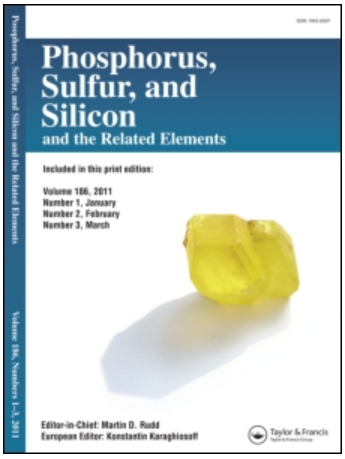

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THE REACTION OF ANHYDROUS HCl/CHLOROFORM WITH DIARYL SULFOXIDES

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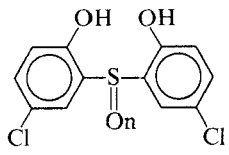
The reaction of variously substituted diaryl sulfoxides with anhydrous HCl in chloroform was examined. The products ranged from the corresponding sulfides to mono- and dichlorinated sulfides and sulfoxides. The same reaction in the presence of phenol afforded primarily the corresponding sulfides accompanied by *o*- and *p*-chlorophenol. The latter reaction is an efficient means for deoxygenating diaryl sulfoxides. The mechanism of the reaction and the nature of the chlorinating species are discussed.

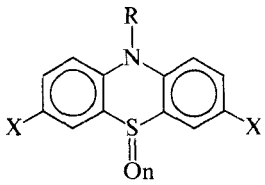
INTRODUCTION

Among the vast number of methods available for the deoxygenation of sulfoxides[1] are the reactions with hydrogen halides (HX). While these reactions of HX with sulfoxides include some of the oldest methods known for reduction, there appears to be controversy and inconsistencies in the literature concerning resulting products and their mechanisms of formation. While the reactions of HI with sulfoxides often lead to clean reductions[1] without accompanying side products, the reactions with HBr and especially HCl are not as direct. It is the reaction of HCl with diaryl sulfoxides about which this work is concerned.

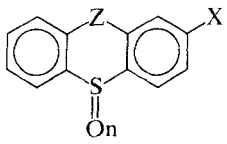
Gazdar and Smiles[2] found that ethanolic HCl reduced **1** primarily to its sulfide **2** accompanied by higher chlorides of **2**. Upon refluxing 10-methylphenothiazine sulfoxide (**3**) in 20% aqueous HCl, Schmalz and Burger[3] isolated the 3-chloro sulfide while the same reaction using **4** afforded both a demethylated tetrachloro sulfide and **5**. Similar results were obtained by Page and Smiles[4] with **3** and phenothiazine sulfoxide (**6**) and with the 10-ethyl derivative **7** by Gilman and Eisch.[5]



1 $n = 1$
2 $n = 0$



	X	R	n
3	H	CH_3	1
4	Cl	CH_3	1
5	Cl	CH_3	0
6	H	H	1
7	H	CH_2CH_3	1



	Z	X	n
8	S	H	1
9	S	H	0
10	S	Cl	0
11	C=O	H	1
12	C=O	H	0

Shine and Dais[6] have shown that the reaction of thianthrene sulfoxide (**8**) in conc. HCl at room temperature afforded both thianthrene (**9**) and 2-chlorothianthrene (**10**) while Castrillon and Szmant[7] found that thioxanthone sulfoxide (**11**) and a hydrazone derivative in conc. HCl/dioxane only afforded thioxanthone (**12**). Thus, it is not clear whether HCl can be used generally for preparative reductive chlorinations or pure reductions of aromatic sulfoxides. To further cloud the issue, the reaction of phenylacetyl chloride with diphenyl sulfoxide was reported by Nagai and Sammes[8] to give both reduction and reductive chlorination while the reaction of acetyl chloride with the same sulfoxide gave quantitative reduction[9] only.

TABLE I

Products resulting from the reaction of HCl with diaryl sulfoxides

Compound	Product mixtures and composition (%)[a,b]					
	Starting material	Sulfide	Monochlorined sulfide	Dichlorinated sulfide	Monochlorinated sulfoxide	Unidentified products
13 $4\text{-}ClC_6H_4S(O)C_6H_4Cl\text{-}4$	83	17	—	—	—	—
14 $C_6H_5S(O)C_6H_5$	25	32	28	3	8	4
15 $4\text{-}CH_3C_6H_4S(O)C_6H_4CH_3\text{-}4$	5	66	10	6	—	13
16 $C_6H_5S(O)C_6H_4OCH_3\text{-}4$	—	36	28	24	6	6
17 $C_6H_5S(O)C_6H_3(OCH_3)_2\text{-}2,4$	—	12	84[c]	—	—	—

[a] The products were identified by comparison of GC retention times with those of authentic materials, where available, and by GC/mass spectrometry.

[b] Compounds **13–16** were reacted for 4 weeks while **17** was reacted for 24 hrs.

[c] This material was actually isolated and characterized (see Experimental).

RESULTS AND DISCUSSION

We have examined the reaction of anhydrous HCl at 0–25° with a variety of diaryl sulfoxides dissolved in chloroform. These conditions are in contrast to suspensions in conc. aqueous HCl, aqueous HCl/dioxane and sat. HCl/ethanol as discussed above and provide for a single phase non-aqueous system. The results of these reactions are shown in Table I. While the percentages are variable from one run to another, a general trend was observed. For **13**, which is deactivated toward electrophilic substitution, the primary product was sulfide with no products resulting from reductive chlorination, for a reaction time of 4 weeks. Much starting material was recovered. For **14–16**, which are more activated than **13** toward electrophilic substitution, reduction and reductive chlorination products were observed for the same reaction period, with less starting material remaining. For **17**, which is highly activated toward electrophilic substitution, reductive chlorination predominated. The reaction was complete within 24 hrs.

Gilman and Eisch[5] tried to distinguish between a nucleophilic attack by chloride ion and an electrophilic attack by chlorine (or chloronium ion) in the reductive chlorination of **7** in aqueous HCl. They added phenol to the reaction medium to trap electrophilic chlorine. However, while bromophenol formed with HBr, no chlorophenol formed with HCl. However, they still concluded that electrophilic chlorination was operable. Shine and Dais[6] performed a similar experiment using **8**, phenol and conc. HCl. They detected chlorine above the surface of the reaction solution and also found that *p*-chlorophenol formed yet concluded from other evidence that nucleophilic substitution by chloride ion was the mechanism for reductive chlorination.

The reaction of anhydrous HCl with **13–17** in chloroform in the presence of equal molar quantities of phenol was performed. Compounds **13–16** were quantitatively reduced to their corresponding sulfides with concomitant formation of a mixture of *o*- and *p*-chlorophenol. Compound **17** underwent both reduction and reductive chlorination accompanied by chlorophenol formation (see Table II). These reactions were all complete within 24 hrs. The formation of *o*- and *p*-chlorophenol (and multiple chlorination products in

TABLE II

Products resulting from the reaction of HCl/Phenol with diaryl sulfoxides

Compound	Product[a]	Yield[b] (%)	mp (°C) bp(°C)/kPa	Lit. mp or bp/kPa
13 4—$ClC_6H_4S(O)C_6H_4Cl$—4	4—$ClC_6H_4SC_6H_4Cl$—4	93	93–95	95[c]
14 $C_6H_5S(O)C_6H_5$	$C_6H_5SC_6H_5$	100	151/1.5	151.5/1.5[d]
15 4—$CH_3C_6H_4S(O)C_6H_4CH_3$—4	4—$CH_3C_6H_4SC_6H_4CH_3$—4	95	56–57.5	57[c]
16 $C_6H_5S(O)C_6H_4OCH_3$—4	$C_6H_5SC_6H_4OCH_3$—4[e]	100	140/.32	138–140/.27[f]
17 $C_6H_5S(O)C_6H_3(OCH_3)_2$—2,4	$C_6H_5SC_6H_3(OCH_3)_2$—2,4 $C_6H_5SC_6H_2(OCH_3)_2Cl$—2,4,5	~50 ~50	oil[g]	

[a] The TLC, GC, and IR of these products were identical to those of authentic sulfides, where available.
[b] Yield of the isolated product of >98% purity as determined by TLC and GC.
[c] *Handbook of Chemistry and Physics*, 55th Edn., Chemical Rubber Co., Cleveland, Ohio, 1974–75.
[d] Beilsteins Handbuch der Organischen Chemie, **6**, 299, Berlin: Springer-Verlag.
[e] This compound was characterized by IR and NMR ($CDCl_3$) since its sulfide was not available.
[f] R. Adams, W. Reefschneider, and M. D. Nair, *Croat. Chem. Acta*, **29**, 277 (1957); CA **53**: 16145f (1959).
[g] The two products were not separated from one another and were identified by GC comparison to authentic materials.

the absence of phenol) indicates that the reductive chlorination is not intramolecular and that chlorination is by an electrophilic species, since *o*- and *p*-chlorophenol are expected from electrophilic attack. That **17** is both reduced and reductively chlorinated in the presence of phenol indicates that the electron rich ring of the sulfide of **17** can compete with phenol for the electrophile.

The mechanism of racemization and reduction of sulfoxides catalyzed by halide ions in aqueous acidic media has been extensively examined.[10] More recently Ciuffarin *et al.* examined the chloride catalyzed racemization[11] and oxygen exchange[12] of non-cleavable sulfoxides[13] in acidic non-aqueous solvents. They proposed a mechanism for racemization as is shown in Eqs. (1)–(4).

$$>S{=}O + H^+ \rightleftharpoons >S^+{-}OH \quad (1)$$

$$>S^+{-}OH + Cl^- \rightleftharpoons >S\begin{matrix}OH\\Cl\end{matrix} \quad (2)$$

$$>S\begin{matrix}OH\\Cl\end{matrix} \overset{H^+}{\rightleftharpoons} >S^+{-}Cl + H_2O \quad (3)$$

$$>S^+{-}Cl \overset{Cl^-}{\rightleftharpoons} >S + Cl_2 \quad (4)$$

It was concluded[12] that the equilibria lie far to the left, that the rate determining step (**4**) is removal of the chlorosulfonium ion, and that the process leading to racemization is the same as that leading to reduction, up to the rate determining step. If this mechanism were operable under our conditions with diaryl sulfoxides, then the chlorosulfonium ion or chlorine would be available for electrophilic chlorination. That the rate of reduction of the sulfoxides in the presence of phenol is so much faster than the reductive chlorination of the sulfoxides in its absence suggests that the equilibria do lie far to the left and only when the chlorinating species can be removed rapidly can the equilibria be shifted to the right. It is not possible at this time to identify the chlorinating species as chlorine or chlorosulfonium ion although it appears that chlorine is present.[6,12]

In conclusion, $HCl/CHCl_3$ can best be used for reductive chlorination of diaryl sulfoxides when the rings are strongly activated toward electrophilic attack. Alternatively, $HCl/CHCl_3$ can best be used for reduction of diaryl sulfoxides (especially in the presence of phenol) when the aromatic groups are not activated toward electrophilic attack.

EXPERIMENTAL

Compounds **13**, **14** and **15** are commercially available from Aldrich Chemical Co. TLC analyses were performed on Analtec, Inc., pre-coated silica gel plates using chloroform as eluent and UV light for visualization and GC analyses on a Hewlett Packard Model 5840A equipped with an 18″ × 1/8″ column of 10% OV-17 on Chromosorb W. Mass spectra were obtained on a Varian MAT 311A equipped with a Finnigan Incas Data System and NMR spectra on a Varian Model A60. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Huffman Labs, Wheatridge, Colo.

4-Methoxydiphenyl Sulfoxide (**16**). This compound was prepared in 90% yield according to the general procedure of Chasar and Pratt[14] using benzenesulfinyl chloride and anisole with anhydrous aluminum chloride in methylene chloride. A hexane wash of the crude material afforded a white solid, mp 86–89°C; IR (Nujol) 1040 (S=O) cm^{-1}; NMR ($CDCl_3$) δ 3.76 (s, 3), 6.92 (d, 2, J = 8.5 Hz), 7.58 (d, 2, J = 8.5 Hz), 7.3–7.7 (m, 5). Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.22; H, 5.21; S, 13.80. Found: C, 67.82; H, 5.00; S, 13.95.

2,4-Dimethoxydiphenyl Sulfoxide (**17**). This compound was prepared in 70% yield according to the general procedure of Chasar and Pratt[14] using benzenesulfinyl chloride and 1,3-dimethoxybenzene with anhydrous aluminum chloride in methylene chloride. Recrystallization of the crude solid from ethyl acetate afforded a white solid, mp 93–96°C; IR (Nujol) 1020 (S=O) cm^{-1}; NMR ($CDCl_3$) δ 3.74 (s, 3), 3.77 (s, 3), 6.39 (d, 1, J = 2.4 Hz), 6.60 (dd, 1, J = 8.0, 2.4 Hz), 7.2–7.8 (m, 6). Anal Calcd. for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38; S, 12.22. Found: C, 64.47; H, 5.95; S, 12.22.

General Procedure for the Reductive Chlorination of Diaryl Sulfoxides

HCl gas is bubbled through a solution of the diaryl sulfoxide in chloroform at 0–25°C. The progress of the reaction is followed by TLC or GC. When the reaction is complete, the chloroform solution is washed with water, dried (Na_2SO_4), and evaporated to afford an oil or solid.

2,4-Dimethoxy-5-Chlorodiphenyl Sulfide. HCl gas is bubbled slowly through a solution of **17** (5.0 g, 0.019 mol) in chloroform (50 ml) for 24 hr. The solution is washed with water, dried (Na_2SO_4) and the solvent evaporated to afford an oil which slowly crystallizes. A washing with cold methanol afforded 3.35 g (63%) of a white crystalline solid, mp 83–87°C; IR (Nujol) no S=O absorption; NMR ($CDCl_3$) δ 3.82 (s, 3), 3.90 (s, 3), 6.53 (s, 1), 7.33 (s, 1), 7.03 (m, 5). Anal. Calcd. for $C_{14}H_{13}ClO_2S$: C, 59.89; H, 4.67; Cl, 12.63; S, 11.42. Found: C, 60.28; H, 4.69; Cl, 12.35; S, 11.63.

General Procedure for the Reduction of Diaryl Sulfoxides with HCL/Phenol

HCl gas is bubbled through a chloroform solution of equimolar quantities of diaryl sulfoxide and phenol at 0–25°. The progress of the reaction is followed by TLC or GC. When the reaction is complete, the chloroform solution is extracted with aq. 2N NaOH solution, water, dried (Na_2SO_4) and evaporated to give the crude sulfide.

The caustic extracts can be acidified with conc. HCl and extracted with chloroform to recover the chlorinated phenols, which are analyzed by GC.

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