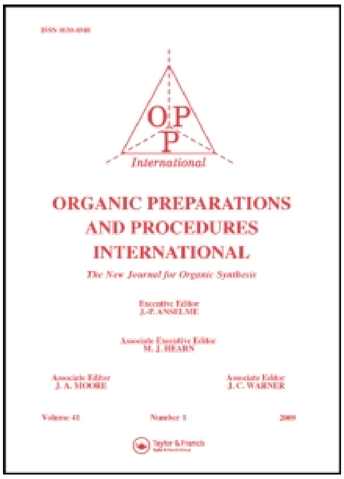

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DEXYGENATION OF SULFOXIDES. A REVIEW

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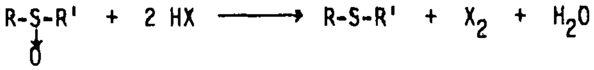
INTRODUCTION

The recent literature indicates an active interest in finding effective methods for the reduction of sulfoxides to sulfides. Much of this interest has been originated from the growing importance of organosulfur compounds in organic synthesis. Sulfoxides are important intermediates in various synthetic transformations. The successful application of these procedures generally requires the removal of the residual sulfoxide moiety. One of the simplest method for achieving such a transformation involves the reduction of sulfoxide to sulfide which is then further reduced by treatment with Raney nickel or a reducing metal system such as lithium in liquid ammonia or amines. In this brief review are tabulated exhaustively the methods of reduction of sulfoxides which have been used up to now together with remarks on the advantages and limitations of these methods. Brief mechanistic discussions are also given.

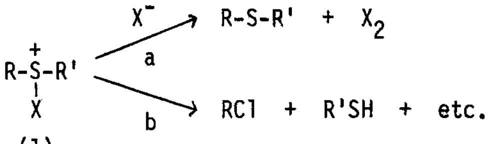
1. Reduction with Hydrogen Halides

Generally this reaction can be described by the following equation.



$$R\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R' \;+\; 2\,HX \longrightarrow R\text{-}S\text{-}R' \;+\; X_2 \;+\; H_2O$$

Reduction of sulfoxides with hydrogen halides involves an intermediate, halosulfonium salt(1).

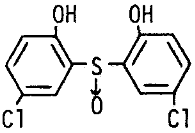


(1)

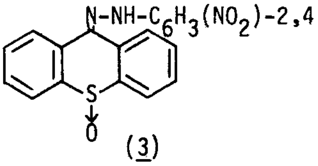
Depending on the nature of X , R and R', the salt(1) can either react with another halide anion to form the sulfide (path a) or decompose (path b) eventually forming the C-S bond cleavage products, such as mercaptans and halogenated hydrocarbons.

a) Hydrogen Chloride

Gazder and Smiles[1] in 1910 found that heating of sulfoxide(2) with HCl in ethanol solution in a sealed tube at 100° for 4-5 hrs gave the corresponding sulfide quantitatively. Recently hydrogen chloride was used for reduction of another heterocyclic sulfoxide(3).[2]



(2)



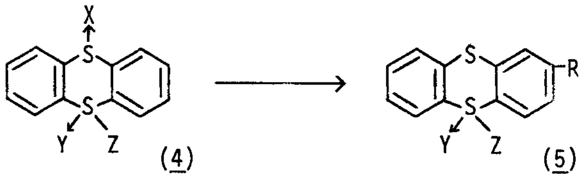
(3)

However, both dibenzyl[3] and di-isoamyl[4] sulfoxides were found to decompose quickly by hydrogen chloride at room temperature.

b) Hydrogen Bromide

In 1911 Fries and Vogt[5] revealed that hydrogen bromide reduces thianthrene 9,10-dioxide(4a) smoothly to the corresponding sulfide(5a). Much later however, it was found by Gilman and Swayampati[6] that the reduction of sulfoxide(4b) gave the brominated sulfide 5b, while the treatment of 9,10,10-trioxide derivative(4c) with 32% hydrobromic acid at reflux gave the corresponding 9-sulfide(5c) in a quantitative yield.

Aida, Furukawa and Oae[7] reported catalytic reductions of both dialkyl and alkyl aryl sulfoxides with HBr-Br_2 system.



(4)

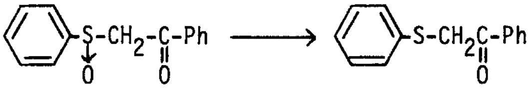
a) X = Y = O, Z = lone pair
b) Y = O, X = Z = lone pair
c) X = Y = Z = O

(5)

a) Y = Z = lone pair, R = H
b) Y = Z = lone pair, R = Br
c) Y = Z = O, R = H

c) Hydrogen Iodide

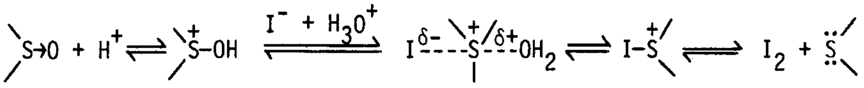
In contrast to hydrogen chloride and hydrogen bromide, reduction with hydrogen iodide only effects the reductive cleavage of sulfur-oxygen bond. This reagent was first used for reduction of sulfoxide(6) to the sulfide by Zincke and Baeumer.[8] Much later Karaulova and Gal'pern[9] reported reductions



(6)

of a broad spectrum of sulfoxides by this method.

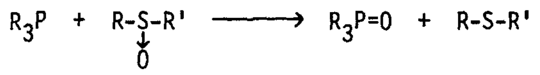
This reduction with iodide is an acid-catalyzed S_N2 type process on the sulfur atom as shown below.[10-13]



Landini et al.[10] and Tamagaki et al.[14] have carried out detail kinetic investigations of this reaction. While the rates of reduction of thianthrene, phenoxathiane and dibenzothiophene oxides were found to be in a linear relation with their basicities, those of alicyclic sulfoxides fall in the following sequence over a 700-fold range; (relative rates), 5-(717) 〉 4-(34.7) 〉 DMSO (32.6) 〉 7-(9.9) 〉 6-(1) membered.[14] Thus the reduction is affected markedly by steric interference around the sulfur atom. Since the reduction occurs under mild conditions, this procedure has been used extensively. Hogeveen and Montanari[10c] have utilized this method for quantitative determination of sulfoxides.

2. Reduction with Trivalent Phosphorus Compounds

The sulfoxide group is capable of oxidizing various compounds. Among these, trivalent phosphorus compounds are known to be oxidized readily to the corresponding phosphoryl derivatives according to the following general equation.



$$R_3P + R\text{-}\underset{\displaystyle O}{\underset{\downarrow}{S}}\text{-}R' \longrightarrow R_3P{=}O + R\text{-}S\text{-}R'$$

Reducing properties of trivalent phosphorus compounds are strongly dependent on the nature of the substituent on the phosphorus atom.

a) Triphenylphosphine

Castrillon and Szmant[15] indicated that sulfoxides may be converted in high yields to the corresponding sulfides by refluxing with triphenylphosphine for 2 hrs in CCl_4. Later they found that this reaction is of acid-catalyzed.[16] In the presence of acids, the reaction time is much shortened and the temperature can be lowered considerably. The most likely mechanism of the reaction is a nucleophilic attack of the phosphorus atom on the acid-complexed sulfoxide oxygen. Thus the rate is dependent on the basicity of the sulfoxide.

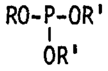
b) Phosphorus Trichloride and Phosphorus Tribromide

In 1969 Granoth *et al*.[17a] found that phosphorus trichloride can reduce diaryl sulfoxides in a smooth exothermic reaction in yields of 67-85%. It was also shown that nitro group present in the aromatic ring, e.g., *p*-nitrophenyl *p*-chlorophenyl sulfoxide, is not attacked under the reaction condition.

Claes *et al*.[17b] found that penicillin sulfoxides were deoxygenated with phosphorus tribromide in DMF solution under cooling.

c) Phosphites

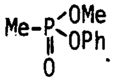
Amonoo-Neizer *et al*.[18] found that triphenyl phosphite(7a) reduces dimethyl sulfoxide to dimethyl sulfide at elevated temperatures. Oae, Nakanishi and Kozuka[19] found that the mode of reaction between the phosphite(7) and the sulfoxide depends on the nature of both R and R' groups. They showed that 7a and 7b have converted alkyl phenyl sulfoxides to sulfides quantitatively at 110°; with 7c, sulfides were formed only 70% yield while the Arbuzov-type rearrangement product 8 was obtained in 30% yield.



$$RO-\underset{OR'}{\underset{|}{P}}-OR'$$

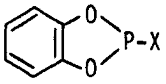
(7)

a) R = R' = Ph;
b) R = Me, R' = Ph;
c) R = Ph, R' = Me



$$Me-\underset{O}{\underset{\|}{P}}(OMe)(OPh)$$

(8)



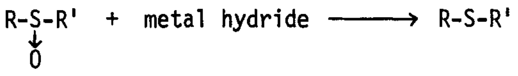
(9)

a) X = OPh;
b) X = Cl

Recently Dreux et al.[20] showed that dialkyl, alkyl aryl and diaryl sulfoxides are reduced smoothly with cyclic phospholane(9a). With catalytic amounts of iodine, deoxygenation was completed within a few minutes above the temperature at which the sulfoxide is soluble in CCl_4 and the yields are in the 87-95% range. Aliphatic sulfoxides are generally reduced faster than aromatic ones. Very recently Chasar and Pratt[21] reported that cyclic chlorophospholane 9b can be used for the facile reduction of sulfoxides at room temperature (yield 72-100%). Since chlorophospholane 9b is the precursor of 9a, this reducing agent is easily accessible.

3. Reduction with Hydrides

Various metallic hydrides have been used for the reduction of sulfoxides in the following manner.



$$R-\underset{O}{\underset{\downarrow}{S}}-R' + \text{metal hydride} \longrightarrow R-S-R'$$

a) Lithium Aluminium Hydride ($LiAlH_4$)

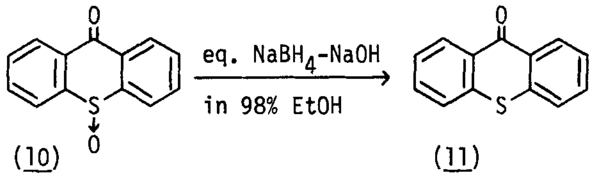
In 1950, Strating and Backer[22] reported that sulfoxides were not reduced by $LiAlH_4$. Soon thereafter, Pitt[23] found that sulfoxides may be reduced to the corresponding sulfides by $LiAlH_4$ in boiling ether. Karaulova and Gal'pern[9,24] and Brown et al.[25] have subsequently used this hydride for the reduction of a broad spectrum of sulfoxides. Serious limitation of this method constitutes the very long time and rather low (about 50%) yield of sulfides.

Recently it has been found that $LiAlH_4$-titanium tetrachloride($TiCl_4$) system reduces sulfoxides under mild conditions in high yields (80-90%) and in less than 2 hrs.[26]

Complex hydrides formed in situ between $LiAlH_4$ and optically active alcohols such as (-)menthol or amino alcohols such as (-)ephedrine and (-)quinine, with general structure $LiAlH_{4-n}(OR^*)_n$ have been used for asymmetric reduction of racemic dialkyl and alkyl aryl sulfoxides.[27]

b) Sodium Borohydride ($NaBH_4$)

It has been shown that sodium borohydride alone is not able to reduce the sulfoxide group, but in the presence of sodium hydroxide, thioxanthone sulfoxide(10) was reduced by $NaBH_4$ to the corresponding thioxanthone(11).[28]



(10) (11)

Chasar[29] found that sulfoxides are reduced efficiently by $NaBH_4$-cobalt chloride($CoCl_2$) system at room temperature in high yields. However, dibenzyl sulfoxide and tetramethylene sulfoxide afforded little or no sulfide upon treatment with this reagent; instead complete decomposition of the starting sulfoxides occurred.

c) Sodium Cyanohydroborate($NaBH_3CN$)-Crown Ether System

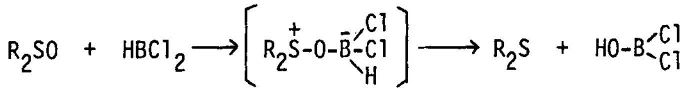
Durst et al.[30] revealed that alkoxysulfonium salts, generated in situ from corresponding sulfoxides by alkylation with methyl fluorosulfonate, were reduced to the sulfides in good yields (71-87%) by treatment with $NaBH_3CN$ in presence of 18-crown-6-ether. Without the crown ether, yields of sulfides were below 5%.

d) Tributyltin Hydride (*n*-Bu_3SnH)

Oae *et al.*[31] reported that tributyltin hydride in presence of an equimolar amount of azobisisobutyronitrile(AIBN) as initiator can reduce diaryl sulfoxides such as diphenyl sulfoxide, thianthrene and phenoxathiane S-oxides; however, this reagent failed to reduce dialkyl and alkyl aryl sulfoxides such as dibutyl and methyl phenyl sulfoxides. Yields of sulfides in this free-radical reaction are strongly dependent on the nature of the sulfoxides. In the case of alkyl sulfoxides the cleavage of sulfur-carbon bond was observed.

e) Dichloroborane ($HBCl_2$)

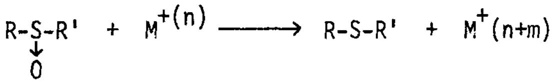
Brown and Ravindran[32] observed that dialkyl sulfoxides are rapidly deoxygenated to the corresponding sulfides in high yields (86-95%) by treatment with dichloroborane in ice-cooled THF solution at 0°. However, the reduction of diphenyl sulfoxide is much slower (90% yield) after 24 hrs at 25°. They also found that this reagent selectively reduces sulfoxides without affecting other reducible functions, such as ketones, esters and amides. The following mechanism was proposed.



$$R_2SO + HBCl_2 \longrightarrow \left[R_2\overset{+}{S}-O-\overset{-}{B}{\scriptstyle\begin{matrix}Cl\\Cl\\H\end{matrix}} \right] \longrightarrow R_2S + HO-B{\scriptstyle\begin{matrix}Cl\\Cl\end{matrix}}$$

4. Reduction with Low Valent Metal Ions

Low valent metal ions are useful reagents for cleavage of semi-polar hetero atom-oxygen bonds and hence they were often used for deoxygenation of sulfoxides. The advantage of this reaction which can be represented by following equation is its high selectivity.



$$\text{R-}\underset{\substack{\downarrow\\ \text{O}}}{\text{S}}\text{-R}' + \text{M}^{+(n)} \longrightarrow \text{R-S-R}' + \text{M}^{+}(n+m)$$

a) Titanium(III) Chloride

Titanium trichloride was at first used by Barnard and Hargrave,[33] and Legault and Groves[34] for the quantitative determination of dialkyl sulfoxides. Recently Ho and Wong[35] have used this reagent on a preparative scale for reduction of such sulfoxides as dibutyl, dibenzyl, methyl phenyl and diphenyl sulfoxides in 68-91% yields.

b) Stannous(II) Chloride

Stannous(II) chloride was also used at first for analytical purposes.[36] Very recently Ho and Wong[37] have reported application of this reagent for the preparative reduction of sulfoxides (yields 63-93%).

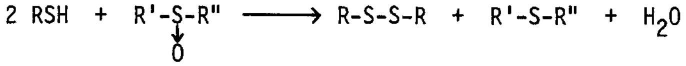
c) Molybdenum(III), Vanadium(II) and Tungsten(III) Compounds

Very recently Olah et al.[38] used low valent molybdenum(III) and vanadium(II) compounds for reduction of sulfoxides such as dialkyl, alkyl aryl and diaryl sulfoxides. The deoxygenation of sulfoxides with activated Mo(III) generated by treatment of $MoCl_3$ with zinc dust in THF solution, was complete within 1 hr at room temperature. Reduction of sulfoxides in aqueous vanadium(II) chloride proceeds more slowly and requires heating for its completion. Yields are in the 78-91% range.

Independently Nuzzo et al.[39] also reported that sulfoxides such as dialkyl, aralkyl, diphenyl sulfoxides, benzylic and allylic sulfoxides are reduced in high yields (70-99%) under mild conditions by various complex ions of molybdenum(II) and (III) and tungsten(III) such as $(NH_4)_4Mo_2Cl_8$, $Cs_3Mo_2Cl_8H$, K_3MoCl_6 and $K_3W_2Cl_9$.

5. Reduction with Sulfhydryl Compounds

Generally this reaction can be described by following equation.

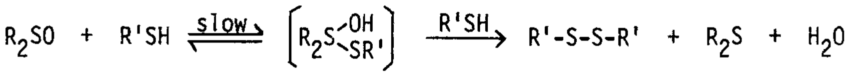


$$2\ RSH + R'\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R'' \longrightarrow R\text{-}S\text{-}S\text{-}R + R'\text{-}S\text{-}R'' + H_2O$$

The rate of the reaction is in general dependent on both acidity of sulfhydryl component and basicity of the sulfinyl oxygen.

a) Mercaptans

Yiannios and Karabinos[40] have shown that DMSO is reduced to DMS by heating with mercaptans. Wallace and Mahon reported also that diisopropyl and tetramethylene sulfoxides are reduced to the corresponding sulfides by heating with mercaptans; amines are catalysts for this reaction. The following mechanism was suggested.[41]



$$R_2SO + R'SH \overset{slow}{\rightleftharpoons} \left[R_2S{<}^{OH}_{SR'}\right] \xrightarrow{R'SH} R'\text{-}S\text{-}S\text{-}R' + R_2S + H_2O$$

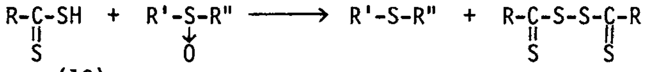
Methionine sulfoxide was easily reduced with dithiothreitol(Cleland's reagent).[42]

An interesting example is the use of optically active thiols, e.g., L-cysteine, (+)2-mercaptopropionic acid, etc., for asymmetric reduction of racemic sulfoxides to obtain optically active sulfoxides with partial preference for one enantiomer.[43]

Dialkyl sulfoxides were easily reduced with hydrogen sulfide(H_2S) to the corresponding sulfides in good yields.[44]

b) Carbodithioic Acid

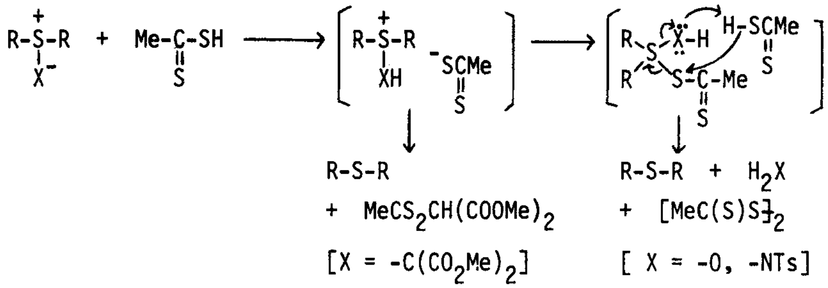
Mikołajczyk and Para[45] and Oae et al.[46] reported independently that DMSO, dialkyl, alkyl aryl and diaryl sulfoxides are quantitatively reduced in an exothermic reaction at room temperature by treatment with carbodithioacid(12).



$$R\text{-}\underset{\overset{\|}{S}}{C}\text{-}SH + R'\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R'' \longrightarrow R'\text{-}S\text{-}R'' + R\text{-}\underset{\overset{\|}{S}}{C}\text{-}S\text{-}S\text{-}\underset{\overset{\|}{S}}{C}\text{-}R$$

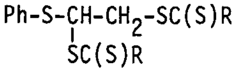
(12)

N-Tosylsulfilimines and sulfonium ylides are also similarly reduced nicely with the same reagent and the general scheme of the mechanism is suggested in the following equation.[46] The reduction of sulfonium ylides



requires one equimolar amount of the acid while in the others two equimolar amounts of the acid are necessary for completion of the reaction.

Unsaturated sulfoxides such as vinyl phenyl sulfoxide gave in this condition α, β-disubstituted sulfide(13). Not only the reduction but also a Michael addition took place (an additive Pummerer reaction).[46]



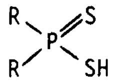
$$\underset{\displaystyle SC(S)R}{Ph\text{-}S\text{-}CH}\text{-}CH_2\text{-}SC(S)R$$

(13)

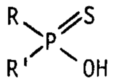
c) Mono- and Dithiophosphoric Acids

Mikołajczyk showed that DMSO was reduced with a few dithiophosphoric acids(14).[47] Independently Nakanishi and Oae revealed upon extensive studies that dialkyl, alkyl aryl and diaryl sulfoxides were easily reduced to the corresponding sulfides quantitatively by treatment with other dithiophosphoric acids(14a and 14b) in an exothermic reaction at room temperature.[48] Both dialkyl and alkyl aryl sulfoxides are reduced in a few minutes while the reduction of diaryl sulfoxides requires a few hours to be completed at room temperature.[48] Other semi-polar bonds such as sulfilimine, sulfonium ylide, amine N-oxide and N-imino groups are also reduced by the reagent.[48] Reduction by monothioacid of phosphorus(15) requires high temperatures and addition of electrophilic catalysts such as p-TosOH and $BF_3 \cdot Et_2O$.[45,47]

Optically active monothioacids of phosphorus have been used by Mikołajczyk and Para for asymmetric reduction of racemic sulfoxides.[49]


(14)

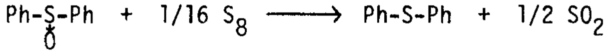
a) R = EtO; b) R = ^{i}PrO;
c) R = MeO; d) R = Ph


(15)

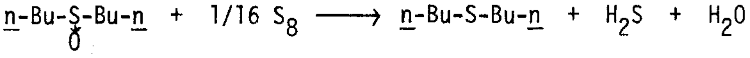
a) R = R' = EtO; b) R = R' = Et;
c) R = EtO, R' = Et;
d) R = R' = OPh

6. Reduction with Sulfur and Organic Sulfur Compounds

Sulfur reacts rapidly with diphenyl sulfoxide at 280° to form sulfide and SO_2.[50]

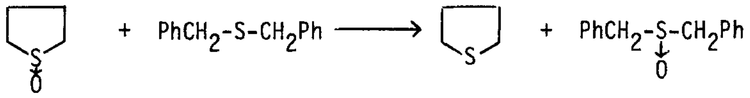

$$\mathrm{Ph\text{-}\underset{O}{\underset{\downarrow}{S}}\text{-}Ph} + 1/16\ S_8 \longrightarrow \mathrm{Ph\text{-}S\text{-}Ph} + 1/2\ SO_2$$

Di-n-butyl sulfoxide also reacts with sulfur at 200° according to the following equation.[51]

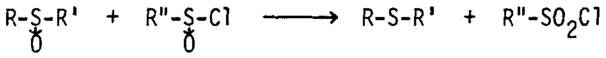

$$\mathrm{\underline{n}\text{-}Bu\text{-}\underset{O}{\underset{\downarrow}{S}}\text{-}Bu\text{-}\underline{n}} + 1/16\ S_8 \longrightarrow \mathrm{\underline{n}\text{-}Bu\text{-}S\text{-}Bu\text{-}\underline{n}} + H_2S + H_2O$$

Benzylic sulfoxides gave many products resulting from C-S bond cleavage under these reaction conditions.[52] It was also shown that diphenyl sulfoxide is reduced by diphenyl disulfide at 250°.[53] Both reactions are considered to be of free radical character.

The reductions of sulfoxides have been achieved by oxygen exchange reaction with sulfides. Searles and Hays[54] have found that the aliphatic sulfides were oxidized to the corresponding sulfoxides in 55-58% yields by heating with DMSO at higher temperature (160-175°). Bordwell and Pitt[55] also found that heating tetramethylene sulfoxide with dibenzyl sulfide gave quantitative yields of tetramethylene sulfide and dibenzyl sulfoxide and the reaction was catalyzed by acids.



Senning[56] and Oae et al.[57] reported another method for reduction of sulfoxides which also represents oxygen transfer reaction, e.g., the reactions between sulfoxides and sulfinyl chlorides.



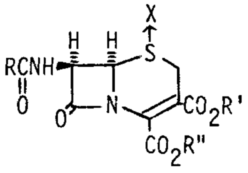
$$R-\underset{O}{\underset{\downarrow}{S}}-R' + R''-\underset{O}{\underset{\downarrow}{S}}-Cl \longrightarrow R-S-R' + R''-SO_2Cl$$

Dialkyl, alkyl aryl and diaryl sulfoxides and benzylic sulfoxides are smoothly reduced by either methanesulfinyl or arenesulfinyl chlorides.[57] Yields of sulfides are excellent (80-90%) and the reaction requires mild conditions. Similarly, reduction of sulfoxides with arenesulfenyl chloride by oxygen transfer was observed in the reaction of thianthrene and phenoxathiane S-oxides with p-nitrobenzenesulfenyl chloride.[57]

7. Reduction by Activation with Acyl Reagent

a) Acetyl Chloride

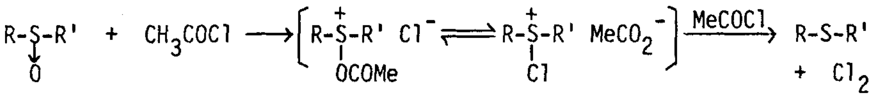
In 1966 Allenmark[58] found that sulfoxides after activation by acetyl chloride are able to oxidize iodide anion to free iodine and this reaction can be used for quantitative determination of sulfoxides. Later, Kaiser et al.[59] reported that 3-cephem sulfoxides(16a) were reduced to the corresponding 3-cephem sulfides(16b) by many reducing agents ($S_2O_4^{-2}$, I^-, Sn^{2+}) when the sulfoxides are activated by a reactive acyl halide.



(16)

a) X = O;
b) X = lone pair

Recently Numata and Oae[60] found that an excess of acetyl chloride reduces various sulfoxides in an exothermic reaction at room temperature generally in yields better than 90%. Only di-n-butyl sulfoxide gave di-n-butyl sulfide in 70% yield. The reaction may be rationalized by following mechanistic scheme.

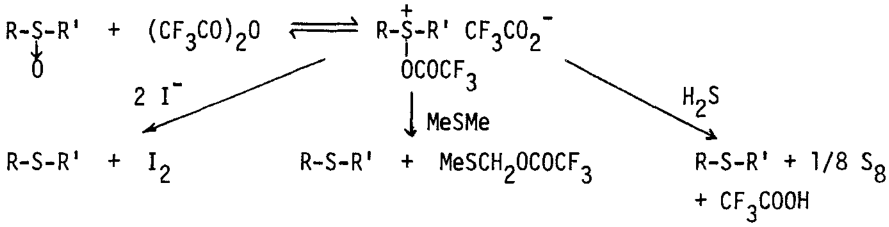


$$R-\underset{O}{\underset{\downarrow}{S}}-R' + CH_3COCl \longrightarrow \left[R-\overset{+}{\underset{OCOMe}{\underset{|}{S}}}-R'\ Cl^- \rightleftharpoons R-\overset{+}{\underset{Cl}{\underset{|}{S}}}-R'\ MeCO_2^-\right] \xrightarrow{MeCOCl} R-S-R' + Cl_2$$

Sulfilimines are also reduced similarly with this reagent.[60]

b) Trifluoroacetic Anhydride

Recently sulfoxides were found to be rapidly reduced to the corresponding sulfides by iodide anion,[61] H_2S,[62] and Me_2S[63] after activation with trifluoroacetic anhydride. The reaction may be rationalized by following scheme.



Yields are very high (above 90%) and the reaction conditions are very mild (0° in case of iodide anion and Me_2S and -60° in case of H_2S). It was found that the system $[(CF_3CO)_2O - H_2S]$ allows the selective reduction of sulfoxides among other sulfinyl compounds such as sulfinic esters and *t*-butyl thiolsulfinates.

8. Reduction by Miscellaneous Method

a) Chlorosilanes

Harpp *et al.*[64] found that aromatic sulfoxides are reduced by an excess of $HSiCl_3$ in high yields (85-100%) at room temperature. Under these conditions, dibenzyl sulfoxide and dialkyl sulfoxides such as $(RCH_2)_2SO$ [R = Et, *n*-Pr], gave in good yields mercaptals(**17**) instead of the sulfides.

$RCH(SCH_2R)_2$ (**17**) R = Ph, Et, *n*-Pr

Diphenyl sulfoxide has been reduced to diphenyl sulfide in 91% yield at room temperature by treatment with hexachlorodisilane ($Cl_3SiSiCCl_3$).[65]

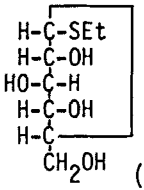
b) Iron Pentacarbonyl [$Fe(CO)_5$]

Alper and Keung[66] found that sulfoxides such as dialkyl, dibenzyl and diaryl sulfoxides are deoxygenated by a slight excess of $Fe(CO)_5$ in diglyme or in di-*n*-butyl ether at 130-135° (yield 48-91%).

Fujisawa et al.[67] reported that sulfoxides and thiolsulfonates are deoxygenated by "reduced iron" at 200° to give the corresponding sulfides and disulfides in good yields, respectively.

c) Sulfite(Na$_2$S$_2$O$_5$) and Sodium Hydrogen Sulfite(NaHSO$_3$)

The sulfoxides of d,l-methionine and α-ethylthioglucoside(18) were reported in 1939 to be reduced to the corresponding sulfides by aqueous sulfite (Na$_2$S$_2$O$_5$).[68] More recently, an aqueous solution of sodium "metabisulfite" was employed in the selective reduction of the sulfoxide group in ω-methylsulfinylacetophenone and the derivatives.[69] Johnson et al.[70] recently used an aqueous solution of sodium hydrogen sulfide for reduction of such simple sulfoxides as dialkyl and alicyclic sulfoxides. But the reaction was found to be slow while the yields were not high.



(18)

d) Thionyl Chloride

In 1894 Loth and Michaelis[71] found that treatment of diphenyl sulfoxide with thionyl chloride gives p-chlorophenyl phenyl sulfide.

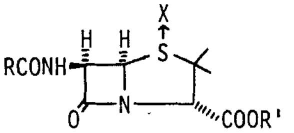
In 1961 Volynskii et al.[72] reported that various sulfoxides were reduced to the corresponding sulfides by thionyl chloride. Very recently Grossert et al.[73] also found that tetramethylene sulfoxide gave the sulfide in 25% yield in the reaction with SOCl$_2$ and a small amount of the 2-chlorosulfide was also formed.

e) Phosphorus Pentachloride and Phosphorus Oxychloride

In 1891 Michaelis and Godchaux[74] found that PCl$_5$ reacts with diphenyl sulfoxide to give p-chlorophenyl phenyl sulfide. Recently Bird[75] investigated the reduction of some aromatic and heterocyclic sulfoxides by phosphorus oxychloride (POCl$_3$) and found that this reaction gives the mixture of sulfides and chlorosulfides.

f) Phosphorus Pentasulfide – Pyridine

Very recently Micetich[76] found that penicillin sulfoxides(19a) and cephalosporin sulfoxides(16a) are smoothly reduced to the corresponding sulfides(19b and 16b) in a phosphorus pentasulfide-pyridine system in over 90% conversion yields in CH_2Cl_2.



(19)

a) X = O;

b) X = lone pair

g) Zinc in Acetic Acid

This is one of the oldest methods for reduction of sulfoxides. In 1910 Gazder and Smiles[1] reported that 2-hydroxy-5-methylphenyl sulfoxide was reduced to the sulfide by zinc dust in hot acetic acid.

h) Iodine-Pyridine-Sulfur Dioxide

Nojima et al.[77] recently found that sulfoxides such as dialkyl, dibenzyl and diphenyl sulfoxides are reduced to sulfides in an iodine-pyridine-sulfur dioxide system in high yields (84-96%) in CH_3CN at 80° in 2 hrs.

i) Catalytic Hydrogenation

Catalytic reduction by molecular hydrogen was at first carried out by James and co-workers.[78] They found that DMSO is reduced by molecular hydrogen under mild condition to DMS and water in presence of rhodium(III) complex such as $RhCl_3 \cdot 3H_2O$ and cis-$RhCl_3(Et_2S)_3$. Recently Ogura et al.[79] reported that one of the best catalysts for this reaction is 5% palladium on charcoal. Yields of sulfides were better than 90% but the reaction requires a very long time (1-4 days) for completion.

j) Photolysis

In aromatic solvents, direct photolysis of aryl sulfoxides gives the corresponding sulfides in excellent yields (nearly 90%), via a triplet excited state. However, photolysis of dialkyl sulfoxides gives no dialkyl sulfide.[80]

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