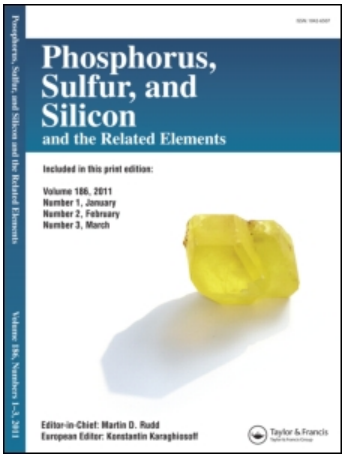

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REACTIONS OF CHLOROTHIOLFORMATE ESTERS WITH DIMETHYL SULFOXIDE

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REACTIONS OF CHLOROTHIOLFORMATE ESTERS WITH DIMETHYL SULFOXIDE.

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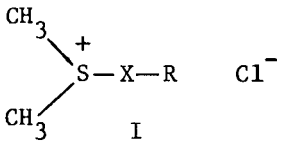
The reaction of an alkyl chloroformate with dimethyl sulfoxide gives the corresponding alkoxysulfonium chloride (I; X = O) and carbon dioxide. However, the corresponding reactions with chlorothiolformate esters do not yield the salts (I; X = S). Phenyl chlorothiolformate reacts with dimethyl sulfoxide according to equation [1].



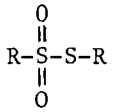
I

[1] $2\text{Ph-S-C}(=\text{O})\text{Cl} + 3\ (\text{CH}_3)_2\text{S}{=}\text{O} \longrightarrow \text{Ph-S-S-Ph} + 2\text{CO}_2 + (\text{CH}_3)_2\text{S}$

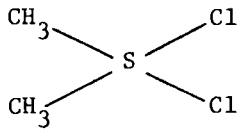
II

$\text{CH}_3\text{-S-CH}_2\text{Cl} + (\text{CH}_3)_2\text{SO.HCl}$

III IV



V



VI

Methyl chlorothiolformate probably reacts similarly, but the disulfide is oxidised by dimethyl sulfoxide to the thiolsulfonate ester (V; R = CH_3). Indeed, the disulfide is produced when the sterically hindered t-butyl chlorothiolformate is used in this reaction.

The results suggest that dimethylsulfur dichloride (VI) is an intermediate in these reactions and that it decomposes to form (III) and hydrogen chloride which immediately reacts with dimethyl sulfoxide to form (IV). Prepared in this way, (IV) is remarkably stable and has a melting

point of 56°C. It has previously been reported that unstable solids are formed when dimethyl sulfoxide is treated with dry hydrogen chloride[2,3].

References.

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