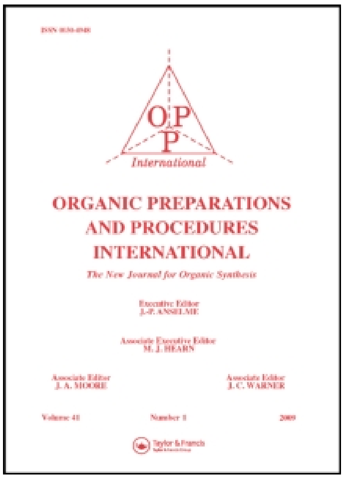


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

α-HALO SULFOXIDES. A REVIEW

Clifford G. Venier[a]; Howard J. Barager III[a]
[a] Department of Chemistry, Texas Christian University, Fort Worth, Texas

To cite this Article Venier, Clifford G. and Barager III, Howard J.(1974) 'α-HALO SULFOXIDES. A REVIEW', Organic Preparations and Procedures International, 6: 2, 77 — 102
To link to this Article: DOI: 10.1080/00304947409355079
URL: http://dx.doi.org/10.1080/00304947409355079

ORGANIC PREPARATIONS AND PROCEDURES INT. 6(2), 77-102 (1974)

α-HALOSULFOXIDES. A REVIEW

Clifford G. Venier* and Howard J. Barager, III

Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129

ORGANIC PREPARATIONS AND PROCEDURES INT. 6(2), 77-102 (1974)

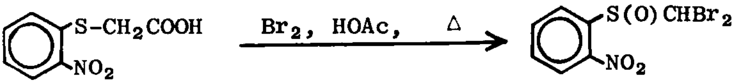
α-HALO SULFOXIDES: A REVIEW[1]

Clifford G. Venier and Howard J. Barager, III
Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129

In recent years, α-halo sulfoxides have appeared more and more frequently in the literature. This survey is meant to quickly summarize methods of preparation, reactions, and uses of α-halo sulfoxides. Because of the unique chemical properties of organofluorine compounds compared to compounds of the other halogens, they will not be included here.* In each section of this review, α-chloro compounds, of which the most is known, will be treated first, followed by the α-bromo and finally the α-iodo derivatives.

INTRODUCTION

The first reported preparation of an α-halo sulfoxide was that of Claasz[2] in 1913 who prepared 2-nitrophenyl dibromomethyl sulfoxide by the reaction in equation 1.

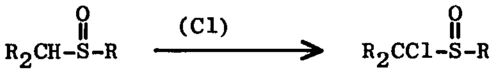


(1)

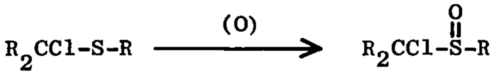
---

* Most of the knowledge of α-fluoro sulfoxides (usually trifluoromethyl derivatives) can be found by consulting the work of Yagupol'skii, which appears primarily in Zh. Obshch. Khim.

Mann and Pope were the first to use both of the most common routes to α-chloro sulfoxides. They reported the chlorination of bis(β-chloroethyl)sulfoxide in 1922,[3] and the oxidation of bis(chloromethyl)sulfide in 1923.[4] These two methods (equation 2 and equation 3) have been expanded greatly over the years, examples of a large number of different chlorinating and oxidizing agents having been reported.



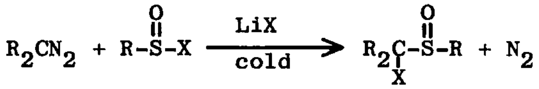
$$R_2CH-\overset{\overset{O}{\|}}{S}-R \xrightarrow{(Cl)} R_2CCl-\overset{\overset{O}{\|}}{S}-R \qquad (2)$$



$$R_2CCl-S-R \xrightarrow{(O)} R_2CCl-\overset{\overset{O}{\|}}{S}-R \qquad (3)$$

Preparations of α-bromo sulfoxides both by oxidation of the corresponding α-bromo sulfides and by bromination of sulfoxides have recently been reported (see below). There is no reason to suspect that either of these routes will be inapplicable to α-iodo sulfoxide preparations, although neither has been reported. In fact, the oxidation of α-iodo sulfides to α-iodo sulfones has been successfully carried out.[5]

Recently, a third general route to α-halo sulfoxides has been developed involving the condensation of diazo compounds with sulfinyl halides[6,7,8] (equation 4).



$$R_2CN_2 + R-\overset{\overset{O}{\|}}{S}-X \xrightarrow[\text{cold}]{\text{LiX}} R_2\underset{X}{C}-\overset{\overset{O}{\|}}{S}-R + N_2 \qquad (4)$$

METHODS OF PREPARATION

The methods which have been used up to now to prepare α-halo sulfoxides are exhaustively tabulated below. In the recent past (since 1968) chlorination of sulfoxides has received the majority of attention. Molecular chlorine, iodobenzene dichloride, sulfuryl chloride, and *t*-butyl hypochlorite all seem to work well. The choice of reagent for a particular new chlorination will probably depend more on the individual chemist's taste than on any inherent superiority of a particular reagent.

The oxidation of α-halo sulfides does have advantages over chlorination of sulfoxides in specific cases. For example, the position of the chlorine can be specified in the synthesis of the α-halo sulfide, so that mixtures of positional isomers can be avoided. The condensation of mercaptans, aldehydes and HCl leads to specifically chlorinated substrates,[5] as does the condensation of sulfenyl chlorides with diazo compounds.[9]

The condensation of diazo compounds with sulfinyl chlorides leads directly to α-chloro sulfoxides. This method has the position specificity of some of the α-chloro sulfide methods, without the necessity of a further oxidation step. Overall yields are high because sulfinyl chlorides can be prepared simply from disulfides or mercaptans by methods developed by Douglass.[10] The reaction of diazo compounds with sulfinyl chlorides(in the presence of lithium iodide) is also useful for the preparation of α-iodo sulfoxides.[7]

1. From Sulfoxides

α-Chloro Sulfoxides

(a) With Molecular Chlorine.-

Chlorination of sulfoxides directly with molecular chlorine yields the α-chloro sulfoxides in the presence of base. Alkyl sulfoxides have been chlorinated in this way in 60 to 90 % yields.[11-14] Martin, Berger, and Peschel[11] showed that the chlorination of methyl chloromethyl sulfoxide leads to methyl trichloromethyl sulfoxide. Iriuchijima and Tsuchihashi have shown the regioselectivity of chlorination for the position alpha to the sulfoxide function in phenyl 2-phenylethyl sulfoxide[12] and have carefully studied the stereochemistry of the chlorination of six-membered ring sulfoxides.[14]

(b) With NaOCl.-

The very first chlorination of a sulfoxide was carried out with this reagent. Mann and Pope chlorinated bis(2-chloroethyl) sulfoxide in a 10% yield.[4]

(c) With Sulfuryl Chloride.-

Tin and Durst[15] reported the chlorination of sulfoxides with sulfuryl chloride, obtaining yields generally in the 70 to 90% range. This chlorination in the absence of base is more regioselective but less stereoselective than typical chlorinations carried out in the presence of pyridine.[16] Iriuchijima and Tsuchihashi have carried out a very careful study comparing the chlorination with sulfuryl chloride to that with chlorine.[14]

(d) With Iodobenzene Dichloride.-

Cinquini, Colonna and their coworkers have carried out extensive investigations of this reagent as a method of preparation of α-chloro sulfoxides.[17-20] They have also reported a detailed study of the mechanism of the reaction.[21] One of the great advantages of this reagent is that α-chloro sulfoxides may be produced directly from sulfides,[17] the iodobenzene dichloride serving as both the oxidizing and chlorinating reagent. Yields in the range of 60 to 90% are obtained, with the yields from sulfides being slightly lower than those from sulfoxides.

(e) With t-Butyl Hypochlorite.-

Iriuchijima and Tsuchihashi[22] showed that this reagent could be used as a "free radical" chlorination agent or, in the presence of pyridine, as an "ionic" reagent. A comparative mechanism study of this reagent, sulfuryl chloride, and molecular chlorine was also carried out by them.[14]

(f) With N-Chloroamides.-

The chlorination of sulfoxides with N-chlorosuccinimide has been reported by Tsuchihashi and Ogura[23] who report differing product composition for the chlorination of methyl benzyl sulfoxide depending on the whether pyridine or potassium acetate is used as a base. The authors suggest that a "free radical" mechanism is responsible for the production of only methyl chlorobenzyl sulfoxide with K_2CO_3, whereas an ionic mechanism is operative when pyridine is used as a base.

(g) With 1-Chlorobenzotriazole.-

In 1972, Cinquini and Colonna[24] reported that 1-chlorobenzotriazole may be used to chlorinate sulfoxides in 70 to 90% yield.

(h) With NOCl.-

Loeppky and Chang[25] have shown that sulfoxides may be converted to α-chloro sulfoxides in 60 to 90% yields when treated with excess NOCl in the presence of pyridine.

(i) With p-Toluenesulfonyl chloride.-

Hojo and Yoshida[26] prepared phenyl chloromethyl sulfoxide from phenyl methyl sulfoxide by treating it with p-toluenesulfonyl chloride and pyridine.

α-Bromo Sulfoxides

(a) With Molecular Bromine.-

The bromination of sulfoxides with molecular bromine and pyridine has been carried out.[17,20,27] Yields could be improved by the use of bromine in conjunction with silver nitrate,[17] but silver ion reverses the stereochemistry of bromination.[20] The stereochemistry of normal sulfoxide bromination has been carefully studied.[28]

(b) With N-Bromoamides.-

Iriuchijima and Tsuchihashi[27] report that N-bromosuccinimide gives better yields of α-bromo sulfoxides than does molecular bromine, the yields ranging from 70-90% for simple compounds.

2. From α-Halo sulfides.

α-Chloro Sulfoxides

(a) With NaOCl.-

In 1926, Muller and Metzger[29] used NaOCl to oxidize bis (α-chloroethyl) sulfide to the corresponding sulfoxide. The method has not been further used.

(b) With Oxygen.-

A 1957 patent[30] described the preparation of a number of aryl 1,2-dichlorovinyl sulfoxides and sulfones by oxidation of the sulfides with oxygen.

(c) With Ozone.-

Böhme and Fischer[31] and later Bordwell and Brannen[32] have prepared α-chloro sulfoxides in good yields by oxidation of α-chlorosulfides with ozone.

(d) With H_2O_2.-

A 1957 patent[33] claims the oxidation of α-chloro sulfides to sulfoxides with H_2O_2. In a description of the use of V_2O_5 as a catalyst for H_2O_2 oxidations of sulfides to sulfoxides in general, Hardy, Speakman and Robson[34] prepared n-dodecyl and phenyl chloromethyl sulfoxides in about 70% yields.

(e) With Peroxyacids.-

Peracetic acid (or H_2O_2 in HOAc) is perhaps the cheapest peroxy acid that one could use for this oxidation. Consequently, its use is covered by a number of patents.[33,35-40] Backer, Strating and Hagenberg[41] report the use of peracetic acid for the oxidation of t-butyl 1,2-dichlorovinyl sulfide to the sulfoxide. Aryl peroxy acids have been used, including, perbenzoic acid,[42,43] m-chloroperbenzoic acid,[44-46] and monoperphthalic acid.[5,47] These aryl peroxy acids seem to give yields in the 70-90% range.

(f) With Nitric Acid.-

The first reported oxidation of an α-chlorosulfide to an α-chloro sulfoxide was by Mann and Pope[3,4] who used HNO_3 for the purpose.

(g) With Dinitrogen Tetroxide.-

Whitaker and Bennett[48] have reported the oxidation of bis(chloromethyl) sulfide to the sulfoxide using N_2O_4.

α-Bromo Sulfoxides

Two of the three diastereomeric bis(α-bromobenzyl) sulfoxides have been prepared in 60-70% yield by the m-chloroperbenzoic acid oxidation of the corresponding sulfide.[49,50]

3. From the Reaction of Sulfinyl Halides with Diazo Compounds.

α-Chloro Sulfoxides

Although a general procedure for the preparation of α-chloro sulfoxides from the reaction of sulfinyl chlorides with diazo compounds has only recently been published,[6] the reaction has appeared in the literature twice previously.

In 1948, a British group[51] reported that two moles of diazomethane add to one mole of thionyl chloride to give bis (chloromethyl) sulfoxide in a 40 % yield, in a reaction which has been shown to go through chloromethanesulfinyl chloride as an intermediate.[52]

Ayca[53] showed that the addition of arenesulfinyl chlorides to excess diazomethane gave the corresponding chloromethyl sulfoxides in low yields. The general procedure developed by Venier, Hsieh and Barager[6] ordinarily gives yields in the range of 70-90 % .

α-Bromo Sulfoxides

Senning and his co-workers[54] produced bromomethyl trichloromethyl sulfoxide in 15 % yield by the reaction of trichloromethanesulfinyl bromide with diazomethane. Venier and Barager[8] have found that the reaction of sulfinyl chlorides with diazo compounds in the presence of lithium bromide gives α-bromo sulfoxides in good yields.

α-Iodo Sulfoxides

The recent report that iodomethyl sulfoxides can be prepared in 60-90 % yields by the reaction of sulfinyl chlorides with diazomethane in the presence of lithium iodide,[7] has been extended to the preparation of other α-iodo sulfoxides.[8]

4. Miscellaneous Methods

α-Chloro Sulfoxides

(a) From Vinyl Sulfoxides.-

Alexander and McCombie[55] added Cl_2 to divinyl sulfoxide to produce bis(1,2-dichloroethyl) sulfoxide.

(b) From α,β-Dichloro Sulfoxides.-

Both Muller and Metzger[29] and Alexander and McCombie[55] reported many years ago that treatment of bis(1,2-dichloroethyl) sulfoxide with base led to bis(2-chlorovinyl) sulfoxide. Recently, Molenaar and Strating[47] have shown this to be in error. The product is, without question, bis-(1-chlorovinyl) sulfoxide.

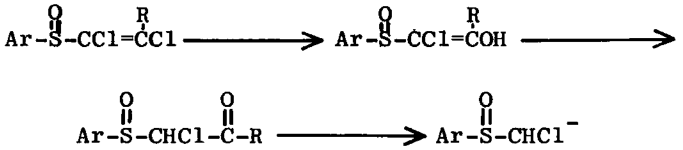
(c) From Sulfenyl Acetic Acids.-

One of the more unique methods for the production of aryl dichloromethyl sulfoxides involves the treatment of arenesulfenyl acetic acids with nitrosyl chloride.[56] It has been postulated that the initial oxidation to sulfinyl acetic acids is followed by dichlorination to sulfinyl dichloroacetic acids, then finally decarboxylation to the dichloromethyl sulfoxides[56] (equation 5).

$$\begin{array}{l} ArSCH_2CO_2H \longrightarrow ArS(O)CH_2CO_2H \longrightarrow \\ ArS(O)CCl_2CO_2H \longrightarrow ArS(O)CHCl_2 \end{array} \qquad (5)$$

(d) From 1,2-Dichlorovinyl Sulfoxides.-

Brown[46] reported that treatment of 1,2-dichlorovinyl sulfoxides with base gives chloromethyl sulfoxides. β-Chlorovinyl sulfoxides are vinylogous sulfinyl chlorides, and thus would be expected to undergo facile hydrolysis to vinylogous sulfinic acids, which are tautomer of β-carbonyl sulfoxides. These derivatives can undergo a reverse acylation giving the α-sulfinyl carbanions (equation 6).

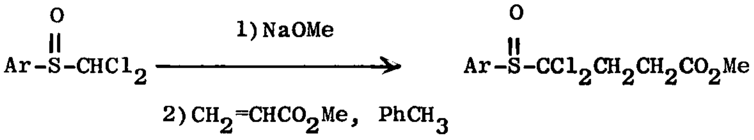


$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CCl{=}\overset{R}{C}Cl} \longrightarrow \mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CCl{=}\overset{R}{C}OH} \longrightarrow$$

$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CHCl{-}\overset{\overset{O}{\|}}{C}{-}R} \longrightarrow \mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CHCl^{-}} \qquad (6)$$

(e) <u>From other α-Chloro Sulfoxides</u>.-

Since strong bases can remove the α-protons of a sulfoxide group in general, one would expect the same to hold for α-chloro sulfoxides which also possess a proton on the α-carbon. These anions should be able to serve as nucleophiles in a wide variety of condensation reactions. Examples of condensations with ketones[45,57] to produce chlorohydrins have been reported, as have examples of Michael addition to activated olefins[58] (equation 7), and alkylation.[59]



$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CHCl_2} \xrightarrow[\text{2) } CH_2{=}CHCO_2Me,\ PhCH_3]{\text{1) NaOMe}} \mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CCl_2CH_2CH_2CO_2Me} \qquad (7)$$

A German patent describes the nitration of preexisting aryl α-chlorovinyl sulfoxides which leads to nitration of the aromatic ring rather than oxidation.[60]

(f) From Sulfenates.-

Braverman and Stabinsky[61,62] and Zefirov and Abdulvaleeva[63,64] reported the isolation of allyl trichloromethyl sulfoxide when allyl alcohol is allowed to react with trichloromethane sulfenyl chloride, probably through an intermediate sulfenate ester. When cinnamyl alcohol is used, the sulfenate could be isolated at -70°, but slowly rearranged to cinnamyl trichloromethyl sulfoxide. Interestingly, since the rearrangement gives the cinnamyl derivative rather than the 1-phenylallyl compound, the sulfenate to sulfoxide rearrangement cannot be a concerted (3,2) sigmatropic shift of the type recently exploited by Evans.[65]

(g) From Addition of Grignards to Sulfonyl Chlorides.-

Sanna and Stefano[66] reported in 1942 that small amounts of ethyl or phenyl trichloromethyl sulfoxide could be isolated when trichloromethanesulfonyl chloride was treated with ethyl- or phenylmagnesium chloride.

α-Bromo Sulfoxides

(a) From Vinyl Sulfoxides.-

Addition of bromine to divinyl sulfoxide yields bis(1,2-dibromoethyl) sulfoxide.[55] Stirling has reported an interesting case in which asymmetry is induced on the α-carbon by bromination of optically active sulfoxide.[67]

(b) From α,β-Dibromo Sulfoxides.-

Treatment of bis(1,2-dibromoethyl) sulfoxide with base leads to bis(1-bromovinyl) sulfoxide.[47]

(c) From Sulfenyl Acetic Acids.-

The first reported α-halo sulfoxide was 2-nitrophenyl dibromomethyl sulfoxide prepared by the treatment of 2-nitrobenzenesulfenyl acetic acid with bromine in acetic acid.[2] Farrar[56] has reported that treatment of thiodiacetic acid with bromine in base leads to hexabromodimethyl sulfoxide.

(d) From Polybromo sulfoxides.-

Treatment of bis(tribromomethyl) sulfoxide with sodium iodide gives tribromomethyl dibromomethyl sulfoxide.[56]

α-Iodo Sulfoxides

Bordwell and Brannen,[32] in connection with a study of nucleophilic displacements at the α-position of a sulfinyl group, characterized p-nitrophenyl iodomethyl sulfoxide as the product when p-nitrophenyl chloromethyl sulfoxide is treated with potassium iodide. Although good yields of iodomethyl sulfoxides are obtained in this way, the reaction is very slow. Refluxing phenyl chloromethyl sulfoxide with sodium iodide in acetone gives only 43 % conversion in 15 hr.[8]

REACTIONS

α-Halo sulfoxides are, after all, just a special class of sulfoxides, and with certain exceptions can be expected to undergo all of the general reactions of sulfoxides. Thus, we shall limit our survey to those reactions which for one reason or another seem to take advantage of the combination of properties peculiar to α-halo sulfoxides. Reactions, such as the oxidation of α-chloro sulfoxides to α-chloro sulfones, though useful, will not be discussed.

1. Metallation

If an α-chloro sulfoxide possesses a hydrogen on the halogen-bearing carbon, the hydrogen is relatively acidic. Upon addition of n-butyl lithium, α-lithio, α-chloro sulfoxides are formed.[47,57,68]

2. α-Sulfinyl Carbanions as Nucleophiles

The anions of α-chloro sulfoxides, preformed as described above or generated in situ with weaker bases, are nucleophilic and so can be alkylated,[59] or serve as nucleophiles in Michael additions[58] or in aldol-like addition to aldehydes and ketones.[45,57,68-70] In the case of addition to ketones, Durst[45,57] found that preforming the carbanion and then allowing it to react with the substrate, followed by aqueous work up led to the isolation of chlorohydrins (equation 8) while Tavares, Estep, and Blezard[69] and Tsuchihashi and Ogura[70] both found

$$PhS(O)CH_2Cl + n\text{-}BuLi \rightarrow PhS(O)CHCl \xrightarrow[2)\ H_2O]{1)\, R_2C=O} PhS(O)CHClCR_2OH \quad (8)$$

that the reaction of α-chloro sulfoxides with ketones in the presence of potassium t-butoxide gave α,β-epoxy sulfoxides. The reaction of methyl chloromethyl sulfoxide with thiobenzophenone in the presence of potassium t-butoxide gave 1,1-diphenyl-2-methanesulfinylethylene rather that the expected thiirane.[70] Kuwajima and Fukuda[68] showed that the α-chloro β-alkoxyl anion formed by the procedure of Durst, when treated with an additional mole of alkyl lithium, gave, among other products, β-keto sulfoxides (equation 9).

$$PhS(O)CHClCRHO^- \xrightarrow[2)\ \text{workup}]{1)\ CH_3Li} PhS(O)CH_2C(O)R \quad (9)$$

3. Nucleophilic Displacement of Halogen.

In some of its reactions the sulfinyl group reacts in analogy to the carbonyl group and in others, like the sulfonyl group. One way in which sulfonyl and carbonyl differ greatly is in their effects as neighboring groups to aliphatic halogen. α-Chloro ketones, e.g., the phenacyl halides, are exceedingly reactive, while α-chloro sulfones possess a chemically inert chlorine. Bordwell and Brannen[32] established some ten years ago that the sulfinyl group showed intermediate behavior in this case, reacting in acetone with potassium iodide with practically the same rate as n-butyl chloride (see Table).

Table. Relative Rates of Reaction with KI in Acetone at 75°.[a]

Compound	Rel. Rate
$PhCOCH_2Cl$	32,000
$CH_3CH_2CH_2CH_2Cl$	(1.0)
$PhSOCH_2Cl$	0.25
$PhSO_2CH_2Cl$	<0.02

[a] Data quoted from Reference 32.

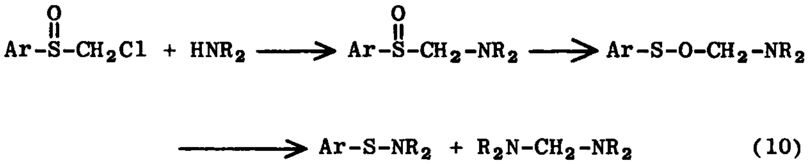
Curiously, without referring to Bordwell and Brannen's earlier work, Hojo and Yoshida[26] report that phenyl chloromethyl sulfoxide is inert to potassium iodide at 60°.*

Displacement of halogen has been extensively studied in both the α-chloro and α-bromo sulfoxides. In the chloro series, the following nucleophiles have been used: alkoxides,[21,71-74] phenoxide,[71] mercaptide[71-74] and amines.[25,73,74] Normal substitution products arise in all cases except the amines. In 1968, Loeppky and Chang noted "extensive alkyl carbon-sulfur cleavage" upon treating phenyl chloromethyl sulfoxide with piperidine.[25] Numata and Oae[73,74] subsequently showed that these cleavage products arise through decomposition of the sulfenate ester derived from the

---

* We[8] find that $PhSOCH_2Cl$ is 43 % converted into $PhSOCH_2I$ by treatment with NaI in acetone at 56° (reflux) for 15 hrs.

first formed sulfoxide by rearrangement (equation 10). This rearrangement is so



$$Ar\text{-}\overset{O}{\overset{\|}{S}}\text{-}CH_2Cl + HNR_2 \longrightarrow Ar\text{-}\overset{O}{\overset{\|}{S}}\text{-}CH_2\text{-}NR_2 \longrightarrow Ar\text{-}S\text{-}O\text{-}CH_2\text{-}NR_2 \longrightarrow Ar\text{-}S\text{-}NR_2 + R_2N\text{-}CH_2\text{-}NR_2 \tag{10}$$

facile that no examples of the α-amino sulfoxides have been prepared by the displacement of halogen.

t-Butoxide does not displace chlorine in the chloromethyl series of compounds, allowing the condensations described above in section 2 to take place.[69-71]

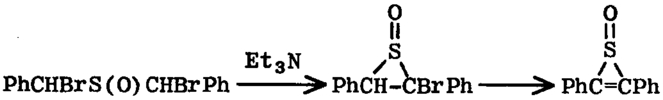
In the α-bromo series, displacements by alkoxides,[20,72-74] mercaptides,[72-74] and amines[73,74] have been carried out. The results were the same as with the chloro compounds, except that the reactions were faster in the bromo series.

4. Elimination reactions

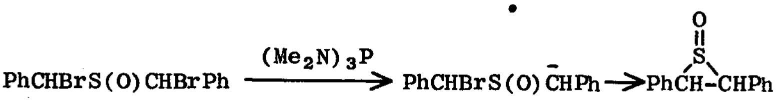
Since most of the work dealing with the reactions of α-halo sulfoxides has been carried out on substrates in which 1,2-eliminations are not available pathways, very little is known about these reactions. Many years ago, Muller and Metzger[29] and Alexander and McCombie[55] reported that 1,2-dichloroethyl sulfoxides eliminate the α-chlorine when treated with Et_3N to give 2-chlorovinyl sulfoxides. Molenaar and Strating[47] have conclusively shown that such eliminations occur with the loss of the more acidic α-hydrogen and β-chlorine to give 1-chlorovinyl sulfoxides.

Recently, Kuwajima and Fukuda[68] have reported that the treatment of the lithium salt of α-chloro-α-alkoxy sulfoxides with methyllithium gives, after work up, β-keto sulfoxides. Whatever the mechanism, this involves elimination of HCl to give the enolate of the final product (see equation 9).

Carpino and Chen[49] have shown that d,l-bis(α-bromobenzyl) sulfoxide undergoes a 1,3-elimination analogous to the Ramberg-Backlund reaction of α-halo sulfones, to give, after a further 1,2-elimination, a thiirene-S-oxide (equation 11). Jarvis, Dutney, and Ammon[50] showed that the meso substrate could be converted to 2,3-diphenylthiirane-1-oxide when treated with hexamethylphosphorous triamide (equation 12).



(11)



(12)

NON-CHEMICAL USES

α-Chloro Sulfoxides

Bis(1,2,2-trichloroethyl) sulfoxide has been reported as a fungicide.[37,75-79] This same compound and bis(2,2,2-trichloroethyl) sulfoxide were 100 % effective against Pythium, Rhizoctonia, Fusarium, and Helminthosporim.[37,77] Recently, Iriuchijima and Tsuchihashi have reported that α-chloro sulfoxides in general may be useful as pharmaceutical intermediates, solvents, cytostatics (against lung cancer) or hypnotics.[14,80]

α-Bromo Sulfoxides

Both bis(tribromomethyl) sulfoxide and tribromomethyl dibromomethyl sulfoxide have been shown to release bromine on exposure to light and can thereby be used as photoactivators.[81-82] In addition, hexabromo-DMSO is effective as a radiation protective agent.[83]

Acknowledgments.- The preparation of this manuscript was made possible through the generous support of The Robert A. Welch Foundation.

REFERENCES

1. Part III in a series "α-Substituted Sulfoxides."
2. M. Claasz, Ber., 45, 1015 (1912).
3. F. G. Mann and W. J. Pope, J. Chem. Soc., 121, 594 (1922).
4. F. G. Mann and W. J. Pope, ibid., 123, 1172 (1923).
5. H. Bohme, H. Fischer, and R. Frank, Ann., 563, 54 (1949).
6. C. G. Venier, H. H. Hsieh, and H. J. Barager, III, J. Org. Chem., 38, 17 (1973).
7. C. G. Venier and H. J. Barager, III, Chem. Commun., 319 (1973).
8. C. G. Venier and H. J. Barager, III, unpublished results.
9. E. Kuhle, Synthesis, 563 (1971).
10. M.-L. Kee and I. B. Douglass, Org. Prep. Proc., 2, 235 (1970) and references therein.

11. D. Martin, A. Berger, and R. Peschel, J. prakt. Chem., 312, 683 (1970).

12. G. Tsuchihashi and S. Iriuchijima, Bull. Chem. Soc. Jap., 43, 2271 (1970).

13. S. Iriuchijima and G. Tsuchihashi, Ger. Patent 2, 110, 519 (1971); C. A., 76, 45932 (1972).

14. S. Iriuchijima and G. Tsuchihashi, Bull. Chem. Soc. Jap., 46, 921 (1973).

15. K. C. Tin and T. Durst, Tetrahedron Lett., 4643 (1970).

16. G. Tsuchihashi, K. Ogura, S. Iriuchijima, and S. Tomisawa, Synthesis, 89 (1971).

17. M. Cinquini and S. Colonna, J. Chem. Soc., Perkin 1, 1883 (1972).

18. G. Barbier, M. Cinquini, S. Colonna, and F. Montanari, J. Chem. Soc. C, 659 (1968).

19. M. Cinquini, S. Colonna, and F. Montanari, Chem. Comm., 607 (1969).

20. M. Cinquini, S. Colonna, and F. Montanari, ibid., 1441 (1970).

21. M. Cinquini, S. Colonna, and D. Landini, J. Chem. Soc., Perkin 2, 296 (1972).

22. S. Iriuchijima and G. Tsuchihashi, Tetrahedron Lett., 5259 (1969).

23. G. Tsuchihashi and K. Ogura, Bull. Chem. Soc. Jap., 44, 1726 (1971).

24. M. Cinquini and S. Colonna, Synthesis, 259 (1972).

25. R. N. Loeppky and D. C. K. Chang, Tetrahedron Lett., 3415 (1968).

26. M. Hojo and Z. Yoshida, J. Amer. Chem. Soc., 90, 4496 (1968).

27. S. Iriuchijima and G. Tsuchihashi, Synthesis, 588 (1970).

28. S. Iriuchijima and G. Tsuchihashi, Bull. Chem. Soc. Jap., 46, 929 (1973).

29. E. Muller and H. Metzger, J. prakt. Chem., 114, 123 (1926).

30. Societe des Usines Chimiques Rhone-Poulenc, Fr. Patent 145,472 (1957); C. A., 53, 21815 (1959).

31. H. Bohme and H. Fischer, Ber., 75B, 1310 (1942).

32. F. G. Bordwell and W. T. Brannen, Jr., J. Amer. Chem. Soc., 86, 4645 (1964).

33. Societe des Usines Chimiques Rhone-Poulenc. Brit. Patent 778,759 (1957); C. A., 52, 1232 (1958).

34. F. E. Hardy, P. R. H. Speakman and P. Robson, J. Chem. Soc. C, 2334 (1969).

35. J. Metimer, U. S. Patent 2,793,234 (1957); C. A., 52, 1229 (1958).

36. Societe des Usines Chimiques Rhone-Poulenc, Fr. Patent, 1,173,117 (1959); C. A., 56, 417 (1962).

37. P. C. Aichenegg and C. P. Emerson, U. S. Patent 3,249,495 (1966); C. A., 65, 3751 (1966).

38. Chemagro Corp., Fr. Patent 1,484,690 (1967); C. A., 68, 49060 (1968).

39. K. Inukai, T. Ueda, and H. Muramatsu, Bull. Chem. Soc. Jap., 39, 2191 (1966).

40. P. C. Aichenegg and C. D. Emerson, U. S. Patent 3,428,687 (1967); C. A., 70, 114605 (1969).

41. H. J. Backer, J. Strating and J. F. A. Hagenberg, Rec. Trav. Chim., 72, 813 (1953).

42. L. N. Lewin, J. prakt. Chem., 127, 77 (1930).

43. L. N. Lewin and I. Chulkov , ibid., 128, 171 (1930).

44. D. L. Tuleen and R. M. White, J. Tenn. Acad. Sci., 42, 111 (1967); C. A., 68, 95441 (1968).

45. T. Durst, J. Amer. Chem. Soc., 91, 1034 (1969).

46. M. S. Brown, J. Org. Chem., 35, 2831 (1970).

47. E. Molenaar and J. Strating, Rec. Trav. Chim., 87, 49 (1968).

48. R. D. Whitaker and C. L. Bennett, Quart. J., Florida Acad. Sci., 28, 137 (1965); C. A., 63, 9436 (1965).

49. L. A. Carpino and H. W. Chen, J. Amer. Chem. Soc., 93, 785 (1971).

50. B. B. Jarvis, S. D. Dutkey, and H. L. Ammon, ibid., 94, 2136 (1972).

51. B. C. Saunders, G. J. Stacey, F. Wild and I. G. E. Wilding, J. Chem. Soc., 695 (1948).

52. C. G. Venier and H. H. Hsieh, unpublished result.

53. E. Ayca, Rev. Fac. Sci. Univ. Istanbul, Ser. C., 22, 371 (1957); C. A., 53, 11287 (1959).

54. A. Senning, et al., Acta. Chem. Scand., 22, 3256 (1968).

55. J. R. Alexander and H. McCombie, J. Chem. Soc., 1913 (1931).

56. W. V. Farrar, ibid., 508 (1956).

57. T. Durst and K.-C. Tin, Tetrahedron Lett., 2369 (1970).

58. H. Timmler and R. Wegler, Ger. Patent 1,166,773 (1964); C. A., 60, 15781 (1964).

59. H. Boehme and W. Stammberger, Ann., 754, 56 (1971).

60. Jean Metivier, Ger. Patent 1,093,355 (1957); C. A., 56, 1396 (1962).

61. S. Braverman and Y. Stabinsky, Chem. Commun., 270 (1967).

62. S. Braverman and Y. Stabinsky, Israel J. Chem., 5, 125 (1967); C. A., 68, 21379 (1968).

63. N. S. Zefirov and F. A. Abdulvaleeva, Vestu. Mosk. Univ. Khim., 11, 725 (1970); C. A., 74, 125046 (1971).

64. N. S. Zefirov and F. A. Abdulvaleeva, Zh. Org. Khim., 7, 947 (1971); J. Org. Chem. U. S. S. R., 7, 962 (1971).

65. D. A. Evans, G. C. Andrews, T. T. Fujimoto and D. Wells, Tetrahedron Lett., 1385 (1973).

66. G. Sanna and S. Stefano, Gazz. Chim. Ital., 72, 305 (1942); C. A., 38, 39533 (1944).

67. D. J. Abbott and C. J. M. Stirling, Chem. Commun., 472 (1971).

68. I. Kuwajima and Y. Fukuda, Tetrahedron Lett., 327, (1973).

69. D. F. Tavares, R. E. Estep, and M. Blezard, Tetrahedron Lett., 2373 (1970).

70. G. Tsuchihashi and K. Ogura, Bull. Chem. Soc. Jap., 45, 2023 (1972).

71. K. Ogura and G. Tsuchihashi, Chem. Commun, 1689 (1970).

72. M. Cinquini, D. Landini and A. Maia, ibid., 734 (1972).

73. T. Numata and S. Oae, Inter. J. Sulfur Chemistry, Part A, 1, 215 (1971).

74. T. Numata and S. Oae, Bull. Chem. Soc. Jap., 45, 2794 (1972).

75. O. L. Wells and M. L. Lacy, Mich. State Univ., Agr. Exp. Sta., Quart. Bull., 423 (1968); C. A., 69, 758897

76. J. T. Mills and H. A. H. Wallace, Can. J. Plant. Sci., 49, 543 (1969); C. A., 71, 111811 (1969).

77. P. C. Aichenegg and C. D. Emerson, U. S. Patent 3,290,380 (1966); C. A., 67, 536785 (1967).

78. D. L. McIntosh, Plant. Dis. Rep., 53, 182 (1969); C. A., 71, 12028 (1969).

79. J. T. Mills and H. A. H. Wallace, Can. J. Plant. Sci., 48, 587 (1968); C. A., 70, 19209 (1969).

80. S. Iriuchijima and G. Tsuchihashi, Ger. Patent 2,110,519 (1971); C. A., 76, 45932 (1972).

81. C. Shunk and T.-Y. Shen, S. Africa Patent 67 04,557 (1967); C. A., 71, 80943 (1969).

82. Konishiroku Photo Industry Co., Ltd., Neth. Appl. 6,614,847; C. A., 67, 59709 (1967).

83. M. J. Ashwood-Smith, Intern. J. Radiation Biol., 3, 41 (1961); C. A., 58, 8216 (1963).

(Received December 14, 1973; in revised form February 25, 1974)