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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

REACTIONS OF CHLOROTHIOLFORMATE ESTERS WITH DIMETHYL SULFOXIDE

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To cite this Article Queen, Alan , Janzen, A. F. , Lemire, A. and Preston, K.(1979) 'REACTIONS OF CHLOROTHIOLFORMATE ESTERS WITH DIMETHYL SULFOXIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 251 – 252

To link to this Article: DOI: 10.1080/03086647908080399

URL: <http://dx.doi.org/10.1080/03086647908080399>

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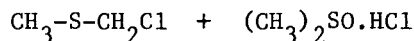
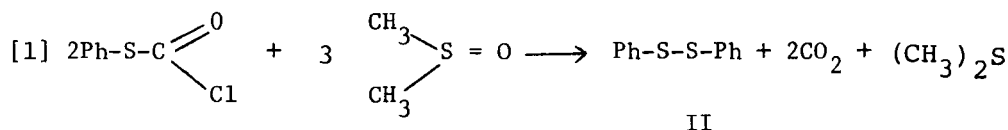
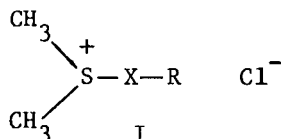
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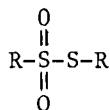
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The reaction of an alkyl chloroformate with dimethyl sulfoxide gives the corresponding alkoxysulfonium chloride (I; X = O) and carbon dioxide. However, the corresponding reactions with chlorothiolfomate esters do not yield the salts (I; X = S). Phenyl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

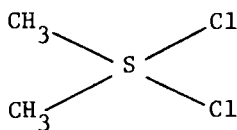


III

IV



V



VI

Methyl chlorothiolfomate probably reacts similarly, but the disulfide is oxidised by dimethyl sulfoxide to the thiolsulfonate ester (V; R = CH₃). Indeed, the disulfide is produced when the sterically hindered t-butyl chlorothiolfomate 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}.

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