Oxidative Chlorination of α-Halogenosulphides as a Synthetic Route to α-Halogenosulphoxides, Sulphinyl Chlorides, and Sulphonyl Chlorides

By J. S. GROSSERT,* W. R. HARDSTAFF, and R. F. LANGLER
(*Chemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada*)

Summary Chlorine is used to cleave and/or oxidize sulphur compounds as a means of furnishing α-polyhalogenosulphoxides, sulphinyl chlorides, or sulphonyl chlorides; a new synthesis of chloromethanesulphonyl chloride is described.

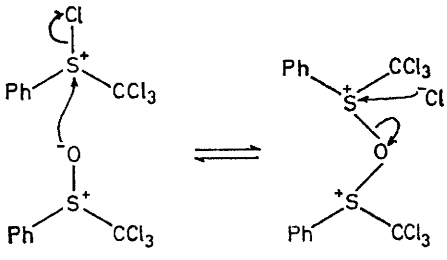
SULPHIDES and sulphoxides have been chlorinated to give α-halogeno-derivatives using a variety of reagents.[1] The elucidation of the mechanism of the oxidative chlorination of α-halogeno-sulphides and -sulphoxides[2] has suggested synthetic potential for some of these reactions. Three synthetic routes have been explored.

(i) $R^1{\cdot}S{\cdot}R^2$ (α-polyhalogeno-sulphides) $\rightarrow R^1{\cdot}SO{\cdot}R^2$. By carrying out chlorination in acetic acid containing water (molar ratio sulphide : water = 1 : 3), we have successfully oxidized some α-polyhalogeno-sulphides to the following sulphoxides (yields in parentheses): $ClCH_2{\cdot}SO{\cdot}CH_2Cl$ (77%), $Cl_2CH{\cdot}SO{\cdot}CH_2Cl$ (65%), $Cl_3C{\cdot}SO{\cdot}CH_2Cl$ (50%), $Cl_3C{\cdot}SOMe$ (62%), $Cl_3C{\cdot}SOPh$ (63%). We have found also that chlorosulphonium chlorides are inert to acetolysis, which makes it possible to accomplish both chlorination and oxidation in one reaction. The starting sulphide was chlorinated; after the addition of water, further chlorination furnished the sulphoxide. In this way bischloromethyl sulphide was reproducibly converted into ααα′-trichlorodimethyl sulphoxide in 50% yield.

(ii) $R{\cdot}SO{\cdot}R$ (α-trichloro-sulphoxides) $\rightarrow R{\cdot}SO{\cdot}Cl$. The intervention of sulphinyl chlorides in the normal cleavage of αα-dichloro-sulphoxides when chlorinated in water,[2] suggested the possibility of a new approach to the preparation of these compounds. We have found that α-trichloro-sulphoxides can be cleaved to give sulphinyl chlorides when chlorinated in methylene chloride. The following sulphinyl chlorides were prepared: $ClCH_2{\cdot}SOCl$ (72% from $ClCH_2{\cdot}SO{\cdot}CHCl_2$); $ClCH_2{\cdot}SOCl$ (81% from $ClCH_2{\cdot}SO{\cdot}CCl_3$); $MeSOCl$ (77% from $MeSO{\cdot}CCl_3$); and $PhSOCl$ (35% from $PhSO{\cdot}CCl_3$).

Since all previous methods for the preparation of sulphinyl chlorides proceed through the corresponding sulphenyl chlorides,[3] this cleavage reaction is a new and potentially useful route to sulphinyl chlorides.

It should be noted that chlorinolysis of $PhSO{\cdot}CCl_3$ did not occur in the presence of the corresponding sulphide. This observation was readily rationalized by invoking a novel degenerate reaction (Scheme).



SCHEME

(iii) $R{\cdot}S{\cdot}CH_2Cl + Cl_2{-}H_2O \rightarrow R{\cdot}SO_2Cl$. Elucidation of the pathway by which 1,3,5-trithian is transformed into methanesulphonyl chloride, has permitted the formulation of a new and general approach to the preparation of sulphonyl chlorides. Chlorination of dimethyl sulphoxide in water yielded 70% dimethyl sulphone. By contrast, the presence of only one chlorine atom in the starting material suppressed sulphone formation to less than 5%. This observation was extended to oxidative chlorination of α-halogeno-sulphides and it was found that the following sulphonyl chlorides could be obtained: R = Me (75%), R = CH_2Cl (70%), R = Ph (68%).

Application of this reaction to $ClCH_2{\cdot}S{\cdot}CCl_3$ (**1**)† gave $ClCH_2{\cdot}SO_2Cl$ (75%); with respect to yield and purity of product, this process is superior to published methods[4] involving either chlorination of 1,3,5-trithian or a 4-step synthesis from Me_2SO_4 and KSCN.

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† Obtainable from $MeSOMe + SOCl_2 \rightarrow MeS{\cdot}CH_2Cl + Cl_2{-}CCl_4 \rightarrow$ (**1**), in 62% overall yield.

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