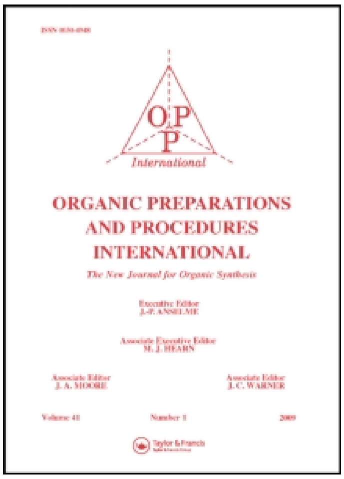

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REDUCTION OF SULFOXIDES. A REVIEW

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REDUCTION OF SULFOXIDES. A REVIEW

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INTRODUCTION

Methods for the reduction of sulfoxides have continuously been exploited and the aim of this review is to compile all the important recent data on the reduction, thus bringing up to date the previous review on this subject published in 1977.[1] It is our intention that these two reviews together will provide a comprehensive coverage of the method for the conversion of sulfoxides to sulfides from the first report on this subject up to the end of 1982.

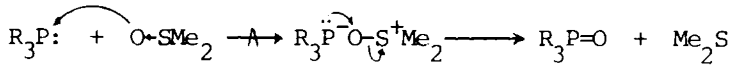
I. TRIVALENT PHOSPHORUS COMPOUNDS

Conversion of trivalent phosphorus compounds to the corresponding pentavalent, four cordinate phosphoryl derivatives can generally be carried out under mild conditions due mainly to the strong affinity of tirvalent phsphorus atom toward oxygen. Accordingly, several reagents, in which trivalent phosphorus atom plays a key role in the reaction, have been used recently for conversion of sulfoxides to corresponding sulfides. Generally, the reaction can be expressed as shown in Eq. 1.

$$R^1\text{-}\overset{O}{S}\text{-}R^2 \quad + \quad R_3P \xrightarrow{\text{(catalyst)}} R^1\text{-}S\text{-}R^2 \quad + \quad R_3P{=}O \qquad (1)$$

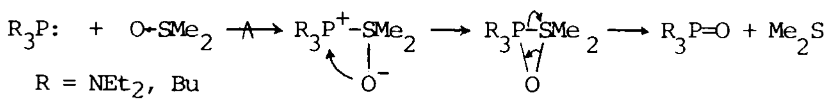
1. <u>Trivalent Phosphorus Compounds</u>

The mechanism of the reduction of the sulfoxides with trivalent phosphorus compounds, when the R group of R_3P is chloride or phenoxy group is depicted in Eq. 2, while that with trivalent phosphorus derivatives, when R is butyl or diethylamino group, is better illustrated by Eq. 3.[2]



$$R_3P: \; + \; O{\leftarrow}SMe_2 \xrightarrow{A} R_3\ddot{P}^{-}\text{-}O\text{-}\overset{+}{S}Me_2 \longrightarrow R_3P{=}O \; + \; Me_2S \qquad (2)$$

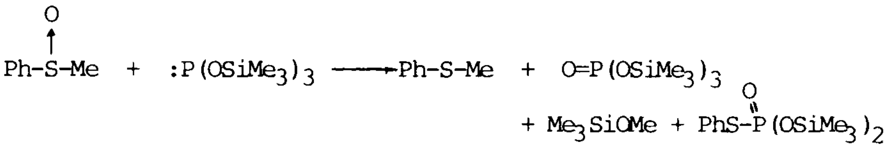
R = Cl, OPh



$$R_3P: \; + \; O{\leftarrow}SMe_2 \xrightarrow{A} R_3\underset{O^-}{\overset{+}{P}}\text{-}SMe_2 \longrightarrow R_3\underset{O}{P}\text{-}SMe_2 \longrightarrow R_3P{=}O + Me_2S \qquad (3)$$

R = NEt_2, Bu

Triphenylphosphine is a weak reducing agent, but the reaction is accelerated by addition of such a Lewis acid as BF_3.[3] Trialkyl phosphite, $P(OR)_3$, cannot reduce sulfoxides, since it isomerizes to $R\text{-}\overset{O}{P}(OR)_2$ upon heating, while tris(trimethylsilyl)phosphite, $P(OSiMe_3)_3$, can function as a strong reducing agent because of the high thermal stability.[4] Hata *et al*. found that heating of methyl phenyl sulfoxide with this reagent at 150^{o} or 8.5 hrs resulted in the formation of the corresponding sulfide in 72% yield while bis(trimethylsilyl)-S-phenylphosphorothioate was formed in 28% yield as a sole phosphorus-containing by-product. The reaction proceeds in the following manner. The reduction obviously involves the initial nucleophilic attack of the phosphite on the sulfur to form a



$$Ph\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}Me \; + \; :P(OSiMe_3)_3 \longrightarrow Ph\text{-}S\text{-}Me \; + \; O{=}P(OSiMe_3)_3 \; + \; Me_3SiOMe \; + \; PhS\text{-}\overset{\overset{O}{\|}}{P}(OSiMe_3)_2 \qquad (4)$$

pentacoordinate intermediate, followed by the ligand coupling.

2. <u>Triphenylphosphine-Iodine-Sodium Iodide</u>

The readily available triphenylphosphine-iodine-sodium iodide system was found to be an useful reagent for the conversion of sulfoxides to corresponding sulfides.[5a] The reaction is relatively rapid and alkyl, aralkyl and dialkyl sulfides are formed in 70-95% yields after heating the corresponding sulfoxides for 10-60 min with this reagent in boiling acetonitrile. Obviously activation of triphenylphosphine by iodine seems to be the essential step of this reduction. The same system reduces both arene- and alkanesulfonic acids and even sulfuric acid and sulfate.[5b] In the excess iodine, alkanesulfonic and -sulfinic acids are directly converted to corresponding alkyl iodides via corresponding thiols.

3. Tris(dimethylamino)phosphine-Iodine-Sodium Iodide

A mixture of tris(dimethylamino)phosphine-iodine-sodium iodide system was found to be more effective than the system based on triphenylphosphine.[6] Thus, for example, diphenyl sulfoxide is completely reduced in 20 min instead of 1 hr, required with the reagent based on triphenylphosphine. In the case of aliphatic sulfoxides, no such catalyst as sodium iodide is necessary. Tris(dimethylamino)phosphine is clearly more useful than triphenylphosphine as a deoxygenation agent because of the facile work-up procedure. Hexamethylphosphotriamide, formed in this reaction as the main by-product, is completely miscible with water. Therefore, sulfides are isolated merely by extraction with ether and no column chromatograpgy is necessary for separation of the product mixture.

4. Phosphorus Triiodide (PI_3)

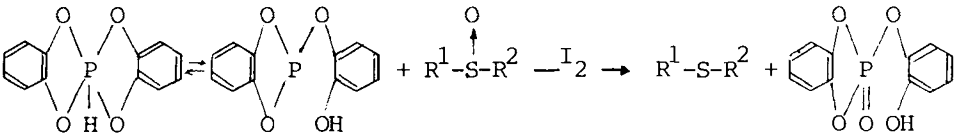
This readily available reagent, formed by treating phosphorus with iodine in carbon disulfide, was used recently for rapid deoxygenation of sulfoxides to corresponding sulfides.[7] The reaction takes place readily even at -78°, forming sulfides in 71-91% yields.

5. Diphosphorus Tetraiodide (P_2I_4)

Denis and Krief[8a] and Suzuki et al.[8b] have found independently that diphosphorus tetraiodide, a cheap, stable, readily prepared and easily handled trivalent phosphorus derivatives, is a useful deoxygenation reagent. P_2I_4 can convert various sulfoxides to corresponding sulfides at room temperature in less than 2 hrs. The work-up procedure is very simple, since all inorganic by-products are water soluble.

6. Phosphorane

Cyclic P-4 phosphorane (A) derived from catechol gives, in dichloromethane solution, a tautomeric form of phosphite (B) in an equilibrium. This trivalent tautomer reacts with sulfoxides in the presence of iodine to give the corresponding sulfides. This reaction is quite fast ($\leqslant$ 2 hrs) and takes place under very mild and neutral condition. Yields of sulfides are in the range of 91-100%.[9]

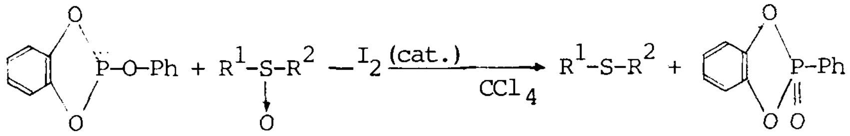


(5)

(A) (B)

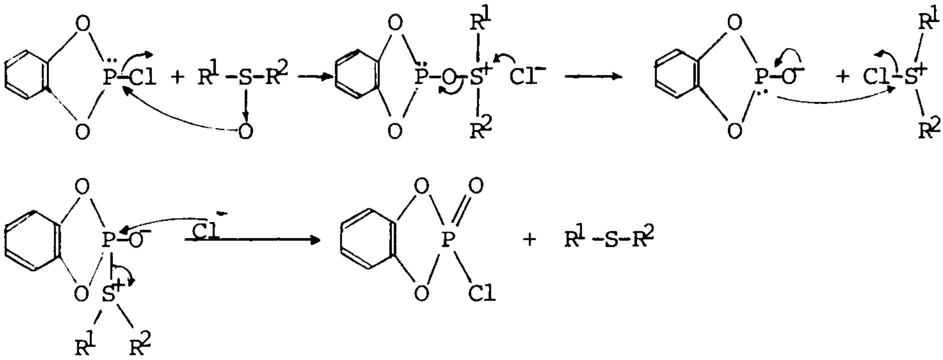
7. 2-Phenoxy(or Chloro)-1,3,2-benzodioxaphosphole

2-Phenoxy-1,3,2-benzodioxaphosphole in the presence of a trace amount of iodine reduces alkyl, aryl and aralkyl sulfoxides to the corresponding sulfides in good yields (more than 90%). However, this reaction requires an elevated temperature (70^{o}) or a longer reaction period (3 hrs), due to the poor solubilities of the sulfoxides in carbon tetrachloride,[10a] whereas 2-chloro-1,3,2-benzodioxaphosphole alone can reduce similar sulfo-



(6)

xides in short period (15-60 min) at room temperature in dichloromethane in excellent yields (90-100%).[10b] This reation may proceed through the following scheme.

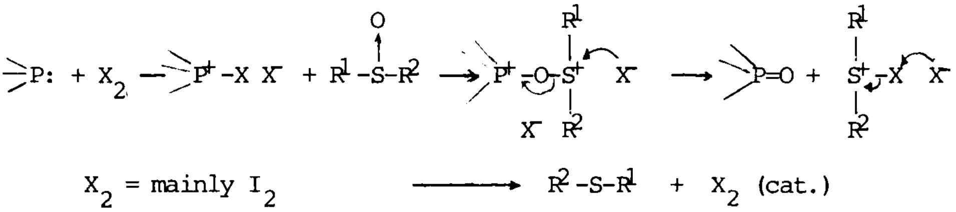


(7)

8. Triphenylphosphine-Carbon Tetrachloride

p-Substituted diaryl sulfoxides, $Ar_2S\to O$ (Ar = p-$CH_3C_6H_5$, etc.), can be reduced to the corresponding sulfides in good yields (80-100%) upon heating with triphenylphosphine in the presence of carbon tetrachloride for 2 hrs.[11] The active species is probably either $Ph_3P{=}CCl_2$ or Ph_3PCl_2 complex or both.

All the reactions depicted in 2, 3, 6, 7 and 8 proceed through the nucleophilic attack of oxygen of sulfoxide on the activated phosphorus atom as shown in the following scheme.

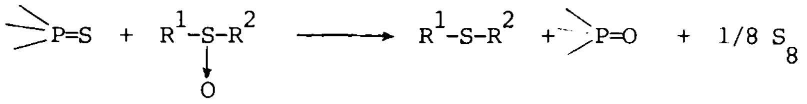


(8)

Meanwhile, in the reactions shown by Euations 4, 5 and 7, the oxygen atom of sulfoxide would directly attack the central phosphorus atom, since the central phosphorus atom in these phosphorus compounds is substantially activated by bonding to electronegative groups.

II. PENTACOVALENT PHOSPHORUS COMPOUNDS

The strong affinity of phosphorus atom toward oxygen seems to be responsible also for the deoxygenation of sulfoxides even in the reaction with several pentacoordinate phosphorus compounds. In the last few years, a few deoxygenation procedures of sulfoxides with thiophosphoryl derivatives have been reported. In this reaction, thiophosphoryl compounds are converted to corresponding phosphoryl derivatives according to the following general scheme (Eq. 9).



$$>P{=}S + R^1\text{-}\underset{\downarrow \atop O}{S}\text{-}R^2 \longrightarrow R^1\text{-}S\text{-}R^2 + >P{=}O + 1/8\ S_8 \qquad (9)$$

1. Phosphorus Pentasulfide

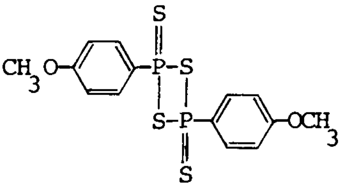
Micetich[12] reported in 1976 the successful reduction of some cephalosporin and penicillin sulfoxides using phosphorus pentasulfide. Subsequently, Still et al.[13] and Baechler et al.[14] applied this reagent generally and found that the conversion of sulfoxides to the corresponding sulfides with P_4S_{10} proceeds smoothly in dichloromethane or carbon disulfide at room temperature, with reaction time generally shorter than 4 hrs. Yields are in the range of 45-99%.

2. Thiophosphoryl Bromide

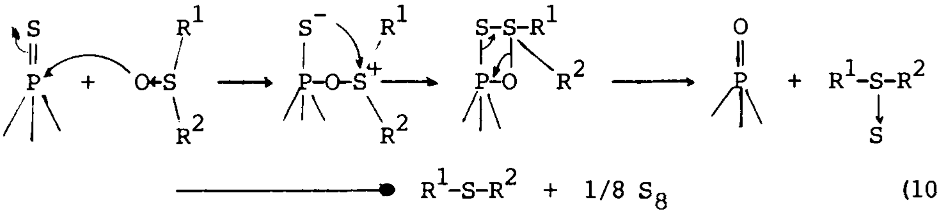
Thiophosphoryl bromide, which is readily available commercially, was found by Still et al.[15] to be, in many ways, a superior reagent to phosphorus pentasulfide in the conversion of sulfoxides to sulfides. It is readily soluble in most organic solvents and thus the reduction can be carried out under homogenous conditions. Although the reaction time required for completion was found to vary somewhat widely (10 min to 24 hrs) with thiophosphoryl bromide, the yields were generally much better (78-99%) than those in the analogous reaction with phosphorus pentasulfide. Thiophosphoryl chloride, however, has no reducing ability.

3. Dimer of p-Methoxyphenylthionophosphosphine Sulfide (Lawesson Reagent)

The dimer of p-methoxyphenylthionophosphine sulfide which is formed readily in high yields by treatment of p-methoxyphenyl-magnesium bromide with phosphorus pentasulfide, was found[16] to convert dimethyl sulfoxide and tetrahydrothiophene oxide to the corresponding sulfides in high yields. In this reaction, the corresponding disulfide, such as dimethyl disulfide and 1,2-dithiane respectively, were also formed in minor yields.



All the reactions described in II.1-II.3 proceed through the nucleophilic attack of the oxygen of the sulfoxide on the phosphorus atom through a transition state shown in the following scheme (Eq.10).

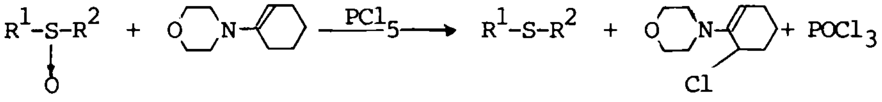


(10)

The driving force in these reductions is undoubtedly the formation of P=O linkage which has a larger (about 10 kcal/mol) bond energy than that of P=S linkage.

4. Phoshorus Pentachloride-Enamine or Amine

Recently phosphorus pentachloride was found to react with various sulfoxides in the presence of 1-morphorino-1-cyclohexene to afford corresponding sulfides and enamine of 2-chlorocyclohexanone.[17] The mechanism of this reaction is not clear. Reaction time was generally found to be shorter than 1 hr even below room temperature and sulfides

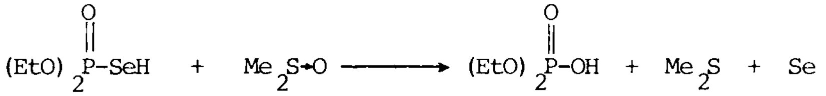


(11)

were isolated in yields of 79-99%.

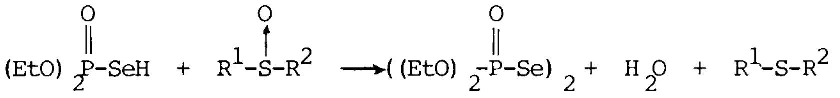
5. O,O-Dimethyl Hydrogen Phosphoroselenate

In 1966 Mikołajczyk[18] reported that O,O-diethyl hydrogen phosphoroselenate reduces dimethyl sulfide to dimethyl sulfide as shown in the following equation.



$$(EtO)_2\overset{O}{\overset{\|}{P}}\text{-SeH} + Me_2S{\rightarrow}O \longrightarrow (EtO)_2\overset{O}{\overset{\|}{P}}\text{-OH} + Me_2S + Se \qquad (12)$$

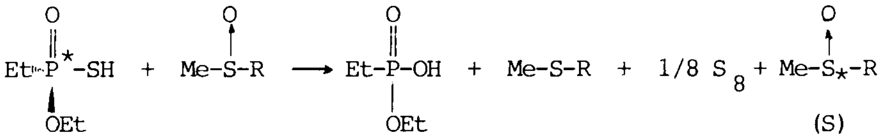
Clives et al.[19] have also used this reagent recently for reduction of various sulfoxides to corresponding sulfides. They found that the treatment of sulfoxides with equivalent amounts of O,O-diethyl hydrogen phosphoroselenate in an inert atmosphere in chloroform solution for 1-24 hrs at room temperature or at refluxing temperature afforded sulfides in 74-97% yields as shown in the following equation.



$$(EtO)_2\overset{O}{\overset{\|}{P}}\text{-SeH} + R^1\text{-}\overset{O}{\overset{\uparrow}{S}}\text{-}R^2 \longrightarrow ((EtO)_2\text{-}\overset{O}{\overset{\|}{P}}\text{-Se})_2 + H_2O + R^1\text{-S-}R^2 \qquad (13)$$

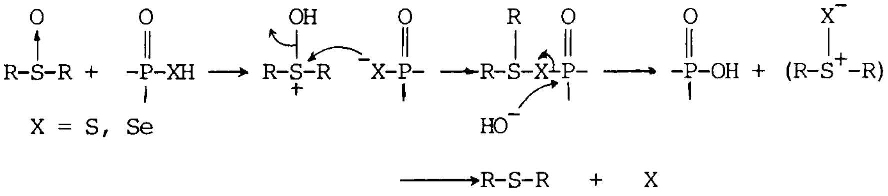
6. O-Ethyl Ethylphophonothioic Acid

O-Ethyl ethylphosphonothioic acid can reduce sulfoxide to sulfide. Milołajczyk[20] was able to recover this optically active sulfoxide (o.p. 3-4%) in the reaction of racemic sulfoxide and optically active O-ethyl ethylphosphonothioic acid.



$$\text{Et-}\underset{OEt}{\overset{O}{\overset{\|}{P^*}}}\text{-SH} + \text{Me-}\overset{O}{\overset{\uparrow}{S}}\text{-R} \longrightarrow \text{Et-}\underset{OEt}{\overset{O}{\overset{\|}{P}}}\text{-OH} + \text{Me-S-R} + 1/8\ S_8 + \underset{(S)}{\text{Me-}\overset{O}{\overset{\uparrow}{S_*}}\text{-R}} \qquad (14)$$

All these reactions may proceed through the following pathway.



$$\text{R-}\overset{O}{\overset{\uparrow}{S}}\text{-R} + \text{-}\overset{O}{\overset{\|}{P}}\text{-XH} \longrightarrow \text{R-}\overset{OH}{\underset{+}{S}}\text{-R}\ \ {}^{-}\text{X-}\overset{O}{\overset{\|}{P}}\text{-} \longrightarrow \text{R-}\overset{R}{\overset{|}{S}}\text{-X-}\overset{O}{\overset{\|}{P}}\text{-} \longrightarrow \text{-}\overset{O}{\overset{\|}{P}}\text{-OH} + (\text{R-}\overset{X^-}{\overset{|}{S^+}}\text{-R})$$

$$HO^- \qquad X = S,\ Se$$

$$\longrightarrow \text{R-S-R} + X \qquad (15)$$

III. ORGANOSILICON COMPOUNDS

In many organosilicon compounds represented by R_3SiX, the central silicon atom is considered to be the hard acid center and nucleophilic substituent, X, usually behaves as a soft base. Therefore, they can react very readily with organic compounds containing oxygen (which is considered to behave as the center of a hard base) forming a very strong silicon-oxygen bond. The anion, X^-, formed in the initial reaction, acts as a strong nucleophile in the subsequent displacement step, to result in the cleavage of the S-O bond, since the reaction is usually carried out in aprotic media. This general scheme has recently been used in a few successful reductions of sulfoxides to corresponding sulfides.

$$R^1\text{-}S_{\to O}\text{-}R^2 + 2\,R_3SiX \longrightarrow R^1\text{-}S\text{-}R^2 + X_2 + R_3SiOSiR_3 \qquad (16)$$

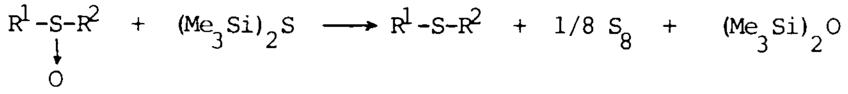
1. Trimethylsilyl Halides

Olah et al.[21] have investigated the reaction of sulfoxides with either iodotrimethylsilane-iodine system, as a source of iodotrimethylsilane. Alkyl, aralkyl and diaryl sulfoxides were found to be reduced effectively upon stirring with two equimolar amounts of either one of these halosilane systems at room temperature in less than 2 hrs. Hexamethyldisiloxane and halogen were formed as by-products while sulfides were obtained in 80-90% yields. Later, Olah et al.[22] found that this reduction of sulfoxides actually proceeds by the reaction with iodotrimethylsilane formed _in situ_ by the addition of chlorotrimethylsilane into a solution of sodium iodide and sulfoxide in acetonitrile. They also found that iodide can be replaced by other "soft" bases such as CN^-, CH_3S^-, S^-, NCS^-, $SO_3^{\,2-}$. Oae _et al_.[23] have found deoxygenation of sulfoxides can also be achieved by treatment with chlorotrimethylsilane-thiol system. Thus treatment of various sulfoxides with RSH/Me_3SiCl (R = Ph, Bu, Pr) in ethyl ether at room temperature under nitrogen atmosphere gave corresponding sulfides in 73-100% yields. When various sulfoxides were allowed to react with two equivalents of chlorotrimethylsilane in the presence of an equivalent amount of powdered zinc at room temperature below 30°, the corresponding sulfides were obtained in 77-94% yields.[24] Zinc chloride and hexamethylsiloxane were formed as by-products.

$$R^1\text{-}S\text{-}R^2 + 2\ Me_3SiCl \xrightarrow{Zn} R^1\text{-}S\text{-}R^2 + (Me_3Si)_2O + ZnCl_2 \tag{17}$$

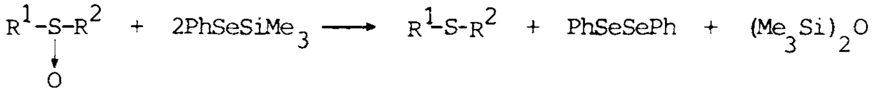
2. Trimethylsilyl Sulfide or Selenide

This new type of silicon reagent have been used for the reduction of sulfoxides by Soysa and Weber,[25] who found actually that either bis(trimethylsilyl) sulfide or hexamethylcyclotrisilatrithiane reacts with sulfoxides in organic solvents ($CHCl_3$, CH_2Cl_2, xylene) to give the corresponding sulfides in high yields (65-100%), along with siloxanes and elemental sulfur as by-products. Thiosulfoxides may be the intermediate



$$R^1\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R^2 + (Me_3Si)_2S \longrightarrow R^1\text{-}S\text{-}R^2 + 1/8\ S_8 + (Me_3Si)_2O \tag{18}$$

in this reaction. It is interesting to note that neither an α-keto nor an α-chloromethyl group directly combined to a sulfinyl function, such as in ω-(methanesulfinyl)acetophenone or chloromethyl phenyl sulfoxide, is reduced by these disilyl or trisilyl sulfide derivatives. Later, Detty[26] reported that sulfoxides were reduced to corresponding sulfides with two equivalents of phenylselenotrimethylsilane in very high yields even when sulfoxides bear various reducible functional groups. The reaction, generally depicted by Eq. 19, is complete within a few minutes, while work up can be carried out without water, to isolate the products. Detty and



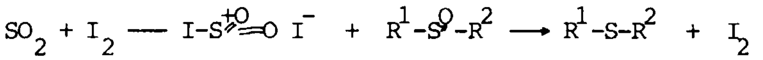
$$R^1\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R^2 + 2PhSeSiMe_3 \longrightarrow R^1\text{-}S\text{-}R^2 + PhSeSePh + (Me_3Si)_2O \tag{19}$$

Seidler have recently reported that bis(trimethylsilyl)sulfide, selenide and telluride, $Me_3SiXSiMe_3$ (X = S, Se, Te), also reduces sulfoxides to sulfides.[27] It is also interesting to note that phenylthiotrimethylsilane can reduce the sulfoxide to the corresponding sulfide in the presence of a catalytic amount of an ammonium halide, while the reaction is very slow in the absence of ammonium halide.[23] These reactions proceed _via_ initial silylation of oxygen of sulfoxide and the subsequent nucleophilic attack of X^- on the activated central sulfur atom as in the reaction shown by Eq. 16.

IV. SULFUR COMPOUNDS

1. Sulfur Oxide-Halogen

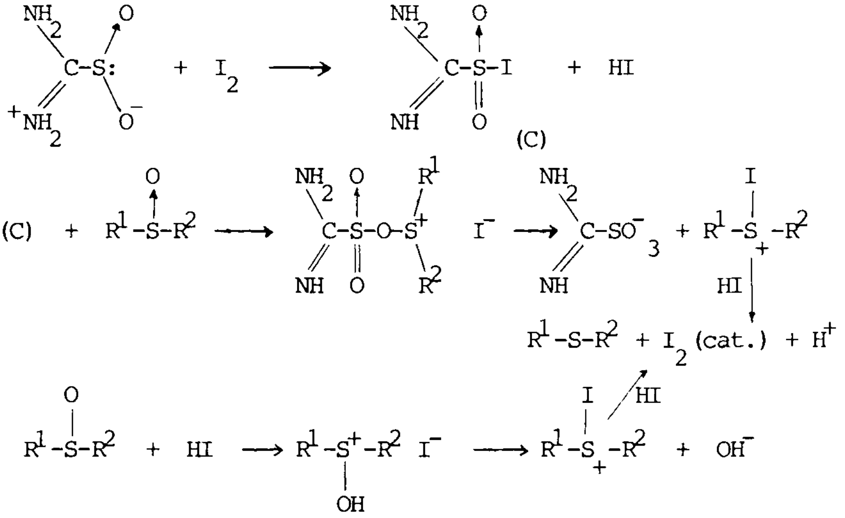
A sulfur dioxide-iodide (or bromine) complex was found to convert sulfoxides to corresponding sulfides when the reaction is carried out at 80° in acetonitrile.[28] Olah et al.[29] recently reported that a mixture of trimethyl (or triethyl)amine-sulfur dioxide along with iodine and sodium iodide in acetonitrile can reduce aliphatic sulfoxides to corresponding sulfides in 78-90% yields at room temperature. Aromatic sulfoxides, however, even upon heating in refluxing acetonitrile, afforded only low yields ($\leq$ 25%) of the corresponding sulfides, whereas a mixture of pyridine-sulfur trioxide complex with sodium iodide reduces both aliphatic and aromatic sulfoxides to corresponding sulfides at room temperature in 80-91% yields. The reaction probably proceeds through the following scheme.



$$SO_2 + I_2 \;—\; I{-}\overset{+O}{S}{=}O\ I^- \;+\; R^1{-}\overset{O}{S}{-}R^2 \longrightarrow R^1{-}S{-}R^2 \;+\; I_2 \qquad (20)$$

2. Formamidinesulfinic Acid

Formamidinesulfinic acid, which is easily prepared by oxidation of thiourea with two equivalent of hydrogen peroxide, was found to reduce sulfoxides to corresponding sulfides in the presence of a catalytic amount of iodine.[30] Thus, dialkyl, alkylaryl and diaryl sulfoxides are all converted to corresponding sulfides in yields exceeding 90% after heating in refluxing acetonitrile for a short time (20 min). The reaction may proceed through the following competitive reactions by both HI and $NH_2C(SO_2H)=NH$.



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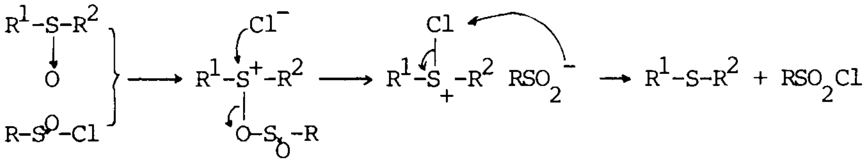
3. Alkane- and Arenesulfinic Acid

Methane- and p-toluenesulfinic acids can reduce dialkyl, alkylaryl and diaryl sulfoxides to corresponding sulfides, while the sulfinic acids are oxidized to the sulfonic acids, in high yields at 40° for 6-20 hrs without solvent, though the reduction of diaryl sulfoxides is slow. Interestingly, the reaction proceeds through a homolytic process.[31]

4. Alkane- and Arenesulfinyl Chlorides

Methanesulfinyl chloride can reduce dialkyl, aralkyl and diaryl sulfoxides at room temperature for 0.5 hr to give the corresponding sulfides and the sulfonyl chlorides in refluxing benzene.[32] p-Nitrobenzenesulfinylchloride can also reduce sulfoxides to sulfides in refluxing benzene.[32]



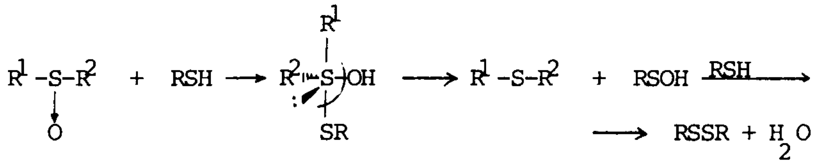
(22)

5. Thiol and Selenol

Thiols are known to be oxidized by dimethyl sulfoxide.[33] Thus, thiols are good reducing agents. Actually, cysteine, cysteamine and glutathione are important also as reducing agents in biological systems. Sulfoxides can be reduced to sulfides by various kinds of thiols.[34] The relative reactivity is as shown below,[35] while relative reducing abilities

$$(CH_3)_2S{\rightarrow}O > (CH_2)_4{-}S{\rightarrow}O > ((CH_3)_2CH)_2S{\rightarrow}O > ((CH_3)_3C)_2S{\rightarrow}O$$

of thiols fall in the following order, ArSH > AralkylSH > AlkylSH. In this reaction, both the acidity of thiol and the basicity of sulfoxide are very important because the addition of either base[36] and acid[37] accelerate the reduction. Therefore, highly acidic dithiocarboxylic acids, $RC\overset{S}{=}SH$ (pK_a = 2.5)[38], dithiophosphoric acids (pK_a = 1.8)[39], can reduce sulfoxide very rapidly. Since the selenol is similar to the thiol but more acidic (pK_a = 5.48), it can reduce sulfoxides very readily to sulfides.[40] All these reactions appear to proceed through the following scheme. Though H_2S,[41] thiols,[42] and dimethyl sulfide[43] are mild reducing agents, the reduction of sulfoxide is accelerated remarkably in the presence of acylating agent such as $(CF_3CO)_2O$.

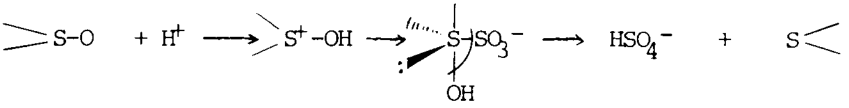

(23)

6. Sodium Metabisulfite ($Na_2S_2O_5$)

The reduction of sulfoxides with $Na_2S_2O_5$[44] is rather convenient, because this reagent is an inorganic compound and reducible functional groups such as C=O, OH, C=C and COOR are not reduced. The mechanism of this reaction is not known, however, the reaction is complete in 20 hrs at 90° in high yields.

7. Sodium Sulfite ($NaHSO_3$)

It is known that the reduction of sulfoxides by $NaHSO_3$ proceeds by the nucleophilic attack of SO_3^{2-} on the sulfur atom of the sulfoxide.[45] The reaction proceeds through the following pathway involving addition of SO_3^{2-}, followed by ligand coupling. The cis-isomer of 2-methylthiolane oxide can be reduced more readily than the trans-derivative.



(24)

V LOW VALENT METAL

1. Chromium(II) Dichloride

Diphenyl and dibenzyl sulfoxides were deoxygenated to corresponding sulfides in low yields (20-24%) upon refluxing with chromium(II) chloride in methanol for 2 hrs.[46]

2. Titanium(II) Chloride

Titanium(II) chloride, which is readily prepared by treating titanium (IV) chloride with zinc dust, was found to be a very useful reagent for the reduction of sulfoxides.[47] Thus, dialkyl, arylalkyl and diaryl sulfoxides are all reduced to corresponding sulfides smoothly at room temperature when zinc dust is added to an etheral solution of sulfoxide and titanium(IV) chloride or alternatively when a dichloromethane solution of sulfoxide is added to an etheal solution of titanium(II) chloride prepared by reduction of titanium(IV) chloride by zinc dust just before use. Later, titanium(II) chloride, prepared by treatment of titanium(IV) chloride with sodium borohydride in diglyme was also found to reduce sulfoxides to sulfides.[48] Low valent titanium compounds, prepared in the reaction between titanium(IV) chloride and lithium hydride[49] or lithium aluminum hydride,[50] also reduce sulfoxides smoothly to corresponding sulfides. Titanium(III) chloride can also reduce sulfoxides smoothly in good yields.[51]

3. Molybdenum Hexacarbonyl

When dialkyl, arylalkyl and diaryl sulfoxides were treated with excess molybdenum hexacarbonyl and acetic acid in refluxing chloroform, the corresponding sulfides were obtained in relatively short periods of time and the yields can be substantial (25-90%).[52]

4. Iron Pentacarbonyl

Iron pentacarbonyl can reduce dialkyl, aralkyl, diaryl sulfoxides to the corresponding sulfides in good yields(50-90%) at 130-135° for 3-8 hrs in diglyme.[53] However, in the case of penicillin sulfoxide, the yield of the reduced sulfide was poor(12%).

5. Cobalt(III) Chloride-Sodium Borohydride

Diaryl and arylalkyl sulfoxides can be reduced to the corresponding sulfides by treatment with $NaBH_4$ in the presence of $CoCl_2$ at room temperature for 2 hrs in ethanol in high yields(95-100%).[53]

6. Others

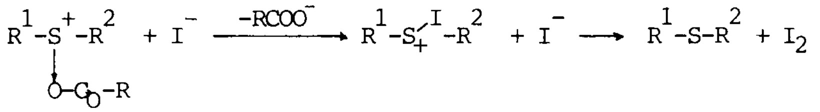
$MoCl_3$-Zn,[55] VCl_2,[55] $K_3W_2Cl_9$,[56] $(NH_4)_4Mo_2Cl_8$ NH_4Cl,[56] $Cs_3Mo_2Cl_8H$[56] K_3MoCCl_6,[56] $SnCl_2$,[57] and Rh(III)H_2[58] can also reduce sulfoxides bearing various functional groups such as epoxy, ketone, ester, nitrile and nitro groups selectively under mild conditions for a few hours in high yields under inert atmosphere, though the mechanism of these reductions are not known at all. Probably the reaction proceeds via the initial coordination of oxygen of sulfoxide to the central metal atom and then one electron transfer from metal to sulfur would take place.

VI. REDUCTION OF SULFOXIDES VIA ACTIVATION OF SULFINYL OXYGEN

The formation of acyloxysulfonium salt in the treatment of sulfoxide with oxalyl chloride was proposed to be a key step in the reduction of sulfoxide with an oxalyl chloride-sodium iodide system. The reaction is usually conducted at 0° or at room temperature by addition of oxalyl chloride to a solution of sulfoxide and sodium iodidide in acetonitrile. Yields of sulfoxides and sodium iodide are generally high(70-90%) while no chlorinated by-product is formed. Diphenyl sulfoxide was found to be reduced efficiently by treatment with other acid chlorides, such as $SOCl_2$, $POCl_3$ and PCl_5, in the presence of sodium iodide.[59] Formation of alkoxysulfonium salts in the reaction between sulfoxides and cyanuric chloride or fluoride is also the initial step of the deoxygenation of sulfoxides by these two reagents. Diaryl sulfoxides were found to undergo facile conversion into the corresponding sulfides when the sulfoxides were treated with cyanuric chloride in refluxing dioxane.[60] Arylalkyl and diaryl sulfoxides, however, were found to react with cyanuric chloride exothermally yielding complex mixtures of chlorinated products.

When cyanuric fluoride was used instead of cyanuric chloride, both arylalkyl and diaryl sulfoxides were converted smoothly to the corresponding sulfides without formation of halogenated by-products.

Similarly, acylating agents such as $(CF_3CO)_2O$,[61] CH_3COCl[62] can also reduce functionalized(e.g. COOH) sulfoxides instantly in quantitative yields. The reduction proceeds throguh the initial formation of an acyloxysulfonium and halide ion,e.g. iodide functions as a reducing agent as shown in Eq.25. Activation of sulfinyl oxygen by protonation seems to



$$R^1\text{-}\underset{O\text{-}C(O)\text{-}R}{\overset{+}{S}}\text{-}R^2 + I^- \xrightarrow{-RCOO^-} R^1\text{-}\overset{I}{S^+}\text{-}R^2 + I^- \longrightarrow R^1\text{-}S\text{-}R^2 + I_2$$

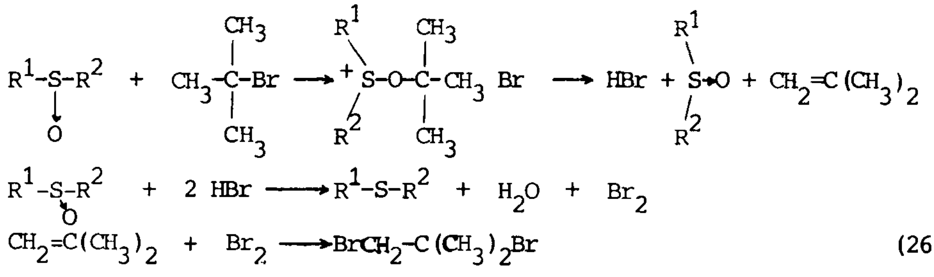
(25)

be an essential step in the reduction of diaryl sulfoxides by anhydrous hydrogen chloride in chloroform solution. Chasar et al.[63a] have found that this system can best be used for the reduction of diaryl sulfoxides in which the aromatic groups are not activated toward electrophilic attack.

When the aromatic ring is activated strongly for electrophilic attack, the main reaction is the reductive chlorination of the starting sulfoxide. However, HBr or HCl generally cannot reduce sulfoxides, though HI can reduce slfoxides to sulfides easily.[63b] Therefore, iodide is an effective reducing agent for various sulfoxides in the presence of an acid to afford the corresponding sulfides in quantitative yields.[64]

In the reduction of substituted aryl methyl sulfoxides with iodide in the presence of acids (Acid/KI,[65] $HClO_4$/KI[66]), the Hammett correlation of the rates of this reaction gave a considerably large negative ρ value ($\sim$-0.9) and the rate, v, of the reduction is lowered markedly by steric bulkiness of the group, R, in $R\text{-}\overset{O}{S}\text{-}Ph$. The rate of the reaction, v, can be expressed as $v = k(\text{sulfoxide})^1(HI)^2$.[65,67] Meanwhile, the rate of reduction of cyclic sulfoxides by HI(KI/$HClO_4$) depends mainly on $S^{\ddagger}$.[68]

The unstable alkoxysulfonium bromide is believed to be the initial intermediate in this sequential reaction which eventually results in the reduction of sulfoxides by heating with an excess of t-butyl bromide at 80°. By this procedure[69] as depicted by Eq. 26, a wide variety of sulfoxides have been reduced through the following path.



$$R^1\text{-}\underset{\underset{O}{\downarrow}}{S}\text{-}R^2 + CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}Br \longrightarrow \overset{R^1}{\underset{R^2}{\overset{+}{S}}}\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_3\ Br \longrightarrow HBr + \overset{R^1}{\underset{R^2}{S}}\!\rightarrow\! O + CH_2{=}C(CH_3)_2$$

$$R^1\text{-}\underset{O}{S}\text{-}R^2 + 2\ HBr \longrightarrow R^1\text{-}S\text{-}R^2 + H_2O + Br_2$$

$$CH_2{=}C(CH_3)_2 + Br_2 \longrightarrow BrCH_2\text{-}C(CH_3)_2Br \qquad (26)$$

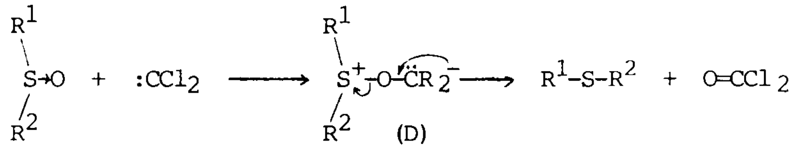
VII. Dichlorocarbene

Sulfoxide can be deoxygenated by carbene species which are electron-deficient. This was first shown by Oda[70] and later studied in detail by Weber.[71] Dichlorocarbene, generated *in situ* (from chloroform and 50%

sodium hydroxide) under phase-transfer conditions can deoxygenate most sulfoxides to the corresponding sulfides in high yields at room temperature for 20 hrs, forming phosgene as the by-product. Yields vary

$$R^1\text{-}S^{O}\text{-}R^2 + :CCl_2 \longrightarrow R^1\text{-}S\text{-}R^2 + COCl_2 \qquad (27)$$

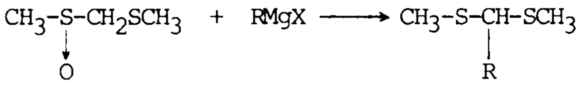
(20-96%) but are generally higher for diaryl sulfoxides than for dialkyl sulfoxides. Very recently Dyer and Evans[72] have carried out a detailed mechanistic study of this reaction and fully confirmed the observation of Soysa and Weber. They also observed a marked steric acceleration with the increase of the steric reqiurement of R group and the retardation of the reduction by resonance interaction of sulfoxide group with aromatic rings. Thus, the reactivities of sulfoxides fall in the following order, $(\underline{t}\text{-Bu})_2S{\to}O > (\underline{i}\text{-Pr})_2S{\to}O > Ph_2S{\to}O > Me_2S{\to}O$.[72] The sterically hindered sulfoxides can be reduced more readily. The reaction proceeds via the following scheme. The rate-determinig step is the decomposition of zwitter ion(D).



$$R^1R^2S{\to}O + :CCl_2 \longrightarrow R^1R^2\overset{+}{S}\text{-}O\text{-}\ddot{C}R_2^{-}\ (D) \longrightarrow R^1\text{-}S\text{-}R^2 + O{=}CCl_2 \qquad (28)$$

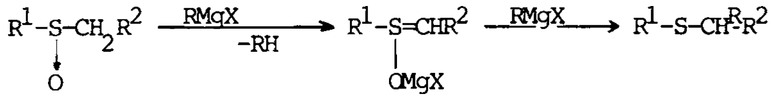
VIII. GRIGNARD REAGENT

As early as 1961, dimethyl sulfoxide was shown to react with the Grignard reagents, RMgX, to give α-alkylated sulfides, $CH_3\text{-}S\text{-}CH_2R$, with concomitant formation of much olefines derived from the Grignard reagent.[73] Later, the following reductive α-alkylation of methylthiomethyl sulfide with the Grignard reagent was reported by Hojo et al..[74]



$$\underset{\downarrow\atop O}{CH_3\text{-}S}\text{-}CH_2SCH_3 + RMgX \longrightarrow CH_3\text{-}S\text{-}\underset{|\atop R}{CH}\text{-}SCH_3 \qquad (29)$$

A similar reaction was already described by Manya in 1970.[75] The reaction is presumed to proceed through the following Pummerer type scheme.



$$R^1\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}CH_2R^2 \xrightarrow[-RH]{RMgX} R^1\text{-}\underset{\substack{|\\ OMgX}}{S}{=}CHR^2 \xrightarrow{RMgX} R^1\text{-S-}\overset{R}{CH}\text{-}R^2 \qquad (30)$$

Recently, Posner and Tang[76] have reported that alkenyl sulfoxides can be reduced to the corresponding sulfides efficiently by treatment with ethylmagnesium bromide and 10% cuprous iodide at 0° for 1 hr. No double bond isomerization was observed during the reduction and also 1, 3-butandienyl sulfoxides were reduced cleanly to 1,3-butadienyl sulfides.

IX. BORONSULFIDE AND BORONSELENIDE

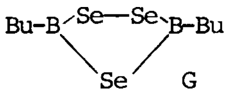
The deoxygenation of sulfoxides was found to be achieved by Baechler et al.,[77a] using a new reagent, i.e. BX_3 (X = S, Se). They have found that treatment of variuos sulfoxides with boron sulfide (B_2S_3) gave the orresponding sulfides in high yields. Recently, the compounds with selenium boron compounds was also used for the same purpose by Clive and Menchen.[77b] The compounds (E, F, G) were found to deoxygenate sulfoxides efficiently and fairly rapidly even at room temperature. Yields were in the range of 74-97%. However,in the reduction of cephalosporin sulfoxide, the corresponding sulfide was isolated in 25% yield only after refluxing in chloroform for 24 hrs.

$B(SeMe)_3$

E

$B(SePh)_3$

F



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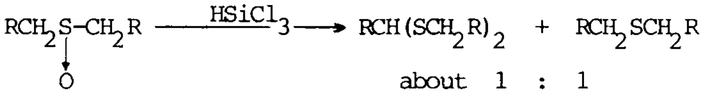
X. HYDRIDE REAGENT

Sulfoxides can be readily reduced by treatment with various aluminium hydride reagents such as $LiAlH_4$, $LiAlH(OMe)_3$, at 0° for a few hours in quantitative yields.[78] This reaction requires two equivalents of hydride species(H:$^-$) to give one equivalent of hydrogen gas and the sulfide, and is considered to proceed by the direct nucleophilic attack of hydride, H:$^-$, on the sulfur atom. One interesting application is a partial asymmetric reduction of racemic sulfoxide with an optically active $LiAlH_{4-n}(OR^{*})_n$ (R^{*} = (+)-quinidine). Thus the recovered sulfoxide was found to retain 0.2-2.7% of optical activity.[79] No boron hydride agent can reduce the sulfoxide group except B_2H_6 which can reduce the sulfoxide slowly;[80] however the alkoxysulfonium group can be reduced not only with $NaBH_4$[81] but also with $NaBH_3CN$[82] which is a weak reducing agent. $NaBH_3CN$ can also reduce keto-sulfoxides to keto-sulfides in good yields.

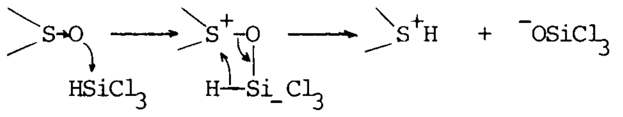
Since silicon has a strong oxygen affinity, Cl_3SiH[83a] can also reduce sulfoxides to sulfides at room temperature to 0° in a few hours; the yields of diaryl sulfides obtained in the reduction of diaryl sulfoxides are high (≧ 85%). However, in the case of dialkyl sulfoxides, the yields of the reduction products are not high and thioacetals are formed as by-products. In the reduction of p-substituted diaryl sulfoxides, the



$$RCH_2\underset{\downarrow\atop O}{S}-CH_2R \xrightarrow{HSiCl_3} RCH(SCH_2R)_2 + RCH_2SCH_2R \qquad (31)$$

about 1 : 1

rate of reaction, v, was shown by v = k(sulfoxide)^1($HSiCl_3$)^1, and the Hammett correlation of the rate gave ρ value of -1.54. Thus the reaction is considered to proceed through the nucleophilic attack of terminal oxygen of the sulfoxide on the silicon as shown below.



$$>S\to O \xrightarrow{HSiCl_3} >\overset{+}{S}-O\cdots H-Si\_Cl_3 \longrightarrow >\overset{+}{S}H + {}^{-}OSiCl_3 \qquad (32)$$

Reduction of diaryl sulfoxides and sulfilimines to corresponding sulfides by both $NaBH_4$ and 1-benzyl-1,4-dihydronicotinamide(BNAH) have been found to proceed in the presence of a catalytic amount of metallo-<u>meso</u>-tetraphenylporphins in excellent yields. The catalytic ability of metalloporphin in the reduction of sulfoxide with BNAH increases with the decrease of the reduction potential of the catalyst, thus in the order of TPPFe(III)$^+$> TPPCo(II) > TPPCu(II).[83b]

XI. PHOTODEOXYGENATION

Non-functionalized diaryl and arylalkyl sulfoxides can be deoxygenated with low pressure Hg arc lamp or Hanovia H-450W medium pressure lamp in high yields in benzene at 45-50° for 10-23 hrs.[84] The singlet oxygen, produced *in situ*, was trapped with cyclohexene in 41% yield. But this reduction can be applied only to certain aryl sulfoxides.

XII. OTHERS

Though a few examples of the reduction of sulfoxides by hydrogenation are known,[85] this method cannot be used in general because of the poisoning of the catalyts by divalent sulfur compounds. In a typical run, the reduction of dibenzyl sulfoxide was carried out in ethanol containing Pd-C with the hydrogen of 79 atmospheric pressure at 80-90° for a few days, and the correspnding sulfide was obtained in 90% yield.

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