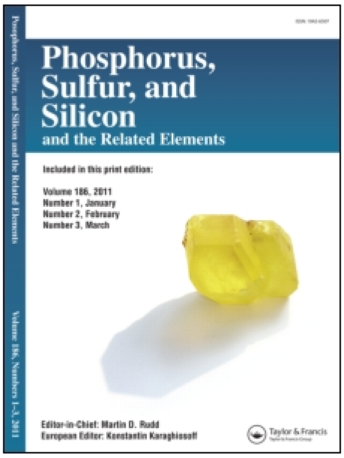

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Reactions of Carbon Monosulfide with Geminal Disulfenyl Dichlorides

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Unlike vicinal disulfenyl dichlorides whose carbon monosulfide diinsertion products readily cyclize with loss of thiophosgene, geminal disulfenyl dichlorides diinsert carbon monosulfide to form stable *gem*-bis(chlorodithioformates).

INTRODUCTION

The preparative use of carbon monosulfide in organic synthesis has been explored by ourselves and collaborating laboratories.[1-3] The single most productive reaction of this kind has been the insertion of CS into sulfur-chlorine bonds according to (1).

$$\text{R–S–Cl} + \text{CS} \rightarrow \text{R–S–C(=S)–Cl} \qquad (1)$$

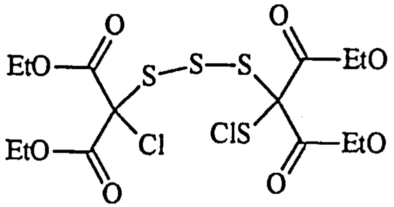
This reaction has so far been carried out with disulfur dichloride,[1] monofunctional sulfenyl chlorides (RSCl),[1] monofunctional chlorodisulfanes (RSSCl),[1] vicinal disulfenyl dichlorides,[3] and other multifunctional oligo(sulfenyl chlorides).[3] This work showed, *inter alia*, that 1,2-alkylene bis(chlorodithioformates) **1**, formed from vicinal disulfenyl dichlorides and CS, are inherently unstable towards spontaneous loss of thiophosgene and formation of the corresponding 1,3-dithiolane-2-thiones (cyclic trithiocarbonates).[3] Off hand, the known stability of cyclic trithiocarbonates of the 1,3-dithietane-2-thione type could suggest a similar thiophosgene loss from geminal analogs of **1** such as **2**, $(EtOOC)_2C[SC(=S)Cl]_2$.

gem-DISULFENYL DICHLORIDES

gem-Disulfenyl dichlorides **3** $R^1R^2C(SCl)_2$ have been prepared in a number of ways.[4] We chose **3a** (**3**, $R^1 = R^2 =$ COOEt)[4c] as our model compound. A CS insertion experiment with **3a** [which was only available in an inseparable mixture with **4**, $(EtOOC)_2C(Cl)SCl$] gave **2** as well as **5**, $(EtOOC)_2C(Cl)[SC(=S)Cl]$ (which could also be obtained from independently prepared **4**[5] and CS), the intriguing unsymmetrical trisulfide **6**, and pentathianedicarboxylic acid diethyl ester, **7**.

This mixture decomposed upon attempted separation, but could be identified by ^1H and ^{13}C NMR as well as MS. Unlike its vicinal counterparts, the geminal compound **2** appears to be stable towards spontaneous loss of thiophosgene.

Upon careful scrutiny and under a variety of conditions no chlorotropic rearrangement of **2** to the isomeric chlorodisulfane **8**, $(EtOOC)_2C(Cl)SSCl]$, could be observed.



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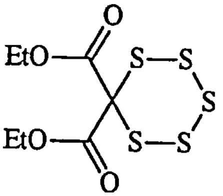

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