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Reactions of Carbon Monosulfide with Geminal Disulfenyl Dichlorides

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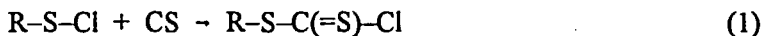
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Unlike vicinal disulfenyl dichlorides whose carbon monosulfide diinsertion products readily cyclize with loss of thiophosgene, geminal disulfenyl dichlorides diinsert carbon monosulfide to form stable *gem*-bis(chlorodithioformates).

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).



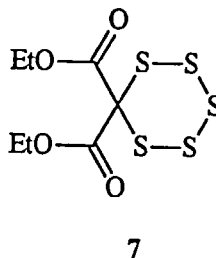
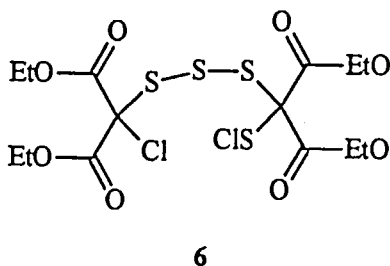
This reaction has so far been carried out with disulfur dichloride,¹ monofunctional sulfenyl chlorides (RSCl),¹ monofunctional chlorodisulfanes (RSSCl),¹ vicinal disulfenyl dichlorides,³ and other multifunctional oligo(sulfenyl chlorides).³ This work showed, *inter alia*, that 1,2-alkylene bis(chlorodithioformates) **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 $3 \text{ R}^1\text{R}^2\text{C}(\text{SCl})_2$ have been prepared in a number of ways.⁴ We chose **3a** ($3, \text{R}^1 = \text{R}^2 = \text{COOEt}$)^{4c} as our model compound. A CS insertion experiment with **3a** [which was only available in an inseparable mixture with **4**, $(\text{EtOOC})_2\text{C}(\text{Cl})\text{SCl}$] gave **2** as well as **5**, $(\text{EtOOC})_2\text{C}(\text{Cl})[\text{SC}(=\text{S})\text{Cl}]$ (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**, $(\text{EtOOC})_2\text{C}(\text{Cl})\text{SSCl}$, could be observed.

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