained from reaction of silica gel and thionyl chloride (*173*). A comparison of the results presented with that reported earlier clearly indicates that chlorinated silica is a more effective reagent for deoxygenation of sulfoxides (Table 22).

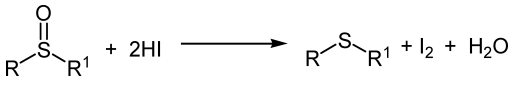
7.2. *Reduction of sulfoxides with iodide/organic acid system in the solid state* (13)

Sulfonic acid–sodium iodide system in liquid phase has been reported in the literature to reduce the sulfoxides to sulfides efficiently (*174*). Furthermore, a novel solid-state reduction of sulfoxides including methionine sulfoxides to the corresponding sulfide by iodide/organic acid system has also been described (Table 23) (*13*). The reduction of methionine sulfoxides, as a protector to S-alkylation, to methionine at the final stage of peptide synthesis and the removal of residual sulfoxides moiety in synthetic applications of optically active sulfoxides have required easy and

Table 22. Reduction of sulfoxides with silica chloride.

Entry	R	R^1	Time (min)[a]	Yield (%)[b]
1	Me	Me	10	90[c]
2	*t*-Bu	*t*-Bu	10	67
3	*s*-Bu	*s*-Bu	10	71
4	Ph	Ph	3	81
5	$PhCH_2$	$PhCH_2$	10	90
6	*n*-Bu	*n*-Bu	10	75

[a]The course of reaction was checked by TLC and GC.
[b]Yield of isolated pure product.
[c]The product was methyl chloromethyl sulfide.



Scheme 32.

Table 23. Reduction of sulfoxides with iodide/organic acid system in the solid state.

Entry	R	R^1	Acid iodide	Time (h)[a]	Isolated yield (%)[b]
1	*n*-Bu	*n*-Bu	T,KI	0.25	73
2	*n*-Bu	*n*-Bu	T,NaI	0.5	73
3	$PhCH_2$	$PhCH_2$	Cl,KI	5.0	77
4	$PhCH_2$	$PhCH_2$	Cl,KI	5.0	67
5	Dibenzothiophene S-oxide		T,KI	4.0	100
6	Dibenzothiophene S-oxide		Cl,KI	96.0	100
7	Ph	Me	T,KI	4.0	97
8	Ph	Me	T,NaI	6.0	86
9	Ph	Ph	Cl,KI	52.0	85
10	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	T,KI	4.0	89
11	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	T,KI	30.0	100
12	4-ClC_6H_4	4-ClC_6H_4	T,KI	4.0	49
13	4-ClC_6H_4	4-ClC_6H_4	T,KI	8.5	91

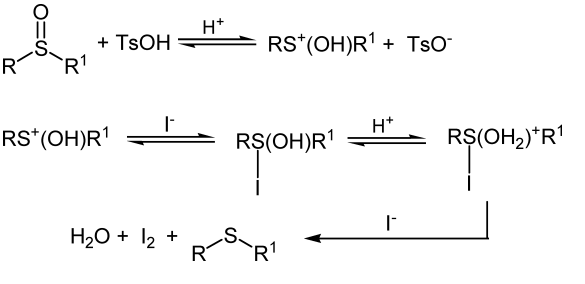
[a]One millimole of sulfoxide was used. The reaction temperature: 30 °C.
[b]Acid, Cl: trichloroacetic acid. T: *p*-toluenesulfonic acid monohydrate. The molar ratio of sulfoxide:acid:iodide=1:3:3.

simple operations. Numerous studies on the reduction of sulfoxides especially with iodide ion in solution have been performed due to its simplicity and effectiveness.

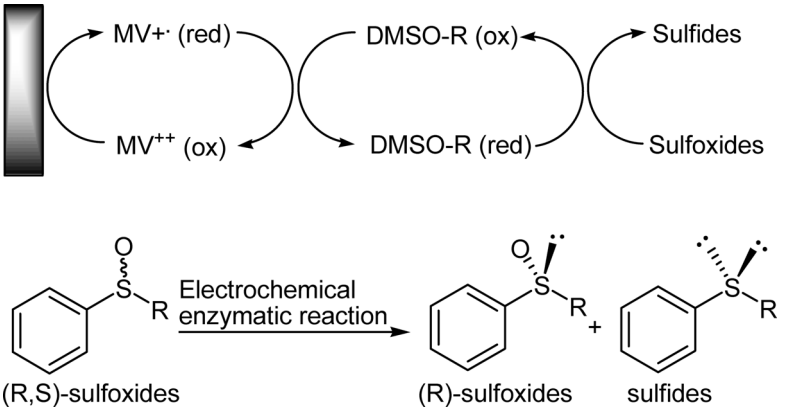
Generally, the reaction is described as presented in Scheme 32.

In the solid state, facile deoxygenation of wide classes of sulfoxides to sulfides in the presence of *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$) or trichloroacetic acid as catalysts in the presence of potassium or sodium iodide occurs efficiently.

Inspection of the data in Table 23 shows that TsOH was a more active catalyst than Cl_3CCOOH, most notably in the reduction of dibenzothiophene S-oxide and diphenyl sulfoxides. This indicates that hydrogen iodide, which can be formed *in situ* from iodide ion and an acid, is ineffective as a reducing agent; therefore, the reaction begins undoubtedly by the protonation of the sulfinyl oxygen followed by the formation of sulfurane intermediate by nucleophilic addition of iodide anion. Subsequently, the adduct is converted by further protonation into the corresponding sulforane, which is decomposed by iodide anion to give the final product (Scheme 33).



Scheme 33.



Scheme 34.

7.3. *Reduction of sulfoxides with DMSO reductase* (16)

Preparation of enantiomerically enriched sulfoxides by an electrochemical enzymatic system utilizing DMSO reductase was studied. This system consists of a glassy carbon electrode as the working electrode, methyl viologen as the mediator, and DMSO reductase from *Rhodobacter sphaeroides* f. sp. *denitrificans* as the catalyst. The (*R*)-enantiomers of chiral sulfoxides in the presence of a variety of functional groups were obtained with high e.e. (>97%) by this system.

However, the microbial preparation of chiral sulfoxides in the presence of a variety of functional groups, which are useful for C−C chain elongation and synthetic modification, resulted in low yield because of the undesirable side reactions.

DMSO-R is the terminal electron acceptor in DMSO respiration (*175*) and catalyzes the deoxygenation of DMSO to dimethyl sulfide. *In vitro*, DMSO-R can accept electrons directly from artificial electron donors such as viologen dyes in the presence of a chemical reductant (sodium dithionite) (*176*). In this study, the system involving a glassy carbon (GC) electrode as an electron donor instead of the chemical reductant was constructed as shown in Scheme 34.

The radical cation of methyl viologen [MV(red)] carries electron to oxidized DMSO-R and then reduced DMSO-R catalyzes the deoxygenation of sulfoxides to the corresponding sulfides. Because of its fast reaction rate, MV was selected as an electron carrier in this system.

As shown in Table 24, sulfoxides with a variety of functional groups were recovered with high e.e.s by this electrochemical enzymatic reaction system. These results show that this system reflects the high enantio- and chemoselectivity of DMSO-R. In the case of 2-phenylsulfinylethanol (Table 24, entry 6), which is a hydrophilic compound due to the hydroxyl and sulfoxide moieties, the recovery yield was improved by MOM (methoxymethyl ether) protection of the hydroxyl group (Table 24, entry 4). Sulfinyl esters (Table 24, entries 3 and 5) were recovered with 99% e.e. in moderate yields; however, the recovery was lower in order to obtain sulfoxides with e.e.s >99%.The concentrations of DMSO-R and the substrate in the reaction mixture were varied depending on the reaction rate of the substrate.

7.4. *Reduction of sulfoxides with 2,6-dihydroxypyridine* (6)

2,6-Dihydroxypyridine was found to be an efficient reagent in the deoxygenation of sulfoxides. The mild reaction conditions were compatible with functional groups such as ester and carbamate (Scheme 35).

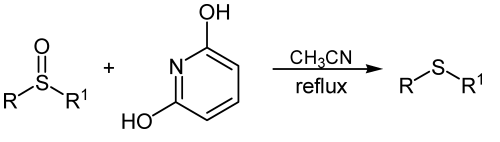
Table 24. Reduction of sulfoxides with DMSO reductase.

Entry	R	R^1	Substrate concentration (mM)	Reaction time (h)	Enzyme concentration (μM)	Recovery yield (%)[b]	e.e. (%)
1	Ph	$CHCH_2$	3.3	3	0.19	29	>99
2	*p*-Tol	Me	3.3	4	0.19	43	>99
3	Ph	CH_2CO_2t−Bu	3.3	4	0.38	38	99
			3.3	5	0.38	31	>99
4	Ph	$(CH_2)_2$−OMOM	3.3	6	0.38	44	>99
5	Ph	CH_2CO_2Me	3.3	4	0.38	40	99
			3.3	6	0.38	37	>99
6	Ph	$(CH_2)_2OH$	3.3	5	0.38	31	92
			3.3	8	0.38	26	>99
7	Ph	CH_2COCH_3	2.2	6	0.38	44	96
			2.2	5	0.76	40	97

Table 25. Reduction of sulfoxides with 2,6-dihydroxypyridine.

Entry	R	R^1	Time (h)	Yield (%)[b]
1	$PhCH_2$	$PhCH_2$	4	98
2	*n*-Bu	*n*-Bu	5	98
3	$-CH_2CH_2CH_2CH_2-$		2	66[a]
4	Ph	Ph	14	24(96)[a,b]
5	Me	$(CH_2)_2CH(NHCbz)(CO_2Me)$	3	90

[a]Yields determined by gas chromatography.
[b]Yield obtained with tetramethylene sulfone (2.0 g) as solvent shown in parenthesis.



Scheme 35.

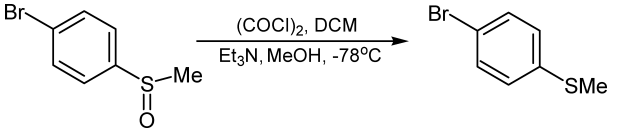
The percent yields shown in Table 25 are from reactions using 0.5 equivalents of 2, 6-dihydroxypyridine. From experiments to determine the stoichiometry of the reaction, it is found that 2,6-dihydroxypyridine could reduce approximately 4 equivalents of sulfoxide. The reaction is compatible with protective functional groups such as those examined with the methionine derivative in Table 25. Under the reaction conditions described, diphenyl sulfoxide gave relatively low yields; however, the use of tetramethylene sulfones as solvent dramatically improved the yield. On the other hand, since tetramethylene sulfones have a high-boiling point and are often difficult to remove from the reaction mixture, it is not a convenient solvent. Not surprisingly, sulfones are not reduced by 2,6-dihydroxypyridine, as seen with many other reducing agents for sulfoxides.

7.5. *Reduction of sulfoxides with $(COCl)_2$, MeOH, Et_3N and dimethyl amino pyridine (DMAP)* (177)

Treatment of 1-bromo-4-(methylsulfinyl)benzene with oxalyl chloride (1 equiv) at −78 °C for 1 h followed by the addition of methanol (1.4 equiv) and then after a further 1 h triethylamine (2 equiv) led to only a small conversion of 1-bromo-4-(methylsulfinyl)benzene (12%) into the relevant (4-bromophenyl)(methyl)sulfane (Scheme 36). As expected, increasing the excess of reagents

resulted in additional amounts of (4-bromophenyl)(methyl)sulfane being generated (Table 26). However, subsequent attempts to improve the yield of (4-bromophenyl)(methyl)sulfane by further increasing the amounts of reagents (Table 26, entry 3) or by inclusion of 2% of DMAP led to little improvement.

In accordance with the mechanism presented in Scheme 37 only sulfoxides containing α-hydrogen atom(s) would be amenable to the aforementioned protocol. Thus, attempts to deoxygenate a sulfoxide not bearing an α-hydrogen such as diphenyl sulfoxide resulted in recovery of unreacted starting material. However, a number of commercially available sulfoxides bearing an α-hydrogen atom could be deoxygenated in high yield (Table 26).

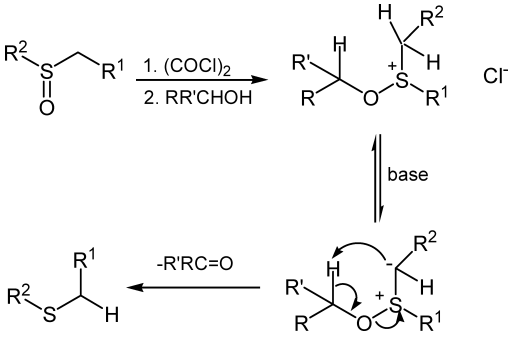


Scheme 36.

Table 26. Reduction of sulfoxides with $(COCl)_2$, MeOH, Et_3N and DMAP.[a]

Entry	R	R^1	GC retention times[b] (min) Sulfoxide/ sulfide	GC	Conversion NMR[c]
1	4-BrC_6H_4	Me	30.21/25.70	100	100
2	4-BrC_6H_4	Me	30.21/25.70	100[d]	100
3	Ph	Me	25.25/19.84	99	100
4	4-$CH_3C_6H_4$	Me	27.70/21.80	100	100
5	$PhCH_2$	Ph	38.26/33.56	[e]	86
6	$-CH_2CH_2CH_2-$		22.76/10.50	99	100
7	*n*-Bu	*n*-Bu	26.30/19.42	[e]	88

[a]Deoxygenation carried out in THF following the standard protocol unless specified otherwise.
[b]GC analysis of the crude reaction mixtures before work-up was performed on a gas chromatograph Perkin-Elmer 8500, 30M BPX5 0.32 mm I.D. wide bore capillary column; oven conditions: initial 50 °C hold for 8 min, ramp 8 °C/min, final 250 °C hold for 12 min.
[c]^1H NMR (400 MHz, $CDCl_3$ or C_6D_6).
[d]Reaction carried out in CH_2Cl_2.
[e]Impossible to estimate due to co-elution of interfering peaks.



Scheme 37.

Part II. Reductive coupling of sulfonyl derivatives to their disulfides

8. Reductive coupling of sulfonyl derivatives with iodide in the presence of boron halides (*178*)

In the absence of n-donor solvents, boron halides are particularly potent Lewis acids. In weakly or non-coordinating solvents (dichloromethane, chloroform, 1,2-dichloroethane), sulfonyl chlorides, sulfonyl bromides, sulfonic acid salts and esters are rapidly reduced by iodide at room temperature in the presence of BBr_3 or BI_3 to yield the corresponding symmetrical disulfides (Table 27).

With BCl_3, the reaction proceeds at a much slower rate; the reduction of sulfonyl halides being partially complete after 16 h at room temperature. With BF_3, sulfonyl chlorides are not reduced at room temperatures, but at 100 °C and under pressure, the reduction is clean and quantitative. In the presence of BBr_3 or BI_3, iodide reduces sulfonyl fluorides, sulfonic acids, and sulfonic acid salts and esters as well, although higher temperatures are required. These methods provide the first general method for the reduction of sulfonic acids and sulfonyl fluorides to disulfides. The reaction is equally applicable to both aliphatic and aromatic sulfonic acids although α-toluenesulfonic acid yields only benzyl bromide and benzyl iodide due to the facile cleavage of the C−S bond in the substrates.

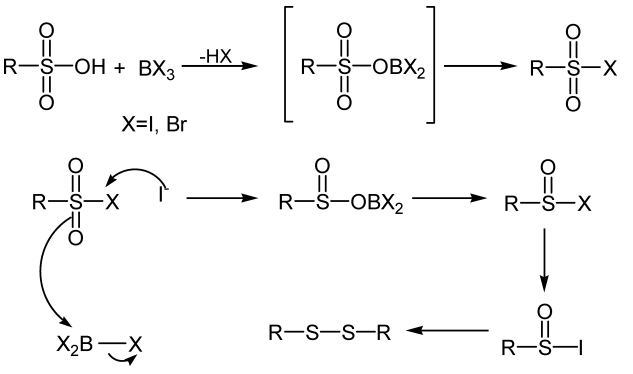
The reaction with sulfonic acids probably proceeds via initial formation of a sulfonyl bromide or iodide as presented by Scheme 38.

9. Reductive coupling of sulfonyl halides with sodium cyanoborohydride (*179*)

The increasing utilization of sodium cyanoborohydride to specific synthetic problems coupled with its selectivity and stability in acidic media (*180–183*), made this reducing agent a reagent of choice for the reductive coupling of sulfonyl chlorides to disulfides (Scheme 39).

Table 27. Reductive coupling of aryl sulfonyl derivatives with iodide in the presence of boron halides.

Entry	R	Reagent	Yield (%)
1	$C_6H_5SO_2Cl$	BI_3	88
		BBr_3/KI/TBAI	93
2	*p*-$CH_3C_6H_4SO_2Cl$	BI_3	88
		BBr_3/KI/TBAI	90
3	*p*-$BrC_6H_4SO_2Cl$	BI_3	88
		BBr_3/KI/TBAI	97
			90
4	*p*-$ClC_6H_4SO_2Cl$	BI_3	98
		BBr_3/KI/TBAI	89
		BCl_3/KI/TBAI	30
		BF_3/KI/TBAI	95
5	*p*-$CH_3C_6H_4SO_2F$	BI_3	98
		BBr_3/KI/TBAI	98
6	*p*-$CH_3C_6H_4SO_2OCH_3$	BBr_3/KI/TBAI	93
7	*p*-$CH_3C_6H_4SO_3H$	BI_3	97
		BBr_3/KI/TBAI	96
8	*p*-$CH_3C_6H_4SO_3H{\cdot}H_2O$	BBr_3/KI/TBAI	96
9	*o*-$CH_3C_6H_4SO_3H$	BBr_3/KI/TBAI	86
10	$C_6H_5SO_3H{\cdot}H_2O$	BBr_3/KI/TBAI	79
11	*p*-$CH_3C_6H_4SO_3Ag$	BBr_3/KI/TBAI	96
12	*n*-$C_4H_9SO_3H{\cdot}H_2O$	BBr_3/KI/TBAI	64
13	*n*-$C_3H_7SO_3H{\cdot}H_2O$	BBr_3/KI/TBAI	71



Scheme 38.

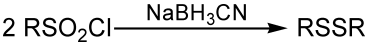
This successful reduction is to be contrasted to the reduction with lithium aluminum hydride (*184*) or sodium borohydride (*185*), which gives thiols or sulfinic acids at lower temperatures.

Most reductions of sulfonyl chlorides with $NaBH_3CN$ can be performed in refluxing dioxane; in some cases, hexamethylphosphoramide (HMPA) was the solvent of choice (Table 28), even though the formation of some *N*, *N*-dimethylsulfonamide (resulting from the decomposition of HMPA by the sulfonyl chlorides) could not be avoided.

Aromatic disulfides were obtained in satisfactory yields, while benzylsulfonyl chloride was reduced in only 45% yield. Trialkylamine-trichlorosilane system (*186*) or $Mo(CO)_6$ in tetramethylurea (*187*) are known to reduce sulfonyl chlorides to the symmetric disulfides. However, the chemoselectivity, the stability of sodium cyanoborohydride, as well as the simple experimental procedure, makes this protocol a highly practical method for reductive coupling of sulfonyl chlorides in comparison with the reported procedures.

10. Reductive coupling of sulfonyl, sulfenyl and sulfinyl derivatives with silicon containing compounds

A variety of silicon derivatives have seen widespread and growing use in the past few years (*164–191*) as protective groups and synthetic mediators. For instance, it is well known (*191, 192*) that



Scheme 39.

Table 28. Reductive coupling of sulfonyl chlorides with sodium cyanoborohydride[a].

Entry	R	Solvent	Time (h)	Yield (%)
1	Benzene-	dioxane	15	78
2	4-Bromobenzene-	dioxane	15	84
3	4-Chlorobenzene-	dioxane	15	76
4	4-Methylbenzene-	dioxane	22	68
5	4-Methoxybenzene-	HMPA	6	60
6	3-Nitrobenzene-	dioxane	15	72
7	2,5-Dimethylbenzene-	HMPA	6	62
8	2-Naphthalene-	HMPA	6	82
9	Benzyl-	dioxane	25	45

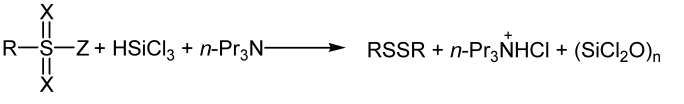
[a]The sulfonyl chloride: $NaBH_3CN$ mole ratio was 1:4 in every case. The use of lower ratios gave poor conversion. The yields are isolated ones based on the sulfonyl chlorides.

acid chlorides react smoothly with alkoxysilanes to produce esters in good yield. Heteroatom analogues of this reaction could be of great utility; however, incomplete synthetic information and virtually no detailed mechanistic data are available for this reaction class (*191, 193, 194*), which in principle encompasses an impressive number of important functionalities.

10.1. *Reductive coupling of sulfenyl, sulfinyl, and sulfonyl derivatives with trichlorosilane in the presence of tri-n-propylamine* (186)

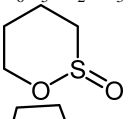
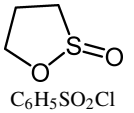
Symmetrical disulfides can be obtained from the reduction of the corresponding sulfenyl, sulfinyl, and sulfonyl chlorides as well as sulfenate and sulfinate esters with the tri-n-propylamine-trichlorosilane system (*n*-PrN-$HSiCl_3$) as presented by Scheme 40 and the reported results in Table 29.

In the cases of two cyclic sulfinate esters (1,2-oxathiolane 2-oxide and 1,2-oxathiane 2-oxide) with *n*-PrN-$HSiCl_3$ the rupture of the heterocycle occurred along with reduction of the sulfinyl oxygen to give the symmetrical hydroxyl disulfides (Scheme 41). It is noteworthy to mention that the reaction does not occur without the addition of the tertiary amine.

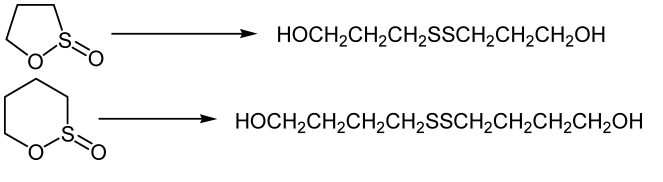


Scheme 40.

Table 29. Reductive coupling of sulfenyl, sulfinyl, and sulfonyl derivatives with trichlorosilane and tri-*n*-propylamine.

Entry	Compound	Time, h (T,°C)	Yield (%)[a,b]
1	C_6H_5SCl	4(20)	53
2	$C_6H_5SOCH_3$	4(20)	88
3	*p*-$CH_3C_6H_4SO_3Cl$	5(20)	91
4	$C_6H_5SO_2CH_3$	4(20)	85
5		4(20)	60
6		4(20)	80
7	$C_6H_5SO_2Cl$	20(20)	67
		6(80)	85
8	$C_6H_5SO_2OCH_3$	15(20)	a,c
		70(80)	

[a]Sulfonate esters (X=Y=O; Z=OR') do not react.
[b]All reactions were carried out in benzene solution.
[c]Starting material recovered.



Scheme 41.

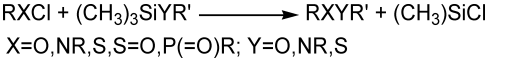
10.2. *Reductive coupling of sulfenyl, sulfinyl, and sulfonyl derivatives with alkoxytrimethylsilane* (195)

Alkoxytrimethylsilane and sulfinyl chlorides have been shown to couple efficiently to afford sulfinate esters; kinetic data indicate that a non-ionic transition state is involved. The parallel reaction between aralkylthiotrimethylsilanes and sulfenyl chlorides gives unsymmetrical disulfides. An attempt to prepare sulfenate esters by the reaction of a sulfenyl chloride and an alkoxytrimethylsilane gave no reaction; in fact, sulfenate esters were shown to be cleaved by either chlorotrimethylsilane or trimethylsilyl cyanide to yield sulfenyl chlorides or thiocyanates, respectively. The reaction of t-butyl hypochlorite with an alkylthiosilane gave disulfide (Scheme 42).

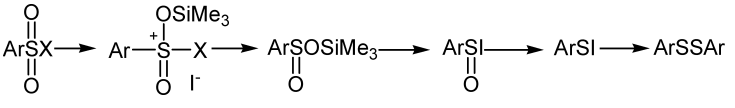
10.3. *Reductive coupling of sulfonyl halides with iodotrimethylsilane* (196)

Sulfonyl halides can be deoxygenated with iodotrimethylsilane to provide disulfides in high yield (Scheme 43).

Sulfinic acids, sulfinic acid salts, alkyl sulfinates, sulfinyl chlorides, and sulfenyl chlorides are all reduced rapidly under the reaction conditions to afford the symmetrical disulfides (Table 30).



Scheme 42.



Scheme 43.

Table 30. Reductive coupling of sulfonyl, sulfinyl, and sulfenyl derivatives to disulfides with iodotrimethylsilane[a].

Entry	Substrate	Yield (%) of disulfide
1	$CH_3CH_2SO_2Cl$	80[b]
2	$C_6H_5CH_2SO_2Cl$	98
3	$C_6H_5SO_2Cl$	100
4	*p*-$CH_3C_6H_4SO_2Br$	90
5	*p*-$BrC_6H_4SO_2Cl$	86
6	*p*-$CH_3C_6H_4SO_2Cl$[c]	79
7	*p*-$BrC_6H_4SO_2Cl$[d]	80
8	*p*-$ClC_6H_4SO_2Cl$	100
9	*p*-$FC_6H_4SO_2Cl$	90
10	*p*-FC_6H_4SOCl	96
11	*p*-FC_6H_4Cl	88
12	*p*-$CH_3C_6H_4SO_2Na$	75
13	*p*-$FC_6H_4SO_2Me$	89

[a]Isolated yield of reaction at 25°C for 16 h in methylene chloride.
[b]Reaction in 1,2-dichloromethane at reflux for 16 h.
[c]Me_3SiCl/NaI in acetonitrile.
[d]$Me_3SiSiMe_3/I_2$ in CH_2Cl_2.

10.4. *Reductive coupling of sulfonyl halides with iodine, chlorotrimethylsilane, and hexamethyldisiloxane* (197)

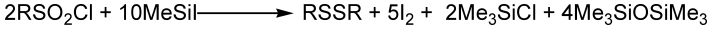
The reaction of sulfonyl chlorides and iodotrimethylsilane in methylene chloride solution proceeds smoothly at room temperature within minutes (in some cases, hours), giving the corresponding disulfide in high yields together with iodine, chlorotrimethylsilane, and hexamethyldisiloxane (Scheme 44).

The reduction of sulfonyl halides can also be carried out with chlorotrimethylsilane in an inert solvent (benzene, chloroform, methylene chloride) and a suspension of sodium iodide even in the absence of a phase transfer catalyst. In this case, however, the reaction requires a much longer time and a higher temperature especially for sterically hindered substrates (Table 31).

The reaction of sulfonyl halides with iodotrimethylsilane is most likely initiated by the formation of the oxonium salt, which can further react in three different pathways (a,b,c) as indicated by Scheme 45.

The relative contribution of each direction is strongly dependent on the nature of X in the sulfoxonium salt. When X=I, the attack of the iodide anion on the iodine atom should be fast, and 'path a' predominates. Additionally, the low electronegativity of iodine facilitates the formation of the sulfoxonium salt (X=I), which, in sum, results in an immediate disappearance of sulfonyl iodide. When X=Cl, the attack of iodide anion on the chlorine atom in the sulfoxonium (X=Cl) takes place more slowly.

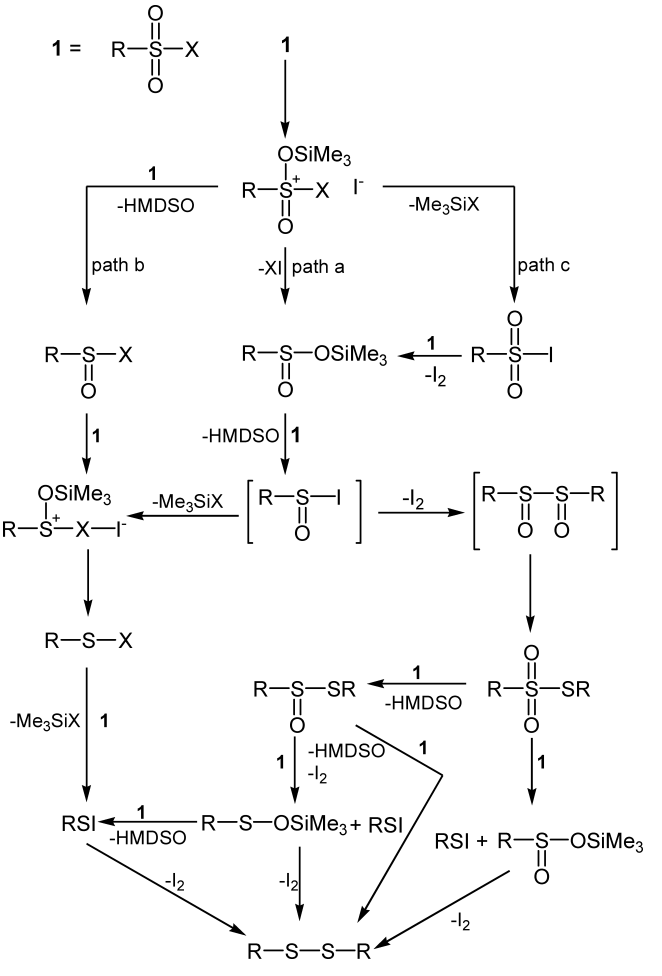
Therefore, it seems reasonable to assume that in this case the reduction may follow also 'path b or c'. At last, when X=F, the formation of the sulfoxonium salt (X=F) is much more difficult due to the high electronegativity of fluorine. This may be responsible for a significantly lower reduction rate as compared with sulfonyl chloride and iodide. Since the attack of iodide anion on the fluorine atom in the sulfoxonium salt (X=F; path a) as well as the fluorine–iodine exchange (path c) due to the higher sulfur–fluorine bond energy in comparison with other sulfur–halogen bonds (*198*) is less probable. It is believed that the fluorine–iodine exchange takes place only as a result of the reaction between sulfenyl fluoride (X=F) and **1** (Scheme 45). Therefore, no formation of thiosulfonate can be observed.



Scheme 44.

Table 31. Reduction of sulfonyl halides and related compounds with iodotrimthylsilane.

Entry	Reduced Compound	Disulfide, Yield (%)
1	$PhSO_2Cl$	94
2	p-$CH_3C_6H_4SO_2Cl$	95
3	o-$CH_3C_6H_4SO_2Cl$	95
4	2,4,6-$Me_3C_6H_2SO_2Cl$	80
5	2,4,6-i-$Pr_3C_6H_2SO_2Cl$	85
6	$PhSO_2I$	97
7	$PhSO_2F$	97
8	$PhSO_2SPh$	97.5
9	$PhSO_2SMe$	Mixture of disulfides
10	PhS(O)SPh	98
11	$CH_3S(O)SPh$	Mixture of disulfides
12	$PhSOCH_3$	96



Scheme 45.

11. Reductive coupling of sulfonyl chlorides with metal containing systems

11.1. *Reductive coupling of sulfonyl chlorides with aluminum iodide* (199)

Aluminum iodide as a strong Lewis acid reduces sulfonyl chlorides to disulfides and sulfoxides to sulfides under mild conditions in CH_3CN (Table 32).

11.2. *Reductive coupling of sulfonyl derivatives with piperidinium tetrathiotungstate* (200)

In an unusually novel reaction, piperidinium tetrathiotungstate has been found to induce reductive dimerization of a variety of sulfonyl derivatives to the corresponding disulfides under very mild conditions (Scheme 46, Table 33).

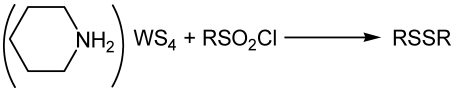
Aryl and alkyl sulfonyl chlorides react rapidly with 1 molar equiv. of piperidinium tetrathiotungstate at room temperature to afford the corresponding disulfide in good yield. It is interesting, however, to note that sulfoxides, sulfones, and sulfonic acids remain unaffected on treatment with piperidinium tetrathiotungstate even after a long reaction time. In terms of reactivity, alkyl sulfonyl chlorides react with piperidinium tetrathiotungstate slower than the aryl

sulfonyl chlorides. Although the thiosulfonate ester reacted very rapidly to give the corresponding disulfides, the disulfone took nearly 12 h to react with piperidinium tetrathiotungstate to give the corresponding disulfide. Hence, it is very unlikely that the α-disulfones are the intermediates in the overall transformation. The fact that thiosulfonate esters react almost instantaneously to give the corresponding disulfides suggest that in the conversion of sulfonyl chlorides to disulfides, thiosulfonate esters are more likely to be intermediates. Since sulfinyl chloride reacts faster than sulfonyl chloride, we believe the overall transformation probably goes through the pathway as indicated in Scheme 47.

Here, the sulfonyl chlorides were converted to the sulfinyl chlorides, which then undergo oxidative coupling to give α-disulfoxide. These α-disulfoxides are known to rearrange readily to the thiosulfonate ester, which undergo reduction to give disulfides.

Table 32. Reductive coupling of sulfonyl chlorides with aluminum iodide.

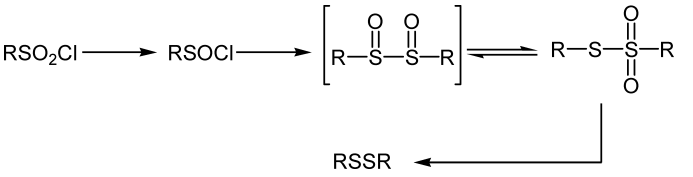
Entry	Substrate	Mole Proportion AlI_3:Substrate	Reaction conditions	Yield (%)
1	p-$CH_3C_6H_4SO_2Cl$	1:1	4 h (r.t.)	82
2	p-$CH_3C_6H_4SO_2Cl$	1:1	3 h (r.t.) 1 h (reflux)	90
3	p-$BrC_6H_4SO_2Cl$	1.4:1	5 h (r.t.) 1 h (reflux)	93
4	2-$C_{10}H_7SO_2Cl$	1.4:1	4 h (r.t.) 1 h (reflux)	95
5	$PhSO_2Cl$	1.4:1	4h (r.t.) 1 h (reflux)	94.5
6	$PhCH_2SO_2Cl$	1.4:1	4 h (r.t.) 45 min (reflux)	82
7	n-$C_4H_9SO_2Cl$	1.4:1	4 h (r.t.) 30 min (reflux)	81



Scheme 46.

Table 33. Reductive coupling of sulfonyl derivatives with piperidinium tetrathiotungstate.

Entry	Substrate	Time, h	Yield (%)
1	$C_6H_5SO_2Cl$	2.0	78
2	p-$CH_3C_6H_4SO_2Cl$	2.0	69
3	p-$BrC_6H_4SO_2Cl$	2.0	53
4	$PhCH_2SO_2Cl$	4.0	59
5	n-$C_4H_9SO_2Cl$	3.0	41
6	p-$CH_3C_6H_4SOCl$	0.5	96
7	p-$CH_3C_6H_4SO_2H$	0.5	98
8	p-$CH_3C_6H_4SO_2SO_2C_6H_4CH_3 - p$	12	88
9	p-$CH_3C_6H_4SO_2SC_6H_4CH_3 - p$	0.5	92
10	$C_6H_5SO_2SC_6H_5$	0.5	67
11	p-$CH_3C_6H_4SO_2SC_6H_5$	0.5	Mixture of disulfides
12	p-$CH_3C_6H_4SO_2SC_6H_5$	1.0	Mixture of disulfides
13	$C_6H_5SOC_6H_5$	24	No reaction
14	$C_6H_5SO_2C_6H_5$	24	No reaction
15	$C_6H_5SO_3H$	24	No reaction



Scheme 47.

In the case of reduction of thiosulfonates by piperidinium tetrathiotungstate one would anticipate the formation of unsymmetrical disulfides starting from thiosulfonate esters having different substituents at the sulfonyl and sulfenyl sulfur. However, in the reaction of thiosulfonate with piperidinium tetrathiotungstate, a mixture of unsymmetrical and both possible symmetric disulfides were always produced (*197, 201*). This could be due to the disproportionation of the unsymmetrical disulfide formed upon reduction or rather by cleavage of the S−S bond in thiosulfonate by piperidinium tetrathiotungstate initially and reformation of the bond later.

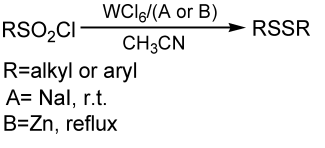
11.3. *Reductive coupling of sulfonyl chlorides with tungsten hexachloride in the presence of NaI or Zn powder* (146)

Reductive coupling of sulfonyl chlorides to their corresponding disulfides has been achieved in the presence of WCl_6/NaI system in anhydrous CH_3CN or zinc powder in anhydrous THF (Scheme 48, Table 34). Sodium benzene sulfinate, as a model compound for sulfinate salts, is also converted to diphenyl disulfide in almost quantitative yield.

The reaction of aryl and alkyl sulfonyl chlorides with WCl_6/NaI proceeds smoothly at room temperature in CH_3CN in excellent yields. WCl_6/Zn powder, even after 20 h, was not able to complete the reaction at room temperature. However, under reflux conditions, the expected disulfides were produced in excellent yields. The transformation of sulfinic acid salts to their disulfides is also of practical importance, and sodium benzene sulfinate was used as a model compound for this study. Both WCl_6/NaI and WCl_6/Zn systems were capable of producing diphenyl disulfide in almost quantitative yield. Deoxygenation of thiosulfonate esters to disulfides was also achieved in high yields using both reducing systems. Application of these methods for the deoxygenation of sulfonic acids, sulfonate esters, and sulfonic acid salts have not been successful so far.

11.4. *Reductive coupling of sulfonyl chlorides with molybdenum pentachloride in the presence of NaI or Zn powder* (147)

Sulfonyl chlorides can be readily reduced to their disulfides with $MoCl_5$/NaI in CH_3CN at room temperature or with $MoCl_5$/Zn powder in refluxing CH_3CN in high yields (Scheme 49, Table 35).

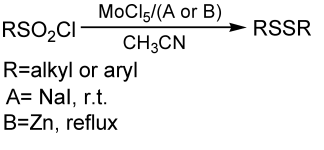


Scheme 48.

Table 34. Reductive coupling of sulfonyl chlorides with tungsten hexachloride.

Entry	Substrate	A or B/ time(min) or (h)	Subst./WCl_6/ reducing agent	Yield(%)[a]
1	$PhSO_2Cl$	A (16)	1:1.2:10	97
		B (20)	1:1.2:3	89
2	p-$CH_3C_6H_4SO_2Cl$	A (17)	1:1.2:10	94
		B (45)	1:1.5:4	88
3	p-$BrC_6H_4SO_2Cl$	A (14)	1:1.2:10	85
		B (40)	1:1.4:4	89
4	2-NaphthylSO_2Cl	A (16)	1:1.2:10	98
		B (80)	1:1.4:4	95
5	CH_3SO_2Cl	A (12)	1:1.2:10	90
		B (120)	1:1.2:3	85
6	$PhSO_2Na$	A (12)	1:1.2:10	95
		B (30)	1:1.4:4	92
7	$PhSO_2SPh$	A (1.5)	1:0.6:5	98
8	p-$CH_3C_6H_4SO_2SC_6H_4CH_3-p$	A (1.5)	1:0.6:5	95
9	p-$CH_3C_6H_4SO_3H$	A (24)	1:1.2:10	No reaction
		B (3)	1:1.4:4	No reaction
10	p-$CH_3C_6H_4SO_3Na$	A (24)	1:1.2:10	No reaction
		B (3)	1:1.4:4	No reaction
11	p-$CH_3C_6H_4SO_3Et$	A (24)	1:1.2:10	No reaction[b]
		B (24)	1:1.2:10	No reaction[b]

A: WCl_6/NaI/MeCN at r.t.
B: WCl_6/Zn/MeCN at reflux.
[a]Yields refer to isolated pure products unless otherwise stated.
[b]The cleavage of ester function was observed.



Scheme 49.

Sulfonyl chlorides, a sodium sulfinate and thiosulfonate esters are also reduced efficiently by $MoCl_5$/NaI $MoCl_5$/Zn/MeCN. Applying these methods for deoxygenation of sulfonic acid, sulfonate esters, and sulfonic acid salts was not successful. Reactions conducted in THF sometimes are accompanied with the formation of a low-molecular weight polymeric material that makes the reaction mixture rather viscous and isolation of the products a time-consuming process.

11.5. *Reductive coupling of sulfonyl chlorides with $ZrCl_4$ or $ZrOCl_2{\cdot}8H_2O$ in the presence of NaI* (158)

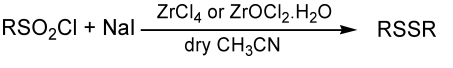
Zirconium tetrachloride/sodium iodide ($ZrCl_4$/NaI) and zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$/NaI) as expedient reagents achieve effective reductive coupling of sulfonyl chlorides to their corresponding disulfides under mild reaction conditions (Scheme 50, Table 36). Reductions conducted in the presence of $ZrOCl_2{\cdot}8H_2O$ require longer reaction times compared to $ZrCl_4$. Reductive coupling of p-toluene sulfonic acid was not successful using these reagents.

Mechanisms have been also proposed for the reaction as indicated by Scheme 51 using $ZrCl_4$/4NaI and $ZrOCl_2{\cdot}8H_2O$/4NaI systems:

Table 35. Reductive coupling of sulfonyl chlorides with molybdenum pentachloride.

Entry	Substrate	A or B/ time(min) or (h)	Subst./WCl_6/ reducing agent	Yield(%)[a]
1	$PhSO_2Cl$	A (12)	1:1.2:10	90
		B (10)	1:0.6:3	93
2	p-$CH_3C_6H_4SO_2Cl$	A (15)	1:1.2:10	85
		B (20)	1:0.8:3	92
3	p-$BrC_6H_4SO_2Cl$	A (11)	1:1.2:10	89
		B (25)	1:0.8:3	90
4	2-NaphthylSO_2Cl	A (10)	1:1.2:10	95
		B (30)	1:0.8:3	95
5	CH_3SO_2Cl	A (12)	1:1.2:10	87
		B (90)	1:0.8:3	81
6	$PhSO_2Na$	A (10)	1:1.2:10	95
		B (15)	1:0.5:3	90
7	$PhSO_2SPh$	A (1.5)	1:0.6:5	95
8	p-$CH_3C_6H_4SO_3H$	A (24)	1:1.2:10	No reaction
		B (180)	1:1.2:5	No reaction
10	p-$CH_3C_6H_4SO_3Na$	A (24)	1:1.2:10	No reaction
		B (180)	1:1.2:5	No reaction
11	p-$CH_3C_6H_4SO_3Et$	A (24)	1:1.2:10	No reaction
		B (180)	1:1.2:5	No reaction

A: $MoCl_5$/NaI/MeCN at r.t.
B: $MoCl_5$/Zn/MeCN at reflux.
[a]Yields refer to isolated pure products unless otherwise stated.



Scheme 50.

11.6. *Reductive coupling of sulfonyl chlorides with $TiCl_4$/Sm* (202)

$TiCl_4$/Sm system reduces sulfonyl chlorides and sodium arylsulfinates to their corresponding symmetric disulfides in moderate to good yields in THF at 60 °C (Scheme 52, Table 37).

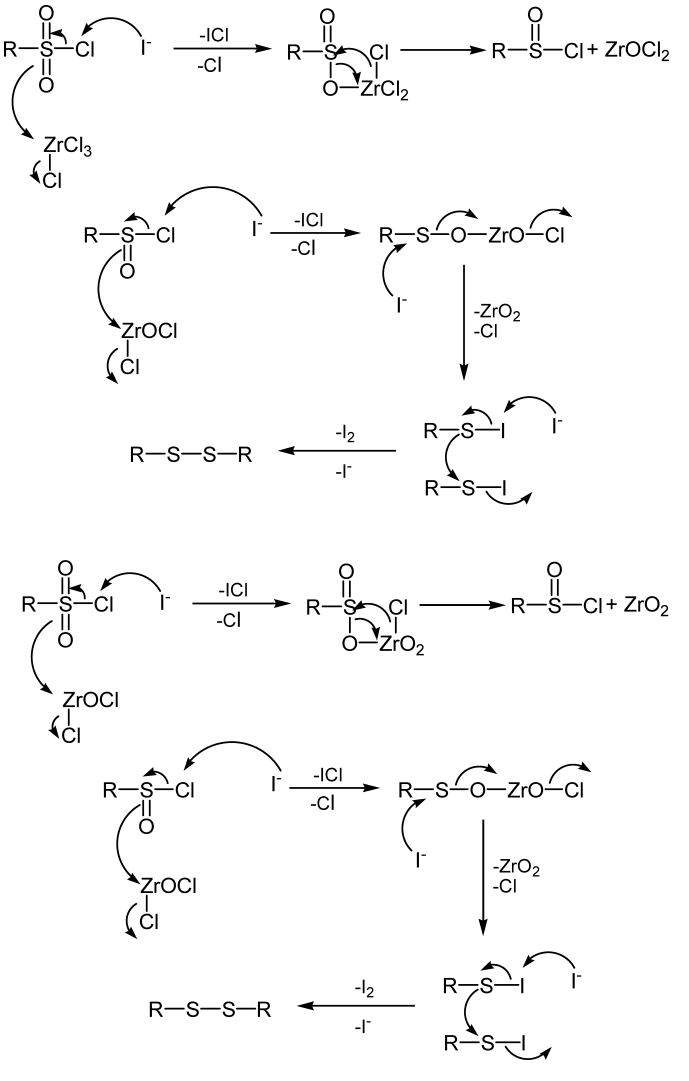
11.7. *Reductive coupling of sulfonyl chlorides with SmI_2/THF/HMPA* (203)

Samarium iodide, which is a powerful single-electron transfer reducing agent, has been extensively applied to organic synthesis in recent years (*204, 205*). It is found that aryl and alkyl sulfonyl halides can be readily reduced with 4 molar equiv. of SmI_2 at 60°C to afford the corresponding disulfides in moderate to good yields (Scheme 53, Table 38).

In these reactions, the halogen atoms on the aromatic ring were not affected. It is worth noting that the addition of HMPA was essential to reduce sulfonyl halides by this method.

11.8. *Reductive coupling of sulfonyl chlorides with Sm/$NiCl_2$/KI system* (206)

Arylsulfonyl chlorides can be readily reduced to corresponding disulfides with Sm/$NiCl_2$/KI system in moderate to good yields at 60 °C (Scheme 54, Table 39). Availability of the starting materials, chemoselectivity, and neutral condition as well as simple operation are the advantages of this method.



Scheme 51.

12. Reductive coupling of sulfonyl derivatives with phosphine containing reagents

12.1. *Reductive coupling of sulfonyl derivatives with polyphosphoric derivatives/potassium iodide/tetra-n-butylammonium iodide system* (207)

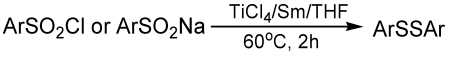
The reduction of sulfonic acid, in which sulfur atom is in the highest oxidation state of all organosulfur compounds, is one of the most challenging problems in organosulfur chemistry. Sulfonic acids, however, can be reduced in multi-step processes through initial conversion of the sulfonic acid to the corresponding sulfonyl derivatives, *i.e.* sulfonyl halide, sulfonic anhydride, sulfonate ester, and sulfonamide and subsequent reduction of these sulfonic acid derivatives with reducing agents to the corresponding thiols or thiol derivatives (Scheme 55, Table 40).

The condensing reagents were tetraphosphoric decaoxide, polyphosphoric acid, and polyphosphate ethyl ester. Acetonitrile and sulfolane are the best solvents in the case of P_4O_{10}/I^- and PPA/I^- systems, respectively, because of the solubility of polyphosphoric derivatives, whereas

Table 36. Reductive coupling of sulfonyl chlorides with $ZrCl_4$ or $ZrOCl_2{\cdot}8H_2O$.[a]

Entry	Substrate	Mediator	Subst./ Mediator/NaI	Time (min)	Isolated Yield(%)
1	$CH_3CH_2CH_2SO_2Cl$	$ZrCl_4$	1:1:4	2	95
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	6	95
2	$PhSO_2Cl$	$ZrCl_4$	1:1:4	3	95
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	7	95
3	*p*-$CH_3C_6H_4SO_2Cl$	$ZrCl_4$	1:1:4	5	94
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	15	90
4	*p*-$BrC_6H_4SO_2Cl$	$ZrCl_4$	1:1:4	3	96
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	7	95
5	2-NaphthylSO_2Cl	$ZrCl_4$	1:1:4	7	95
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	20	95
6	*p*-$NO_2C_6H_4SO_2Cl$	$ZrCl_4$	1:1:4	15	94
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	25	94
7	2-OH,3,5-$Cl_2C_6H_3SO_2Cl$	$ZrCl_4$	1:1:4	6	88
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	12	87
8	*p*-$CH_3C_6H_4SO_3H$	$ZrCl_4$	1:1:4	24 h	–
		$ZrOCl_2{\cdot}8H_2O$	1:2:4	24 h	–

[a]The reactions were performed under reflux conditions.

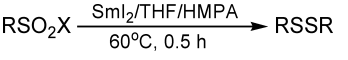


Scheme 52.

Table 37. Reductive coupling of sulfonyl chlorides with $TiCl_4/Sm$.

Entry	Substrate	Yield (%)[a]
1	$C_6H_5SO_2Cl$	65
2	*p*-$CH_3C_6H_4SO_2Cl$	62
3	*p*-$ClC_6H_4SO_2Cl$	74
4	*p*-$BrC_6H_4SO_2Cl$	77
5	3-CH_3-4-$ClC_5H_3SO_2Cl$	61
6	$PhCH_2SO_2Na$	83
7	*p*-$CH_3C_6H_4SONa$	80
8	*p*-$ClC_6H_4SO_2Na$	76

[a]Yields of isolated products.



Scheme 53.

acetonitrile, sulfolane, or chloroform may be a choice solvent in the reduction with the PPE/I^- system. Of the three systems, the reduction with P_4O_{10}/I^- or PPE/I^- gives the corresponding disulfides in higher yields than the PPA/I^- system in the presence of tetra-*n*-butylammonium iodide. In the absence of tetra-*n*-butylammonium iodide, the yields of the disulfide are more satisfactory in the reduction with PPA/I- than the former systems. It is worthy to note that *d*-camphor-10-sulfonic acid, which is a highly sterically hindered aliphatic sulfonic acid, was reduced to the corresponding disulfide in a high yield.

Table 38. Reductive coupling of sulfonyl chlorides with SmI_2/THF/HMPA.

Entry	Substrate	Yield (%)[a]
1	$C_6H_5SO_2Cl$	73
2	*o*-$CH_3C_6H_4SO_2Cl$	62
4	*p*-$CH_3C_6H_4SO_2Br$	75
6	*p*-$BrC_6H_4SO_2Cl$	72
7	3-CH_3-4-$ClC_5H_3SO_2Cl$	77
8	2,4,6-$(CH_3)_3C_6H_3SO_2Cl$	66
10	$C_6H_4CH_2SO_2Cl$	58
11	n-$C_4H_9SO_2Cl$	54

[a]Isolated yields.

$$ArSO_2Cl \xrightarrow[60^{o}C,\ 3h]{Sm/NiCl_2/KI} ArSSAr$$

Scheme 54.

Table 39. Reductive coupling of sulfonyl chlorides with $Sm/NiCl_2/KI$.

Entry	Substrate	Yield (%)[a]
1	$C_6H_5SO_2Cl$	70
2	*o*-$CH_3C_6H_4SO_2Cl$	60
3	*p*-$CH_3C_6H_4SO_2Cl$	62
4	*p*-$ClC_6H_4SO_2Cl$	74
5	*p*-$BrC_6H_4SO_2Cl$	68
6	3-CH_3-4-$ClC_5H_3SO_2Cl$	74
7	2,4,6-$(CH_3)_3C_6H_3SO_2Cl$	68
8	*p*-$CH_3OC_6H_4SO_2Cl$	63

[a]Isolated yields.

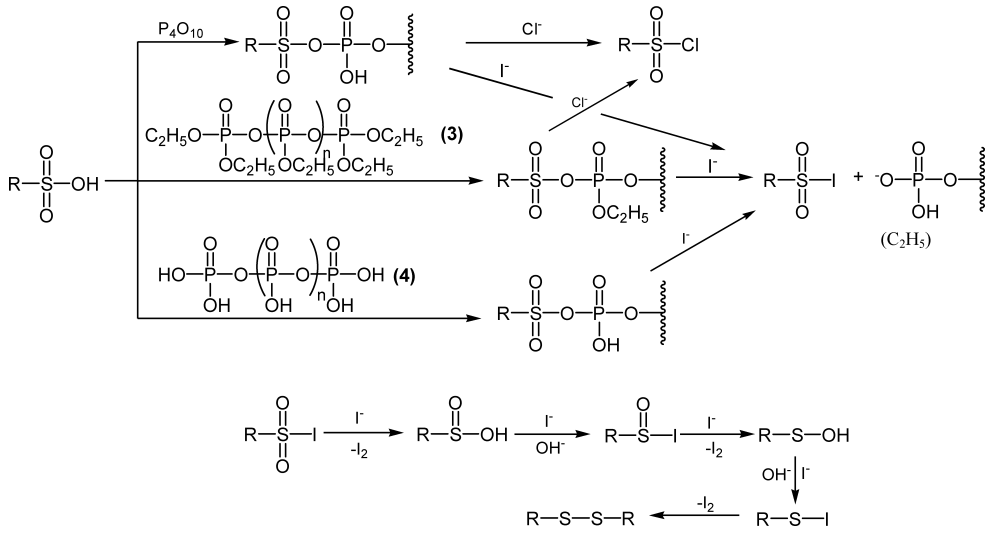
12.2. *Reductive coupling of sulfonyl derivatives with Silphos [$PCl_{3-n}(SiO_2)_n$] as a heterogeneous reagent* (84)

Reductive coupling of sulfonyl chlorides, sodium sulfinates, and thiosulfonates to their corresponding disulfides were carried out by a heterogeneous phosphine reagent, Silphos [$PCl_{3-n}(SiO_2)_n$], and molecular I_2 in dry refluxing CH_3CN in high yields. Applying this method for deoxygenation of sulfonic acid, sulfonate esters, and sulfonic acid salts was not successful (Scheme 56, Table 41).

In comparison with the literature methods using phosphorus containing reagents, Silphos is easily prepared, and in an easy work up, the produced Silphos oxide can be readily removed by a simple filtration.

13. Oxidative coupling of sulfonyl, sulfinyl chlorides and thiosulfonates with molybdenum–persulfide complex (*208*)

There is much interest in the study of complexes containing molybdenum and sulfur (*209–211*), not least because of the coordination of molybdenum by a group of sulfur atoms in each of



Scheme 55.

Table 40. Reductive coupling of sulfonyl derivatives with polyphosphoric derivatives/ potassium iodide/ tetra-*n*-butylammonium iodide system.

Entry	Substrate	Amounts (mmol) of reagents used[a] 1/2,3, or 4/KI/(n-C_4H_9)N^+I^-	Reaction conditions Solvent(15–20 mL)/ temprature/time	Yield (%)[b]
Using Tetraphosphorus Decaoxide (2; P_4O_{10}):				
1	p-$CH_3C_6H_4SO_3H$	6/33.81/30/1.5	CH_3CN/reflux/14 h	57
2	p-$ClC_6H_4SO_3H$	6/42.24/36.15/1.5	CH_3CN/reflux/24 h	40
3	2,4-$(CH_3)_2C_6H_3SO_3H$	6/42.24/36.15/1.5	CH_3CN/reflux/14 h	55
4	p-$CH_3C_6H_4SO_3Na$	6/42.24/36.15/1.5CH_3	CN/reflux/34 h	60
5	p-$CH_3C_6H_4SO_3H.H_2O$	6/33.81/30/0	CH_3CN/reflux/14 h	33
Using Polyphosphoric Acid (4; PPA):				
1	p-$CH_3C_6H_4SO_3H$	6/48/48/1.5	sulfolane/95–100 °C/8 h	65
		6/48/48/0	sulfolane/95–100 °C/8 h	75
2	p-$ClC_6H_4SO_3H$	6/48/60/1.5	sulfolane/95–100 °C/10 h	47
		6/48/48/0	sulfolane/95–100 °C/8 h	58
3	2,4-$(CH_3)_2C_6H_3SO_3H$	6/48/48/1.5	sulfolane/95–100 °C/8 h	68
		6/48/48/0	sulfolane/95–100 °C/8 h	70
4	p-$CH_3C_6H_4SO_3Na$	6/48/48/1.5	sulfolane/95–100 °C/23 h	58
		6/48/48/0	sulfolane/95–100 °C/21 h	55[c]
5	n-$C_8H_{17}SO_3H.H_2O$	6/48/48/1.5	sulfolane/80 °C/5 h	66
Using Polyphosphoric Acid Ethyl Ester (3; PPE):				
1	p-$CH_3C_6H_4SO_3H.H_2O$	6/35.6/48/1.5	$CHCl_3$/reflux/1.5 h	60
		6/35.6/48/0	$CHCl_3$/reflux/2 h	12
2	$PhSO_3H.H_2O$	6/47.4/48/1.5	$CHCl_3$/reflux/2 h	43
3	p-$(CH_3)C_6H_4SO_3Na$	6/35.6/48/1.5	$CHCl_3$/reflux/6 h	43
4	n-$C_8H_{17}SO_3Na$	6/47.4/48/1.5	$CHCl_3$/reflux/2 h	47
5	d-Camphor-10-sulfonic acid	6/47.4/48/1.5	$CHCl_3$/reflux/5 h	74

[a]The molecular masses of 2,3, and 4 were taken as 142, 500, 338, respectively.
[b]Yield of isolated product.
[c]Small amount of thiolsulfonate obtained as by-product.

the molybdenum-containing enzymes such as nitrogenase, sulfite oxidase and xanthine oxidase (*212–214*). Developments in molybdenum–sulfur chemistry serve to demonstrate the structural diversity possible for combination of these elements.

$$RSO_2Cl + Silphos \xrightarrow[MeCN,\ reflux]{I_2} RSSR + filterable\ Silphos\ oxide$$

Scheme 56.

Table 41. Reductive coupling of sulfonyl derivatives with silphos $[PCl_{3-n}(SiO_2)_n]/I_2$[a].

Entry	Substrate	Reaction time (h)	Yield (%)[b]
1	$PhSO_2Cl$	10	96
2	p-$CH_3C_6H_4SO_2Cl$	10	92
3	p-$BrC_6H_4SO_2Cl$	12	88
4	2-NaphthylSO_2Cl	8	98
5	CH_3SO_2Cl	12	85
6	$PhSO_2Na$	12	95
7	$PhSO_2SPh$	5	94
8	p-$CH_3C_6H_4SO_2OH$	24	No reaction
9	p-$CH_3C_6H_4SO_3Na$	24	No reaction
10	p-$CH_3C_6H_4SO_3Et$	24	No reaction

[a]Molar ratio of substrate/I_2 (1:2) in the presence of 1.2 g of Silphos.
[b]Isolated yield.

$$RSOCl + RSO_2Cl + (NH_4)_2Mo_2S_{12} \longrightarrow RSSR$$

Scheme 57.

Table 42. Oxidative coupling of sulfonyl and sulfinyl chlorides in the presence of molybdenum–persulfide complex and under nitrogen atmosphere.

Entry	Substrate	Reaction Time (h)	Yield (%)
1	$PhSO_2Cl$	8	90
2	PhSOCl	8	68
3	p-$CH_3C_6H_4SO_2Cl$	8	67
4	p-$CH_3C_6H_4SO_2OH$	20	No reaction
5	$PhSO_2SPh$	4	81

The reaction of sulfinyl and sulfonyl chlorides with $(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2]$ has been found to afford sulfides and disulfides in good to excellent yields (Scheme 57). However, toluenesulfonic acid did not react and only starting material was recovered even after prolonged reflux (20 h) (Table 42).

Although no intermediates have been isolated to date, it seems probable that the reaction pathway involves the formation of, in the sulfinyl case, an α-disulfide (which could be expected to rearrange to the thiosulfonate) (*215*) or, in the sulfonyl chloride system, the α-disulfone. These intermediates would then be reduced to the disulfide. Support for this pathway was obtained when a sample of benzenthiosulfonate was refluxed in CH_3CN with $(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2]$ for 4 h under a nitrogen atmosphere to yield 81% of diphenyl disulfide (Table 42, entry 5).

14. Concluding remarks

Reduction of oxygenated sulfur atom in organic compounds is a challenging problem in organic reactions. Many methods have been introduced for the reduction of the sulfoxides moiety. Because of the importance of sulfoxides as a chiral auxiliary, mild stereoselective reduction of sulfoxides is still at the beginning of its development and remains a challenging problem in organic synthesis.

The reduction of derivatives of sulfonic and sulfinic acids is a challenging problem. Reduction of their halides is more studied than the other derivatives of these acids and milder and more selective methods with higher efficiency should be developed. Reduction of sulfonic acid in which sulfur atom is at its highest oxidation state is a very difficult process and is very important from an industrial point of views. However, very few methods are available. Therefore, introduction of new methods for this transformation is desirable. Reduction of sulfones is not also an easy task and development of new protocols in this area is also of high demand.

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