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THE REACTION OF SULFOXIDES WITH HYDROGEN CHLORIDE

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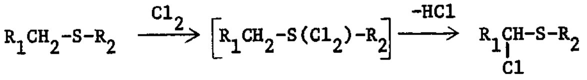
The reversible formation of sulfodichloride intermediates (1) has been proposed to explain the

$$R_1R_2SO \; + \; 2HCl \rightleftharpoons \underset{1}{[R_1R_2SCl_2]} \; + \; H_2O \qquad \text{(Eq. 1)}$$

racemization of optically active sulfoxides by hydrogen chloride in organic solvents (Eq. 1).[1,2] Mislow[2] has suggested that the symmetrization of the sulfodichloride may be the result of its being either a slightly distorted trigonal bipyramid with a plane of symmetry or a set of rapidly interconverting enantiomeric chlorosulfonium chlorides. Recently Allegra and co-workers[3] have suggested that loss of chirality of 1 may arise from rapid, reversible dissociation to the achiral sulfide and chlorine (Eq. 2).

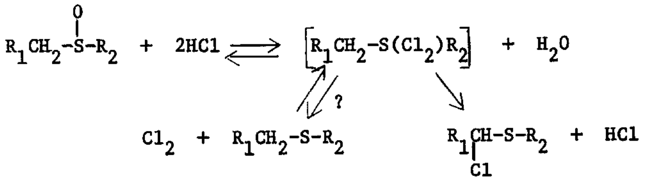
$$R_1R_2SCl_2 \rightleftharpoons R_1R_2S \; + \; Cl_2 \qquad \text{(Eq. 2)}$$

Sulfodichlorides (chlorosulfonium chlorides) are also intermediates in the chlorination of sulfides to afford α-chlorosulfides (Eq. 3).[4,5] If sulfodichlorides are indeed intermediates in



$$R_1CH_2\text{-}S\text{-}R_2 \xrightarrow{Cl_2} [R_1CH_2\text{-}S(Cl_2)\text{-}R_2] \xrightarrow{-HCl} R_1\underset{Cl}{CH}\text{-}S\text{-}R_2 \qquad \text{(Eq. 3)}$$

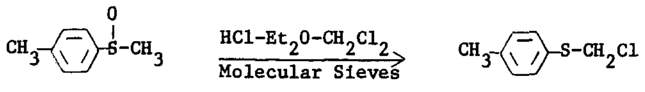
the hydrogen chloride catalyzed racemization of sulfoxides, they should lead to the same products, α-chlorosulfides, that are observed in the chlorination of sulfides. This mode of reaction should be facilitated by removal of water, forcing the equilibrium to the right (Eq. 4).



$$R_1CH_2\text{-}\overset{O}{S}\text{-}R_2 \; + \; 2HCl \rightleftharpoons [R_1CH_2\text{-}S(Cl_2)R_2] \; + \; H_2O \qquad \text{(Eq. 4)}$$

$$Cl_2 \; + \; R_1CH_2\text{-}S\text{-}R_2 \qquad R_1\underset{Cl}{CH}\text{-}S\text{-}R_2 \; + \; HCl$$

Indeed, treatment of methyl p-tolyl sulfoxide[6] with HCl in CH_2Cl_2, with removal of H_2O, afforded a 77% yield of the α-chlorosulfide, chloromethyl p-tolyl sulfide (2). In a



2

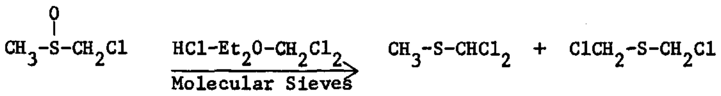
similar manner DMSO was converted into chloromethyl methyl sulfide (3) in 73% yield.

$CH_3-\overset{O}{\overset{|}{S}}-CH_3 \longrightarrow CH_3-S-CH_2Cl$

3

The formation of α-chlorosulfides from sulfoxides on treatment with HCl lends support to the intermediacy of sulfodichlorides in the racemization of sulfoxides and provides a convenient method for the conversion of certain sulfoxides into α-chlorosulfides, an important class of synthetic intermediates.[7]

The selectivity of this reaction closely parallels that observed in the chlorination of sulfides. Böhme and Gran[8] have shown that chlorination of chloromethyl methyl sulfide afforded dichloromethyl methyl sulfide (5) as the only isolated product. Preferential formation of 5 also resulted on treatment of chloromethyl methyl sulfoxide with HCl.

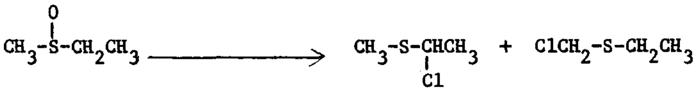


$CH_3-\overset{O}{\overset{|}{S}}-CH_2Cl \xrightarrow[\text{Molecular Sieves}]{HCl-Et_2O-CH_2Cl_2} CH_3-S-CHCl_2 + ClCH_2-S-CH_2Cl$

5 6

95:5[9]

Böhme and Gran isolated 1-chloroethyl methyl sulfide (7) as the only product in the chlorination of ethyl methyl sulfide.[10] Preferential formation of 7 also resulted on treatment of ethyl methyl sulfoxide with HCl.



$CH_3-\overset{O}{\overset{|}{S}}-CH_2CH_3 \longrightarrow CH_3-S-\underset{Cl}{\underset{|}{C}}HCH_3 + ClCH_2-S-CH_2CH_3$

7 8

3:1[11]

The general procedure used in the above reactions can be illustrated by the following specific example.

Chloromethyl *p*-Tolyl Sulfide (2). — A stirred mixture of methyl *p*-tolyl sulfoxide (18 g; 0.117 mole), CH_2Cl_2 (300 ml), and 3A molecular sieves (20 g) was treated dropwise with a saturated solution of HCl in Et_2O. After stirring at room temperature for an additional two hours, the solution was decanted from the molecular sieves. The solvent was removed on a rotary evaporator and the residue was vacuum distilled to afford 15.6 g (77% yield) of **2**, bp, 88°/0.2 mm.

It was noted that in all cases the reaction mixtures developed a faint yellow color reminiscent of Cl_2. This would be in accord with the before mentioned suggestion of Allegra and co-workers[3] and the recent equilibrium studies of Wilson and Chang.[12]

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