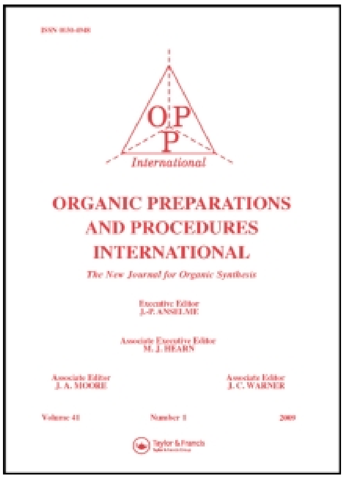

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SYNTHESIS OF SULFOXIDES. A REVIEW

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INTRODUCTION

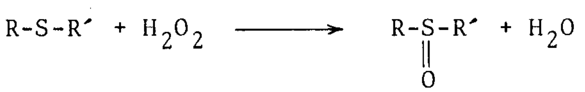
The preparative application of organic sulfoxides in modern organic synthesis is a subject of considerable current interest. For this reason much attention was directed toward the elaboration of efficient methods for the preparation of sulfoxides. Earlier methods for the synthesis of sulfoxides have been reviewed up to 1955.[1] Johnson and Sharp[2] in their review on the chemistry of sulfoxides for the period 1961--1966 have also collected some methods of synthesis of sulfoxides. Recently, in the book "Organic Sulfur Chemistry" edited by Oae the most important methods of synthesis of sulfoxides are summarized[3]. The intention of this review is to present exhaustively the methods for the preparation of sulfoxides and to briefly discuss their scope, limitations and mechanisms.

1. OXIDATION OF SULFIDES

The oldest very convenient and most widely applied sulfoxide synthesis consists of the oxidation of sulfides to sulfoxides. Since 1865, when Märcker[4] first described the synthesis of dibenzyl sulfoxide by oxidation of dibenzyl sulfide with nitric acid, the oxidation of sulfides to sulfoxides has been the subject of extensive study and various synthetic procedures are now available. They will be discussed below with indication of their advantages and limitations.

1.1. Oxidation by Hydrogen Peroxide

Hydrogen peroxide alone or in the presence of various catalysts is the most commonly used reagent to convert sulfides to sulfoxides. Generally, this reaction can be described by the following equation.

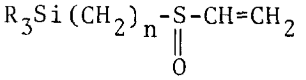


$$R\text{-}S\text{-}R' + H_2O_2 \longrightarrow R\text{-}\underset{\underset{O}{\|}}{S}\text{-}R' + H_2O \qquad (1)$$

The major difficulty encountered in the preparation of sulfoxides by this method is a facile over-oxidation to the corresponding sulfones.

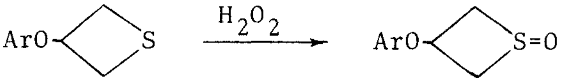
1.1.1. Hydrogen Peroxide

Gazdar and Smiles[5] and Hinsberg[6] reported independently in 1908 that sulfides may be oxidized quantitatively to sulfoxides by hydrogen peroxide in acetone or aqueous solution at romm temperature. This reagent has been used for the synthesis of aliphatic, aromatic and heterocyclic sulfoxides.[7,8] The only drawback is the relatively long reaction time needed for completion of the oxidation. Since this procedure is very mild it can be successfully applied to the preparation of the acid sensitive sulfoxides, such as allyl sulfoxides[9] or silyl-substituted vinyl sulfoxides[10] of structure I.



$R_3Si(CH_2)_n-\underset{\underset{O}{\|}}{S}-CH=CH_2$ I

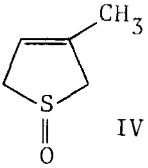
Sander[11] found that treatment of thietane II with hydrogen peroxide gave thietane sulfoxide III in 65% yield.



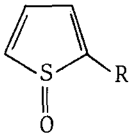
II III (2)

Mesityl ferrocenyl sulfoxide was prepared from the corresponding sulfide by oxidation with hydrogen peroxide in aqueous potassium hydroxide solution at pH 7-9.[12] Prilezhajeva et al.[13] found that unsaturated sulfides can be oxidized selectively to sulfoxides by hydrogen peroxide in acetic anhydride at room temperature in 68-89% yield.

3-Methyl-2,5-dihydrothiophene-1-oxide (IV) was prepared[14] in 57% yield from the corresponding sulfide with hydrogen peroxide in acetone solution at 0^o.



IV

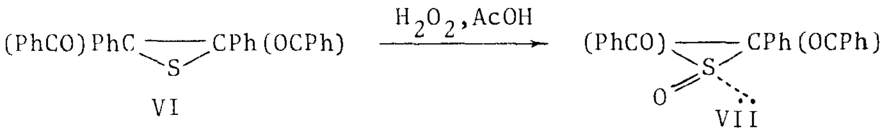


V

By the same procedure the sulfoxides derived from thiophene as well as the substituted thiophene sulfoxides V were also obtained.[15]

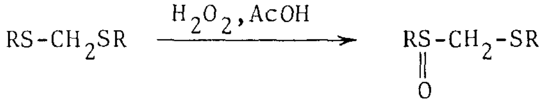
1.1.2. Hydrogen Peroxide in the Presence of Acid

Oxidation of sulfides to sulfoxides by hydrogen peroxide has been found to be subject to acid catalysis.[5] Sulfuric, perchloric[16] and acetic acids[5] are most commonly used as catalysts. By means of this procedure some sulfoxides of more than routine interest were synthesized.[17] Dittmer and Levy[18] found, for instance, that oxidation of dibenzoyl stilbene episulfide (VI) with hydrogen peroxide in acetic acid gave two diastereomers of sulfoxide VII.



VI VII (3)

Oxidation of dithioacetals VIII to the corresponding monooxides IX using hydrogen peroxide in acetic acid was reported by Tsuchihashi[19] and Schill.[20]



$$\mathrm{RS\text{-}CH_2SR} \xrightarrow{\mathrm{H_2O_2,AcOH}} \underset{\underset{\mathrm{O}}{\|}}{\mathrm{RS}}\mathrm{\text{-}CH_2\text{-}SR} \qquad (4)$$

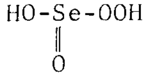
VIII IX

1.1.3. Hydrogen Peroxide in the Presence of Vanadium Pentoxide

Sulfides are oxidised to sulfoxides with hydrogen peroxide in absolute t-butyl alcohol containing a catalytic amount of vanadium pentoxide at 15°.[21] Conversion of sulfides to sulfones takes place at 45°. The oxidation of sulfides to sulfoxides by this method is very advantageous and was applied to the oxidation of labile sulfides such as α-chlorosulfides and α-acetoxysulfides. From the synthetic point of view, it is interesting to note that vanadium pentoxide, in addition to its catalytic action, functions also as an indicator in this reaction. In the presence of hydrogen peroxide, the reaction mixture is orange while in the absence of hydrogen peroxide a pale yellow color is observed. Thus, it is possible to perform the oxidation reaction as a titration ensuring that an excess oxidant is never present.

1.1.4. Hydrogen Peroxide/Selenium Dioxide System

Recently Drabowicz and Mikołajczyk[22] reported a highly selective and rapid oxidation of sulfides to sulfoxides using hydrogen peroxide/selenium dioxide system. The reaction takes place immediately upon addition of a solution of hydrogen peroxide and selenium dioxide to a solution of sulfide in methanol at room temperature. Dialkyl, aralkyl and diaryl sulfoxides are obtained in 80-95% yield. As far as the nature of the reagent is concerned, it is most probable that perseleninic acid acid (X) is the true oxidizing agent.



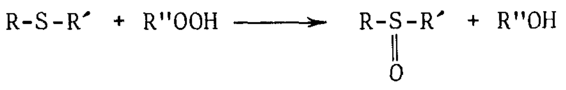
$$\mathrm{HO{-}\underset{\substack{\| \\ O}}{Se}{-}OOH}$$

X

In this context it is interesting to note that Reich *et al.*[23] recently described the oxidation of methyl phenyl sulfide to the corresponding sulfoxide by means of phenylperseleninic acid and much earlier Melnikov[24] indicated that sulfides may be converted to sulfoxides by refluxing with selenium dioxide for a few hours in chloroform.

1.2. Oxidation with Organic Peroxides

In 1954 Bateman and Hargrave[25] found that cyclohexyl methyl sulfide may be oxidized quantitatively to the sulfoxide by means of cyclohehyl or *t*-butylhydroperoxide in alcohol or hydrocarbon solvent. It was later reported[26] that organic peroxides react with unsaturated sulfides at 50-55° affording sulfoxides according to Eq.5.

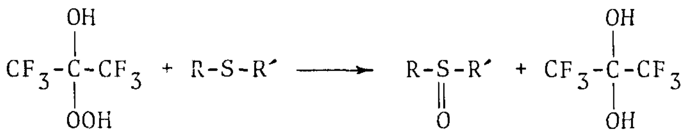


$$\text{R-S-R}' + \text{R}''\text{OOH} \longrightarrow \text{R-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-R}' + \text{R}''\text{OH} \qquad (5)$$

The yields of sulfoxides thus obtained were between 5-100% and strongly dependent upon the structure of both sulfide and hydroperoxide.

Horner and Jürgens[27] and later Pryor and Bickley[28] reported that benzoyl peroxide in the presence of sulfides decomposes to give sulfoxides. This reaction has been shown to occur as an ionic proccess. However, till now it has not found wider application.

Very recently Ganem et al.[29] showed that 2-hydroperoxyhexafluoro-2-propanol (XI) is a convenient reagent for the conversion of sulfides into the corresponding sulfoxides under mild conditions. The reaction takes place quickly below room temperature and affords sulfoxides almost quantitatively.



$$\text{CF}_3\text{-}\overset{\text{OH}}{\underset{\text{OOH}}{\text{C}}}\text{-CF}_3 + \text{R-S-R}' \longrightarrow \text{R-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-R}' + \text{CF}_3\text{-}\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{-CF}_3 \qquad (6)$$

XI

1.3. Oxidation with Peracids

Lewin[30] in 1928 reported the oxidation of sulfides to sulfoxides by perbenzoic acid at ordinary temperatures. A variety of other peracids may be used for this conversion which has been the subject of mechanistic studies.[31] The use of a variety of optically active peracids for oxidation of asymmetric sulfides resulted in the formation of optically active sulfoxides.[32] However, asymmetric oxidation using chiral peracids affords low optical yields. Peracids used for asymmetric oxidation of sulfides have been exhaustively tabulated in reviews by Nudelmann.[33]

1.4. Oxidation with Nitrogen Containing Compounds

1.4.1. Nitric Acid

Nitric acid is the first oxidizing agent which was used to achieve the sulfide to sulfoxide conversion. As mentioned above, Märcker[4] in 1865 had first prepared dibenzyl sulfoxide by oxidation of dibenzyl sulfide with nitric acid. Soon after, many dialkyl sulfoxides were prepared in the same way.[34] Polard and Robinson[35] and more recently Bordwell and Boutan[36] used nitric acid in acetic anhydride to prepare aralkyl sulfoxides.

A recent detailed study revealed that sulfides may react with nitric acid to give sulfoxides, sulfones and their nitro derivatives.[37] Under suitable conditions, however, the nitric acid oxidation of sulfides leads to selective formation of sulfoxides. This may be due to the salt formed from sulfoxide and nitric acid which is resistant to further oxidation at room temperature.[36]

1.4.2. Acyl Nitrates

In 1976 Low *et al.*[38] reported that dialkyl and aralkyl sulfides react rapidly with acetyl and benzoyl nitrates at low temperatures (-76^{o}) to give sulfoxides in high yield.

It is noteworthy that an excess of the oxidizing agent did not lead to sulfones. Acetyl nitrate was prepared from acetic anhydride and concentrated nitric acid. Benzoyl nitrate was obtained from the condensation between benzoyl chloride and silver nitrate. Both reagents were found to give satisfactory results.

1.4.3. Nitronium Hexafluorophosphate

Very recently Olah *et al.*[39] found that treatment of dialkyl, aralkyl and diaryl sulfides with nitronium hexafluorophosphate at -78° in methylene chloride resulted in the formation of sulfoxides in good yields (46-95%). In the case of oxidation of diphenyl sulfide, small amounts of the ring nitration products were observed.

1.4.4. Thallium (III) Nitrate

Nagano *et al.*[40] found that treatment of dialkyl and diaryl sulfides with thallium (III) nitrate (2.2 equivalents) at room temperature in chloroform-acetic acid (3:1) resulted in the formation of sulfoxides in high yields (82-92%). However, in chloroform-acetic anhydride (3:1), the exclusive formation of sulfones was observed.

1.4.5. Ceric Ammonium Nitrate

Ho and Wang[41] demonstrated that ceric ammonium nitrate is an efficient reagent for the conversion of diaryl sulfides into the corresponding sulfoxides under very mild conditions. Overoxidation, even in the presence of an excess of the reagent, was not observed. However, this reagent is not suitable for the oxidation of dialkyl sulfides possessing α-hydrogens. This is most probably due to the Pummerer reaction of the sulfoxides formed which occurs under these conditions.

Very recently Ho[42] reported an improved procedure consisting in the use of catalytic amounts of cerium (IV) salts together with a cooxidant (BrO_3^-), which recycles the spent cerium (III) ions. This catalytic procedure can also be applied to the oxidation of dialkyl sulfides.

1.4.6. Nitrogen Tetroxide

Oxidation of organic sulfur compounds by "nitrous fumes" was first reported by Pummerer[43] in 1910. In 1927 Bell and Bennett[44] found that oxidation of 1,4-dithiane by "nitrous fumes" gave the *trans* isomer of 1,4-dithiane α-disulfoxide. This observation was later confirmed by Whitaker.[45] In 1953, Horner[46] used dinitrogen tetroxide in carbon tetrachloride to convert methyl phenyl sulfide to the corresponding sulfoxide in 95% yield. Soon thereafter, it was found by Addison and Sheldon[47] that alkyl sulfides are readily oxidized by liquid dinitrogen tetroxide to sulfoxides without concomitant formation of sulfones. They showed that dinitrogen tetroxide forms molecular addition compounds with alkyl sulfoxides and suggested that their formation prevents further oxidation at sulfur. Dinitrogen tetroxide may be used for oxidation of α-chloro sulfides provided that formation of N_2O_3 is prevented by scavenging the reaction mixture with oxygen.[48]

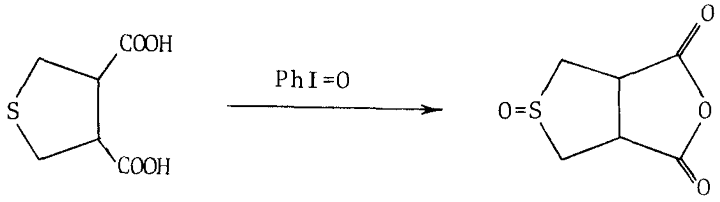
1.5. Oxidation with Iodobenzene Derivatives

1.5.1. Iodosobenzene

Ford-Moore[49] reported in 1949 that iodosobenzene is a very convenient reagent for the conversion of β-hydroxy sulfides to the corresponding sulfoxides (Eq.7).

$$R\text{-}S\text{-}R' + PhI{=}O \longrightarrow R\text{-}\underset{\underset{O}{\|}}{S}\text{-}R' + PhI \qquad (7)$$

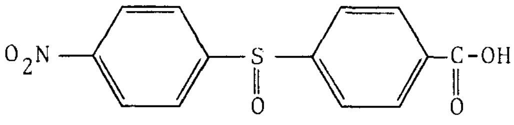
An interesting example of oxidation of cyclic dicarboxylic acids *cis*-XII and *trans*-XII by iodosobenzene has been described by Tokaya *et al.*[50] They found that, whereas *trans*-XII gave the expected sulfoxide, *cis*-XII was oxidized to sulfoxide XIII with simultaneous dehydration.



cis-XII XIII (8)

1.5.2. Iodobenzene Diacetate

This reagent was first used by Szmant and Suld[51] for the synthesis of *p*-(nitrophenylsulfinyl)-benzoic acid (XIV).

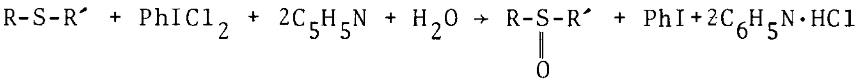


XIV

The oxidation of the sulfide was carried out in boiling acetic acid for 24 hrs using an equivalent amount of iodobenzene diacetate; sulfoxide XIV was obtained in 90% yield. However, oxidation of benzyl phenyl sulfide and dibenzyl sulfide by iodobenzene diacetate was found to be less efficient and gave the corresponding sulfoxides in 51 and 21% yield, respectively.[52]

1.5.3. Iodobenzene Dichloride

Montanari and coworkers[53] found that sulfides were selectively oxidized to sulfoxides by iodobenzene dichloride in aqueous pyridine according to Eq.9.



$$\text{R-S-R}' + \text{PhCl}_2 + 2\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightarrow \text{R-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-R}' + \text{PhI}+2\text{C}_6\text{H}_5\text{N}\cdot\text{HCl} \qquad (9)$$

This procedure may be applied to the preparation of a wide range of sulfoxides such as aliphatic, aromatic and heterocyclic sulfoxides. The reaction is almost instantaneous and affords sulfoxides in yields over 80%. It can be used to synthetize sulfoxides having ^{18}O in the sulfinyl group.

1.6. Oxidation with Sodium Metaperiodate

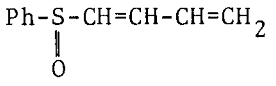
In 1962, Leonard and Johnson[54] reported the selective oxidation of sulfides to sulfoxides by sodium metaperiodate (Eq.10).

$$\text{R-S-R}' + \text{NaIO}_4 \longrightarrow \text{R-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-R}' + \text{NaIO}_3 \qquad (10)$$

This reagent was applied to the preparation of acyclic, cyclic, aliphatic, aromatic and heterocyclic sulfoxides. Usually, the oxidation reaction is carried out at 0$^{\text{o}}$ in a methanol-water solution and is complete in 3-12 hrs affording yields of about 90% or higher.

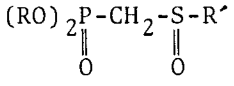
Hall et al.[55] prepared benzylpenicillin and phenoxymethyl penicillin sulfoxides from the corresponding benzyl esters by oxidation with sodium metaperiodate in dioxane solution with phosphate buffer. A general procedure for the synthesis of penicillin sulfoxides was reported later by Essery et al.[56] which consists in the direct oxidation of penicillines or their salts with sodium metaperiodate in aqueous solution at pH 6.5-7.0.

More recently, 1-butadienyl phenyl sulfoxide (XV)[57] and α-phosphoryl sulfoxides (XVI)[58] were obtained from the corresponding sulfides on treatment with sodium metaperiodate.



$Ph\text{-}\underset{\underset{O}{\|}}{S}\text{-}CH{=}CH\text{-}CH{=}CH_2$

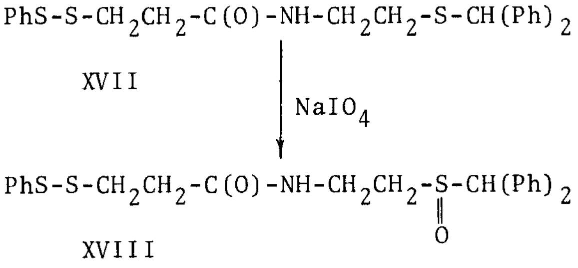
XV



$(RO)_2\underset{\underset{O}{\|}}{P}\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{S}\text{-}R'$

XVI

It is interesting to note that the selective oxidation of the thioether group in the presence of the disulfide bond was observed when a methanolic solution of XVII was treated with an aqueous solution of sodium metaperiodate.[59]



$$\begin{array}{l} PhS\text{-}S\text{-}CH_2CH_2\text{-}C(O)\text{-}NH\text{-}CH_2CH_2\text{-}S\text{-}CH(Ph)_2 \quad \text{XVII} \\ \Big\downarrow NaIO_4 \\ PhS\text{-}S\text{-}CH_2CH_2\text{-}C(O)\text{-}NH\text{-}CH_2CH_2\text{-}\underset{\underset{O}{\|}}{S}\text{-}CH(Ph)_2 \quad \text{XVIII} \end{array} \qquad (11)$$

The selective oxidation of sulfides to sulfoxides can also be carried out with water-insoluble tetrabutylammonium periodate in boiling chloroform.[60]

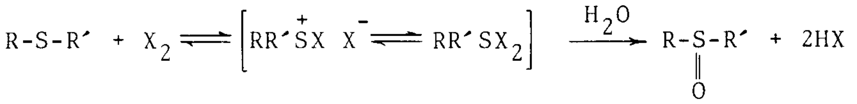
In 1978 Lin and Tong[61] reported a modified procedure for the rapid and simple oxidation of sulfides to sulfoxides using aluminia-supported sodium metaperiodate. Oxidation of unsymmetrical sulfides by this reagent in optically active alcohols as solvent was found to give optically active sulfoxides[62] (optical purity below 8.9%).

Sugimoto *et al.*[63] and Ogura *et al.*[64] found that oxidation of unsymmetrical sulfides and thioacetals with sodium metaperiodate in the presence of bovine serum albumin occurs in an asymmetric way to give chiral sulfoxides of high optical purity (up to 81%) and in good yields (27 to 87%).

1.7. Oxidation by Halogens and Compounds Containing "Electropositive"Halogens

1.7.1. Halogens

Molecular halogens have long been know to form addition compounds with organic sulfides which can be subsequently hydrolyzed to sulfoxides as shown in Eq.12.



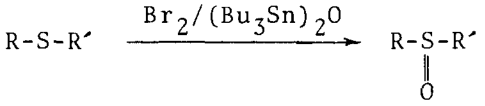
$$R\text{-}S\text{-}R' + X_2 \rightleftharpoons \left[RR'\overset{+}{S}X\ \overset{-}{X} \rightleftharpoons RR'SX_2\right] \xrightarrow{H_2O} R\text{-}\underset{\underset{O}{\|}}{S}\text{-}R' + 2HX \qquad (12)$$

The synthesis of sulfoxides by this method has been discussed.[1] However, it should be recognized that undesired side-reactions such as cleavage of C-S bonds or formation of C-Cl bonds very often predominate over sulfoxide formation.[17,65] In the case of aryl sulfides, halogenation of the aromatic ring is also observed.[66]

Recently, Drabowicz and Mikołajczyk[67] demonstrated that sulfoxides can be obtained in high yields and free of the above mentioned side-products if the reaction of sulfides with bromine or chlorine as well as the subsequent hydrolysis of the addition compounds is carried out under two-phase conditions (CH_2Cl_2/H_2O) using potassium hydrogen carbonate. Oxidation of penicillin by chlorine under two-phase conditions was mentioned earlier by Spray[68] in a very short footnote.

The rate of formation of sulfoxides from sulfides and iodine in aqueous solution has been found to be relatively slow. It may be accelerated by certain nucleophiles, e.g. phthalate ion. Higuchi *et al.*[69] found that oxidation of methyl benzyl sulfide with iodine in the presence of optically active 2-methyl-2-phenylsuccinate as a buffer gave methyl benzyl sulfoxide which was optically active and had 6.35% optical purity.

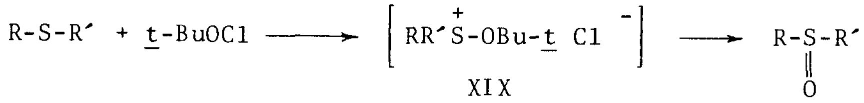
A very important modification of this method was reported by Ueno *et al.*[70] in which oxidation of sulfides by bromine can be carried out under anhydrous conditions. They found that treatment of sulfides with bromine and then with hexabutyldistannoxane in organic solvent, at room temperature afforded sulfoxides in high yields without sulfone contaminations even with an excess of oxidizing agent.



$$R\text{-}S\text{-}R' \xrightarrow{Br_2/(Bu_3Sn)_2O} R\text{-}\underset{\underset{O}{\|}}{S}\text{-}R' \qquad (13)$$

1.7.2. *t*-Butyl Hypochlorite

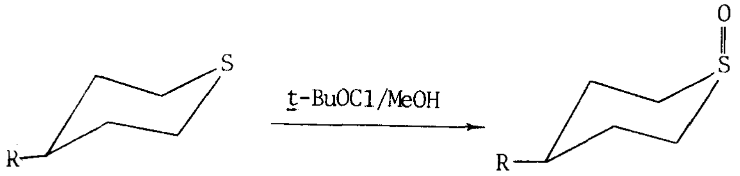
In 1964 Skell and Epstein[71] showed that sulfides react with *t*-butyl hypochlorite at low temperatures to give at first alkoxysulfonium salts XIX which decompose to sulfoxides at room temperature.



$$\text{R-S-R}' + \underline{\text{t}}\text{-BuOCl} \longrightarrow \left[\text{RR}'\overset{+}{\text{S}}\text{-OBu-}\underline{\text{t}}\ \overset{-}{\text{Cl}}\right] \longrightarrow \underset{\substack{\|\\ \text{O}}}{\text{R-S-R}'} \qquad (14)$$

XIX

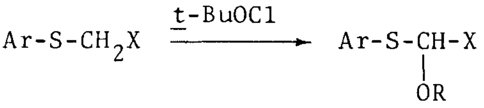
Johnson and McCants[72] reported that oxidation of cyclic sulfides XX by t-butyl hypochlorite in methanol gave in all cases cis-sulfoxides XXI.



(15)

XX XXI

The reaction of sulfides XXII bearing the ethynyl or carbomethoxy group α to sulfur with t-butyl hypochlorite in methanol or ethanol gives high yields of the corresponding α-alkoxy derivatives XXIII rather than sulfoxides.[73]

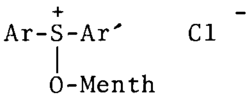


$$\text{Ar-S-CH}_2\text{X} \xrightarrow{\underline{\text{t}}\text{-BuOCl}} \underset{\substack{|\\ \text{OR}}}{\text{Ar-S-CH-X}} \qquad (16)$$

XXII XXIII

$X = CH{\equiv}C\text{-}, CO_2CH_3$ $R = Me, Et$

Oae et al.[74] found that hydrolysis or thermolysis of O-menthyloxysulfonium salts(XXIV), prepared in situ by reaction of sulfides with t-butyl hypochlorite in the presence of menthol, gave optically active diaryl sulfoxides with optical purity of up to 20%.



$$\underset{\substack{|\\ \text{O-Menth}}}{\text{Ar-}\overset{+}{\text{S}}\text{-Ar}'}\quad \overset{-}{\text{Cl}}$$

XXIV

1.7.3. N-Halo Compounds

Oae *et al.*[75] found that treatment of aromatic sulfides with one equivalent of N-bromosuccinimide (NBS) in dioxane-water (7:3) solution at room temperature afforded the corresponding sulfoxides in high yields. The reaction of NBS with dialkyl sulfides and aralkyl sulfides under the same experimental conditions resulted in C-S bond cleavage and gave no sulfoxides.Harville[76] reported, however, that even dialkyl sulfides are efficiently oxidized to sulfoxides without concomitant C-S bond cleavage by N-bromo-or N-chlorosuccinimide in methanol at low temperatures.

Recently, Kunieda *et al.*[77] utilized N-bromocaprolactam in alcohols for oxidation of sulfides. In the presence of optically active alcohols, this reaction produces optically active sulfoxides but in low yields and optical purity.

Benes[78] found that bis-(2-chloroethyl)sulfoxide and the corresponding sulfimide, $PhSO_2NS(CH_2CH_2Cl)_2$, are simultaneously formed in the reaction between chloramine-B and bis-(2-chloroethyl)-sulfide in aqueous solvent. The amount of sulfoxide increases with increasing concentration of water in the reaction mixture.

Sulfides are quickly and efficiently converted into sulfoxides by 1-chlorobenzotriazole in methanol at -78°[79] in yields of 68-98%; formation of sulfones was not observed. 1-Chlorobenzotriazole cannot be used for the conversion of di-*t*-butyl sulfide and dibenzyl sulfide into their sulfoxides since C-S bond breaking takes place at an intermediate stage. Treatment of benzyl *p*-tolyl sulfide with 1-chlorobenzotriazole followed by sequential addition of menthol and silver tetrafluoroborate produced an optically active menthyloxysulfonium salt. Its hydrolysis leads to optically active benzyl p-tolyl sulfoxide.[80]

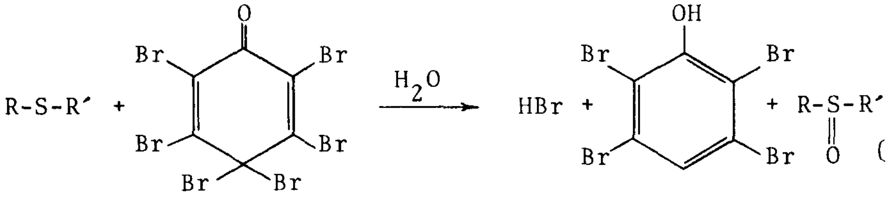
Oae *et al*.[81] reported oxidation of a number of sulfides with the bromine complex of tertiary amines in 70% aqueous acetic acid as solvent. Pyridine-bromine and 1,4-diazabicyclo [2,2,2]-octane-2-bromine complexes gave satisfactory results.

1.7.4. Sulfuryl Chloride

Traynelis *et al*.[82] showed that the low temperature reaction of sulfuryl chloride with sulfides leads to the formation of chlorine-sulfide complexes which are then readily hydrolyzed to the corresponding sulfoxides in 60-97% yields. Very recently Hojo[83] found that treatment of aralkyl and diaryl sulfides with equivalent amount of sulfuryl chloride in the presence of a wet silica gel at room temperature gave sulfoxides in an almost quantitative yield without formation of any chlorinated products. With dialkyl and benzyl sulfides, this reaction was carried at ice bath temperatures in order to avoid α-chlorination. Allylic sulfoxides were also prepared by this method without chlorination at the allylic position.

1.7.5. 2,4,4,6-Tetrabromocyclohexadienone

Calo *et al*.[84] reported that sulfides could be oxidized efficiently to the corresponding sulfoxides uncontaminated by sulfones by means of 2,4,4,6-tetrabromocyclohexadienone in dioxane-water or tetrahydrofuran-water solution at room temperature.


(17)

1.8. Photochemical Oxidation

Photochemical synthesis of sulfoxides was reported for the first time by Foote and Peters[85] in 1971. They found that dialkyl sulfides undergo sensitized photooxidation to give sulfoxides in a smooth reaction (Eq.18).

$$2\ R_2S + O_2 \xrightarrow[\text{sens.}]{h\nu} 2\ R_2SO \qquad (18)$$

Sinnreich *et al.*[86] reported direct photooxidation of aliphatic sulfides in hexane solution and as solids. The yields of sulfoxides were quantitative. Only di-*t*-butyl sulfide was not oxidized under these conditions. Very recently, the direct photooxidation of sulfides as well as the photochemical oxygen transfer from selenoxides to sulfides was described by Tezuka *et al.*[87] The formation of 3-*t*-butylsulfinylcyclobutane and 4-*t*-butylsulfinylcyclohexane in the photochemical oxygen transfer from aza-aromatic N-oxides to the corresponding sulfides has been reported by Boyd *et al.*[88]

1.9. Oxidation by Miscellaneous Reagents

In 1926, Knoll[89] found that chromic acid oxidizes sulfides to sulfoxides. However, this oxidation procedure is not selective and sulfones are also formed.[90] Their formation may be reduced by the use of pyridine as solvent.[91]

Oxidation of di-*n*-butyl sulfide with activated manganese dioxide in ligh petroleum gave di-*n*- butyl sulfoxide exclusively.[91] However, the reaction was very slow at room temperature and a 71% yield was obtained after 85 hrs. This method is also suitable for oxidation of diallyl sulfides although after 76 hrs, diallyl sulfoxide was isolated in only 13% yield.

Böhme *et al.*[92] reported that lead tetraacetate in acetic acid solution oxidizes dibenzyl sulfide and methyl phenyl sulfide to sulfoxides.

Selenoxides readily convert dialkyl sulfides into sulfoxides in acetic acid solution being themself reduced to selenides.[93]

$$R'-\underset{\displaystyle \overset{\|}{O}}{S}-R' \quad (\text{no}) $$

(19)

The yields of sulfoxides are strongly dependent on the steric effects of alkyl groups. The reaction does not occur in methanol or benzene.

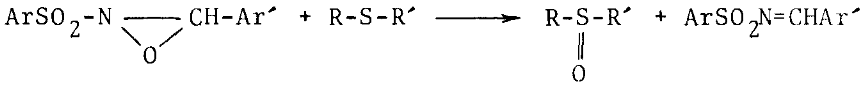
Recently, Faehl and Kice[94] reported that dibenzyl and dibutyl sulfides can be cleanly oxidized to the corresponding sulfoxides by aromatic seleninic acids in the presence of strong acid catalyst in acetonitrile solution. The stoichiometry of the reaction is shown below.

$$R_2S + 2/3\ ArSeO_2H \xrightarrow{H^+} R_2S{=}O + 1/3\ ArSe{-}SeAr + 1/3\ H_2O \qquad (20)$$

Diphenyl sulfoxide was obtained when a solution of diphenyl sulfide was treated with potassium hydrogen sulfate in ethanol and acetic acid.[95]

Horner *et al*.[96] reported oxidation of sulfides with ozone. However, the reaction of bis-(2-hydroxyethyl) sulfide with 1.5 equivalent of ozone gave a 1:1 mixture of the corresponding sulfoxide and sulfone.[97]

Recently, Davis *et al*.[98] reported the selective oxidation of sulfides under aprotic conditions by 2-arenesulfonyl-3-aryloxaziridines. The reaction (Eq.21) is instantaneous at room temperatures giving sulfoxides in yields exceeding 90%.

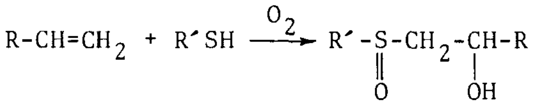


(21)

Oxidation of unsymmetrical sulfides by optically active oxaziridines was found to give optically active sulfoxides. Their optical purity was, however, low.[99]

2. COOXIDATION OF ALKENES AND THIOLS

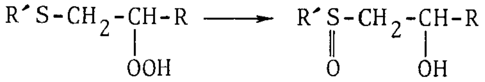
Kharasch and coworkers[100] were the first to show that thiols and olefins cooxidize in an atmosphere of oxygen at room temperature to yield substituted 2-sulfinylethanols XXV according to the equation shown below.



$$R\text{-}CH{=}CH_2 + R'SH \xrightarrow{O_2} R'\text{-}\underset{\overset{\|}{O}}{S}\text{-}CH_2\text{-}\underset{\overset{|}{OH}}{CH}\text{-}R \qquad (22)$$

XXV

Ford[101] as well as Oswald[102] demonstrated that cooxidation of thiols with styrenes or indene by air in a hydrocarbon solvent provides substituted 2-mercaptoethylhydroperoxides XXVI which rearrange to 2-sulfinylethanols XXV.



$$R'S\text{-}CH_2\text{-}\underset{\substack{|\\OOH}}{CH}\text{-}R \longrightarrow R'\underset{\substack{\|\\O}}{S}\text{-}CH_2\text{-}\underset{\substack{|\\OH}}{CH}\text{-}R \qquad (23)$$

XXVI XXV

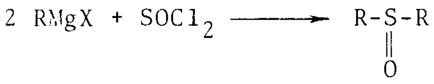
It was later shown[103] that cooxidation is strongly accelerated by chloride and bromide ions.

Recently, Tsuchihashi _et al._[104] reported that fluorescent irradiation is effective and most suitable for the cooxidation of arenethiols and α,β-unsaturated nitriles, α,β-unsaturated esters and 1-alkenes which are not conjugated with electron attracting groups.

3. REACTION OF ORGANOMETALLIC COMPOUNDS WITH SULFUROUS ACID DERIVATIVES

3.1. Thionyl Chloride

Strecker[105] reported in 1910 that reaction of thionyl chloride with two equivalents of phenylmagnesium bromide or benzylmagnesium bromide afforded diphenyl or dibenzyl sulfoxides. The corresponding sulfides were found to be by-products of this reaction.



$$2\ RMgX + SOCl_2 \longrightarrow R\text{-}\underset{\substack{\|\\O}}{S}\text{-}R \qquad (24)$$

Recently, dicyclohexyl[106] and bis-(2-methoxyphenyl)sulfoxide[107] were prepared by this reaction in 85 and 42% yield, respectively.

3.2. Sulfites

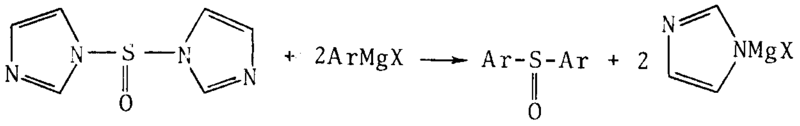
Strecker[105] was the first to show that diethyl sulfite reacts with two equivalents of Grignard reagent in ether solution to yield symmetrical sulfoxides as shown below.

$$2\ R'MgX + RO\text{-}\underset{\underset{O}{\|}}{S}\text{-}OR \longrightarrow R'\text{-}\underset{\underset{O}{\|}}{S}\text{-}R' + 2\ ROMgX \qquad (25)$$

Bert[108] has recommended the use of di-n-butyl sulfite as starting material for the preparation of sulfoxides. Gilman *et al*.[109] prepared diphenyl sulfoxide in 74% yield from diphenyl sulfite and phenylmagnesium bromide.

3.3. Sulfindiamide

Bast and Andersen[110] reported the synthesis of symmetrical diaryl sulfoxides using N,N-thionyl diimidazole (XXVII) and Grignard reagents in yields of 35-81%.

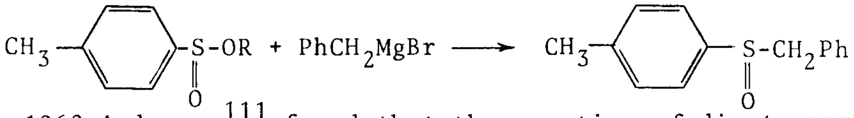


(26)

4. REACTION OF ORGANOMETALLIC COMPOUNDS WITH SULFINIC ACID DERIVATIVES

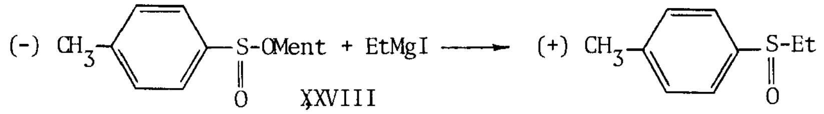
4.1. Sulfinic Acid Esters

Gilman *et al*.[109] first reported in 1926 that the reaction between sulfinic acid esters and Grignard reagents produced sulfoxides in ca. 60% yield.



(27)

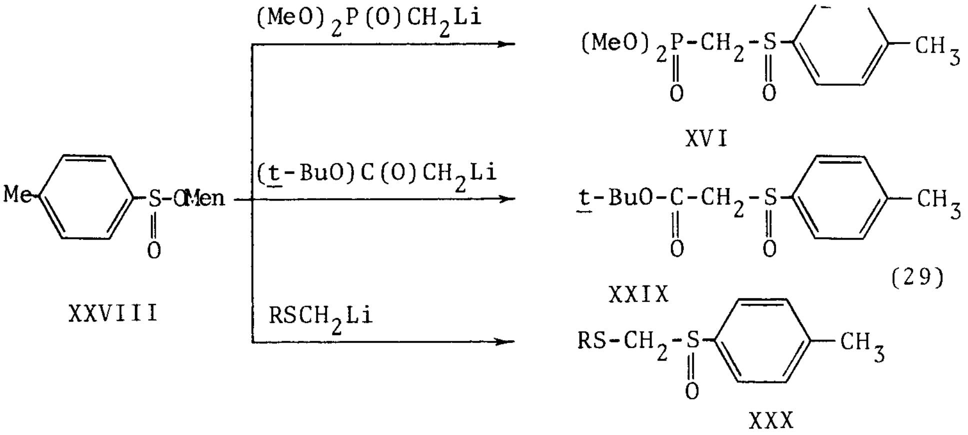
In 1962 Andersen[111] found that the reaction of diastereomerically pure O-menthyl p-toluenesulfinate (XXVIII) with ethylmagnesium iodide gave optically active ethyl p-tolyl sulfoxide (Eq.28). This method has been used to prepare optically active dialkyl[112], aralkyl[112], diaryl[113] and unsaturated sulfoxides[114].



(28)

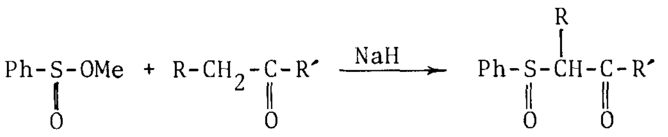
Harpp *et al.*[115] have recently summarized this area and shown that a major by-product is the sulfide derived from the initially formed sulfoxide. The authors recommend organocopperlithium reagents for the conversion of sulfinate esters into the corresponding sulfoxides.

The Andersen synthesis has also been utilized for preparation of optically active α-phosphoryl sulfoxides (XVI)[116], α-keto sulfoxides (XXIX)[117] and monooxides of dithioacetals (XXX)[118].



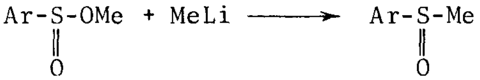
(29)

Monteiro and De Sonza[119] prepared a series of racemic α-keto sulfoxides by treatment of carbonyl compounds with an equivalent amount of methyl benzenesulfinate and sodium hydride in anhydrous ether at room temperature(Eq.30). The yields of sulfoxides XXXI vary from 50 to 83%. Jacobus and Mislow[120] and Montanari *et al.*[121] showed that the reaction of aryl sulfinates with methyllithium yielded methyl aryl sulfoxides (Eq.31).



$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{S}{-}OMe} + \mathrm{R{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}R'} \xrightarrow{\mathrm{NaH}} \mathrm{Ph{-}\underset{\underset{O}{\|}}{S}{-}\overset{\overset{R}{|}}{C}H{-}\underset{\underset{O}{\|}}{C}{-}R'} \qquad (30)$$

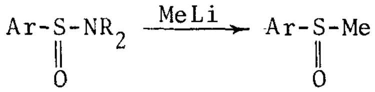
XXXI



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}OMe} + \mathrm{MeLi} \longrightarrow \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}Me} \qquad (31)$$

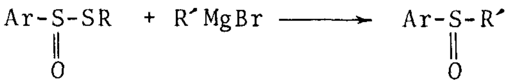
4.2. Sulfinamides and Thiosulfinates

Three groups (Montanari[121], Mislow[122] and Wudl[123]) demonstrated that optically active sulfinamides are suitable precursors to optically active sulfoxides (Eq.32).



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}NR_2} \xrightarrow{\mathrm{MeLi}} \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}Me} \qquad (32)$$

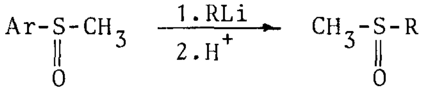
Fava *et al.*[124] and Mikołajczyk and Drabowicz[125] found that treatment of aryl thiosulfinates with an excess of Grignard reagents gave sulfoxides in moderate yields.



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}SR} + \mathrm{R'MgBr} \longrightarrow \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}R'} \qquad (33)$$

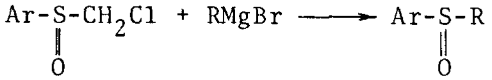
4.3. Sulfoxides

Johnson *et al.*[126] reported the preparation of optically active unsymmetrical dialkyl sulfoxides by the reaction of optically pure methyl phenyl sulfoxide and methyl *p*-tolyl sulfoxide with alkyllithium reagents followed by quenching with a proton source.



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}CH_3} \xrightarrow[2.\,\mathrm{H^+}]{1.\,\mathrm{RLi}} \mathrm{CH_3{-}\underset{\underset{O}{\|}}{S}{-}R} \qquad (34)$$

Hojo *et al.*[127] found that chloromethyl sulfoxides react with Grignard reagents with the replacement of the chloromethyl group giving alkyl or aryl sulfoxides in 55-99% yield.

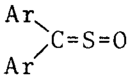


$$\underset{\displaystyle O}{\underset{\|}{Ar\text{-}S}}\text{-}CH_2Cl + RMgBr \longrightarrow \underset{\displaystyle O}{\underset{\|}{Ar\text{-}S}}\text{-}R \qquad (35)$$

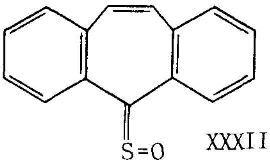
α-Chloroethyl and α-chloroisopropyl sulfoxides, though less important synthetically, can be used in place of α-chloromethyl sulfoxides.

4.4. Sulfines

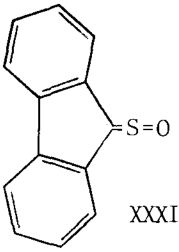
Schultz and Schlessinger[128] examined the reaction of diaryl sulfines as well as the sulfines derived from dibenzotropone and fluorenone with methyl and phenyllithium.



XXXII



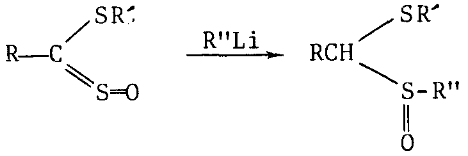
XXXIII



XXXIV

They found that treatment of XXXII and XXXIII with an equivalent of lithium reagent in benzene solution at 25° gave the sulfoxides in high yields (70-80%), whereas the reaction of methyllithium with sulfine XXXIV gave a mixture of various products from which the desired sulfoxide was isolated in low yield.

Recently, Zwanenburg *et al.*[129] described the reaction between sulfine XXXV and alkyllithium leading to S-oxides of dithioacetal XXXVI.

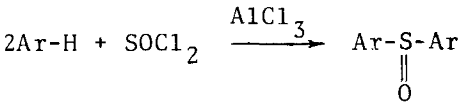


XXXV XXXVI (36)

5. REACTION OF AROMATIC COMPOUNDS WITH SULFINYL CHLORIDES

5.1. Thionyl Chloride

In 1887 Colby and Mc Laughlin[130] found that treatment of arenes with thionyl chloride in the presence of aluminium trichloride produces diaryl sulfoxides probably via the arenesulfinyl chloride.



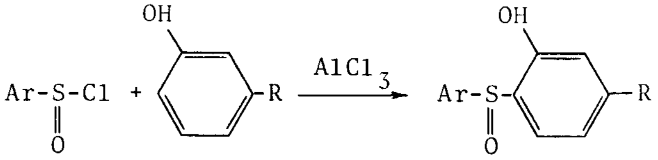
$$2\text{Ar-H} + \text{SOCl}_2 \xrightarrow{\text{AlCl}_3} \text{Ar-}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{-Ar} \qquad (37)$$

Highly reactive aromatic compounds such as naphthyl ethers react with thionyl chloride in the absence of the catalyst.[131]

5.2. Sulfinyl Chlorides

The preparation of sulfoxides by the reaction of aromatic compounds with sulfinyl chlorides is relatively unexplored. Douglas and Farah[132] reported a 26% yield of methyl phenyl sulfoxide from benzene and methylsulfinyl chloride in the presence of aluminium trichloride. Phenyl p-tolyl sulfoxide had been prepared from benzene and p-toluenesulfinyl chloride but the details of this procedure are not reported.[133]

Very recently Chasar and Pratt[134] reported the synthesis of o-substituted diaryl sulfoxides obtained as shown below.

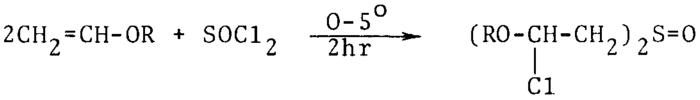


(38)

Phenyl 1-azulyl sulfoxides have also been prepared from phenylsulfinyl chloride and azulenes in the presence of pyridine at -30° in acetonitrile solution.[135]

6. ADDITION OF SULFINYL CHLORIDES TO UNSATURATED COMPOUNDS

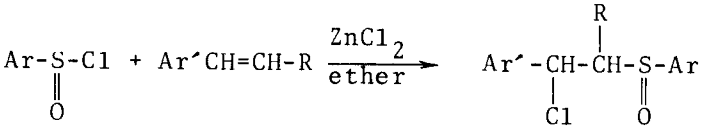
Thionyl chloride and enol ethers react to give high yields of bis (β-chloro-β-alkoxy ethyl) sulfoxides(XXXVII).[136]



$$2CH_2{=}CH\text{-}OR + SOCl_2 \xrightarrow[2hr]{0\text{-}5^o} (RO\text{-}\underset{\displaystyle Cl}{\underset{|}{C}}H\text{-}CH_2)_2S{=}O \qquad (39)$$

XXXVII

p-Toluenesulfinyl chloride and benzenesulfinyl chloride react with aromatic conjugated olefins in the presence of zinc chloride to give 1-chloro-1-phenyl-2-arenesulfinylethanes (XXXVIII) in 37-80% yield.[137]

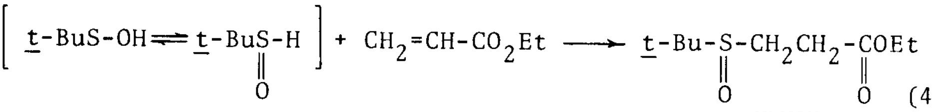


$$Ar\text{-}\underset{\displaystyle O}{\underset{\|}{S}}\text{-}Cl + Ar'CH{=}CH\text{-}R \xrightarrow[ether]{ZnCl_2} Ar'\text{-}\underset{\displaystyle Cl}{\underset{|}{C}}H\text{-}\overset{\displaystyle R}{\overset{|}{C}}H\text{-}\underset{\displaystyle O}{\underset{\|}{S}}\text{-}Ar \qquad (40)$$

XXXVIII

7. ADDITION OF SULFENIC ACIDS TO UNSATURATED COMPOUNDS

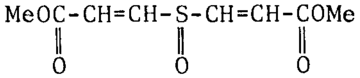
t-Butylsulfenic acid generated thermally from di-t-butyl sulfoxide adds readily at room temperature to ethyl acrylate giving the corrsponding sulfoxide XXXIX.[138]



$$\left[\, t\text{-}BuS\text{-}OH \rightleftharpoons t\text{-}Bu\underset{\displaystyle O}{\underset{\|}{S}}\text{-}H \,\right] + CH_2{=}CH\text{-}CO_2Et \longrightarrow t\text{-}Bu\text{-}\underset{\displaystyle O}{\underset{\|}{S}}\text{-}CH_2CH_2\text{-}\underset{\displaystyle O}{\underset{\|}{C}}OEt \qquad (41)$$

XXXIX

Addition of t-butylsulfenic acid to methyl propiolate gave bis-adduct XL by a double elimination-addition reaction.

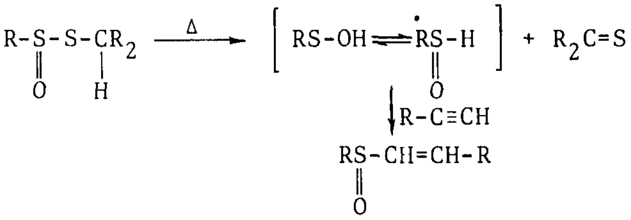


$$\mathrm{MeO}\underset{\underset{O}{\|}}{\mathrm{C}}\mathrm{-CH{=}CH-}\underset{\underset{O}{\|}}{\mathrm{S}}\mathrm{-CH{=}CH-}\underset{\underset{O}{\|}}{\mathrm{C}}\mathrm{OMe}$$

XL

Modifications of addition of t-butylsulfenic acid to olefines were studied by Jones *et al.*[139]

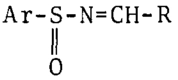
Recently, Block and O'Connor[140] showed that pyrolysis of alkyl thiosulfinates affords alkanesulfenic acids which can be trapped by acetylenes leading to α,β-unsaturated sulfoxides XLI in moderate to high yields (27-91%).



XLI

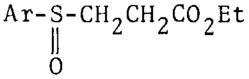
(42)

Recently Davis *et al.*[141] reported that a convenient way to generate arenesulfenic acids is the thermolysis of N-alkylidenearenesulfinamides (XLII). They found that heating XLII for 24 hrs at 80-115° in methyl propiolate or ethyl acrylate afforded methyl trans-arenesulfinylacrylates (XLIII) and ethyl arenesulfinylpropionates (XLIV) in 56-82% yields.



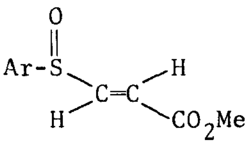
$$\mathrm{Ar-}\underset{\underset{O}{\|}}{\mathrm{S}}\mathrm{-N{=}CH-R}$$

XLII



$$\mathrm{Ar-}\underset{\underset{O}{\|}}{\mathrm{S}}\mathrm{-CH_2CH_2CO_2Et}$$

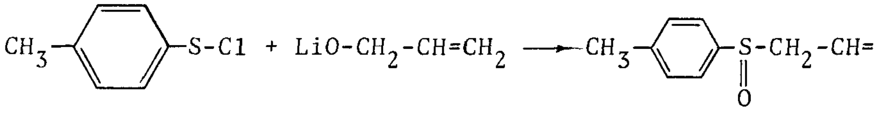
XLIV



XLIII

8. REARRANGEMENT OF SULFENIC ACID ESTERS

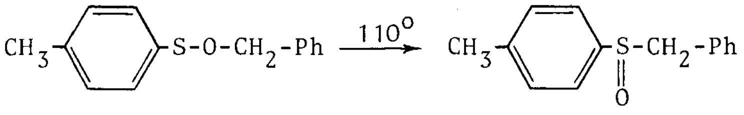
The spontaneous rearrangement of alkyl p-toluenesulfenates to sulfoxides was first recorded by Mislow and coworkers in 1966.[142] They found that p-toluenesulfenyl chloride and lithium allyloxide in ether at room temperature gave allyl p-tolyl sulfoxide (XLV).



(43)

XLV

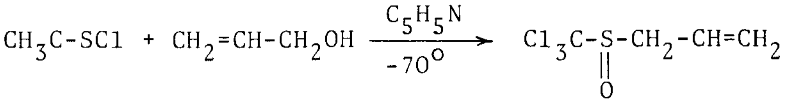
In the case of benzyl p-toluenesulfenate (XLVI) complete conversion to the sulfoxide XLVII required temperature above 110°.



(44)

XLVI XLVII

Braverman and Stabinsky[143] obtained allyl trichloromethyl sulfoxide (XLVIII) from allyl alcohol and trichloromethanesulfenyl chloride in ether at -70° in the presence of pyridine.

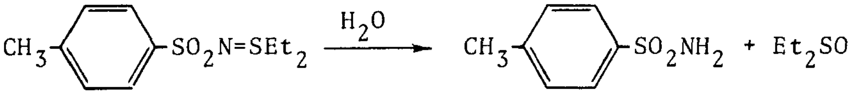


$$CH_3C\text{-}SCl + CH_2{=}CH\text{-}CH_2OH \xrightarrow[-70^{o}]{C_5H_5N} Cl_3C\text{-}\underset{\underset{O}{\|}}{S}\text{-}CH_2\text{-}CH{=}CH_2 \qquad (45)$$

XLVIII

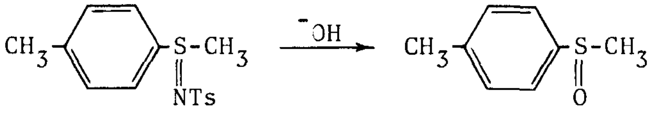
9. HYDROLYSIS OF SULFIMINES

Hydrolysis of sulfimines has rather limited application as a route to sulfoxides. In 1921 Nicolet and Willard[144] hydrolyzed N,N-diethyl p-toluenesulfonylsulfimine (XLIX) to the corresponding sulfonamide and an oily substance believed to be diethyl sulfoxide because of a facile formation of diethyl sulfide upon reduction.


(46)

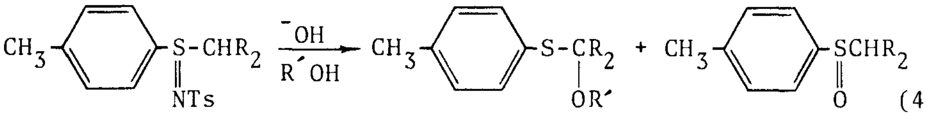
XLIX

Day and Cram[145] demonstrated that hydrolysis of optically active sulfimine (L) with methanolic KOH gave optically active methyl p-tolyl sulfoxide with inversion of configuration at sulfur.


(47)

L

According to Oae et al.[146] alkaline hydrolysis of p-tolyl alkyl N-tosylsulfimines (LI) results in the predominant formation of α-alkoxyalkyl sulfides LII.

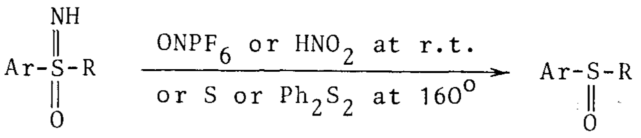

(48)

LI LII

Appel and Buchner[147] observed that unsubstituted dimethylsulfimine and diethylsulfimine are rapidly hydrolyzed to the corresponding sulfoxides.

10. DEIMINATION OF SULFOXIMINES

Cram and coworkers[148] found that optically active alkyl aryl sulfoximines LIII are stereospecifically converted into sulfoxides by nitrosyl hexafluorophosphate in nitromethane. Similar, stereospecific deimination may be achieved with sulfur or diphenyl disulfide at 160°.[149]

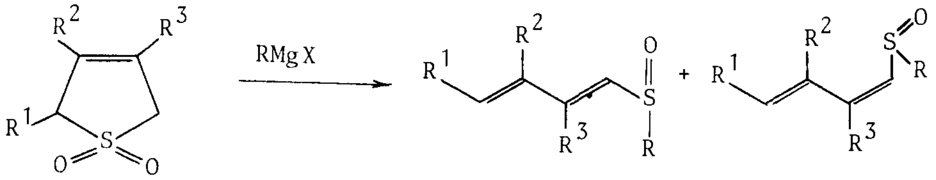


$$\mathrm{Ar{-}\overset{\overset{NH}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R} \xrightarrow[\text{or S or Ph}_2\text{S}_2\text{ at }160^{\circ}]{\text{ONPF}_6\text{ or HNO}_2\text{ at r.t.}} \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}R} \qquad (49)$$

LIII

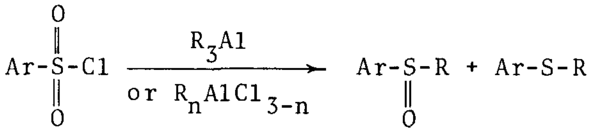
11. MISCELLANEOUS METHODS

It was reported that sulfolenes LIV react with two moles of alkyl or arylmagnesium halides to produce isomeric butadienylic sulfoxides LV in 20 to 66% yields in which Z-configuration predominated.[150]



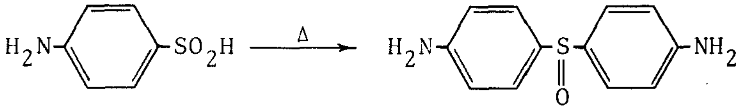
LIV LV (50)

The reaction of aromatic sulfonyl chlorides with trialkyl aluminium or alkylaluminium chloride was found to give alkyl aryl sulfoxides together with the corresponding sulfides.[151]



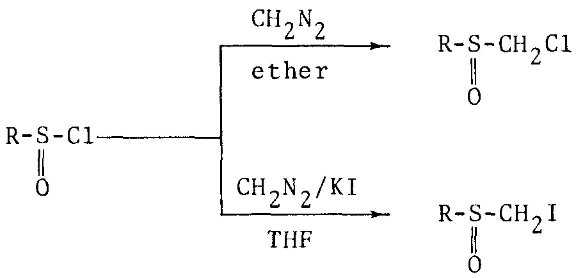
$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}Cl} \xrightarrow[\text{or } R_nAlCl_{3-n}]{R_3Al} \mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}R} + \mathrm{Ar{-}S{-}R} \qquad (51)$$

Lepape[152] reported that p-aminobenzenesulfinic acid is readily converted upon heating into p,p′-diaminodiphenyl sulfoxide in 57% yield.



(52)

The effective procedures for the synthesis of α-halogenosulfoxides reported recently by Venier *et al.*[153,154] are based on the reaction between sulfinyl chlorides and diazocompounds (Eq.53).



(53)

It was found that treatment of alkane- or arenesulfinyl chlorides with diazomethane in ether solution gives α-chlorosulfoxides in high yields. Later on, Venier *et al.*[154] reported that this reaction, when carried out in the presence of iodide ion, yields the corresponding α-iodosulfoxides. The chemistry of α-halogenosulfoxides was discussed by Venier and Barager[155] in their review published in 1974.

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