Pathway of the Oxidative Chlorination of 1,3,5-Trithian

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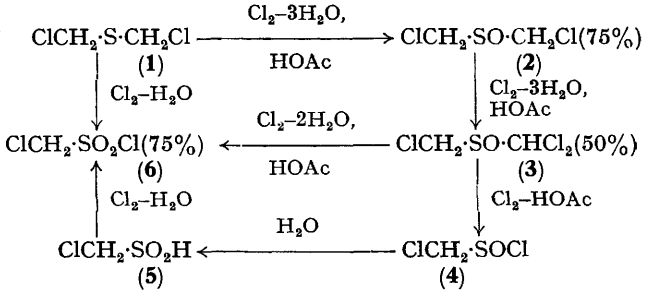
Summary Chlorination of 1,3,5-trithian in water–acetic acid proceeds through bischloromethyl sulphide which subsequently undergoes stepwise degradation through chloromethanesulphinyl chloride to give chloromethanesulphonyl chloride.

DURING the preparation of chloromethanesulphonyl chloride from molecular chlorine and 1,3,5-trithian,[1,2] it became apparent that the reaction did not proceed directly to the desired product. Two previous attempts to unravel the pathway of this reaction concluded either that bischloromethyl disulphide might be the intermediate,[2] or that chloromethanesulphenyl chloride might be a short-lived intermediate.[3]

We have reinvestigated this reaction under controlled conditions, *i.e.* we have chlorinated a 1,3,5-trithian–water mixture (1 : 5 molar ratio) in acetic acid solvent, and have isolated and identified a variety of products along with the key intermediate, bischloromethyl sulphide (**1**; 53% yield). Also, we have found that (**1**) may react further in a stepwise and controlled manner as shown in the Scheme.

The intermediacy of (**4**) in the conversion of (**3**) into (**6**) was demonstrated by its observation after chlorination of (**3**) in anhydrous acetic acid; (**4**) hydrolyses readily[4] to give (**5**). We have observed comparable reaction pathways for the conversion (**3**) → (**6**) in both anhydrous acetic acid and in acetic acid–water mixtures.



SCHEME

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