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AN UNUSUAL REARRANGEMENT, AND FURTHER TRANSFORMATIONS, IN THE CHLORINATION OF ALKOXYTHIOCARBONYLSULFENYL SUBSTRATES

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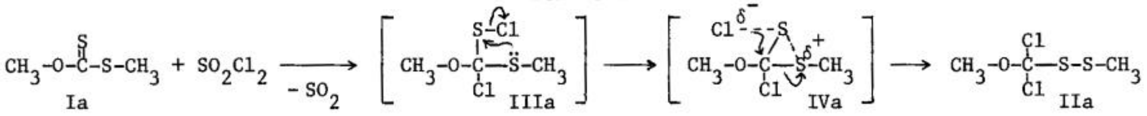
Abstract: Treatment of alkoxythiocarbonylsulfenyl substrates with one equiv. of sulfuryl chloride, expected to provide alkoxychlorothiochloromethylsulfenyl derivatives, gave directly alkoxydichloromethyldisulfanyl products *via* a rapid intramolecular rearrangement.

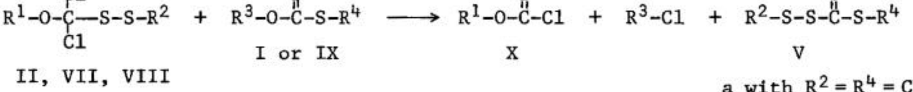
The addition of chlorine to a thiocarbonyl group to yield chloromethanesulfenyl chlorides is well precedented[2]. Relatedly, sulfenyl chlorides have recently been shown[3] to react with thiocarbonyl substrates to give chloromethyl disulfanes as the initial addition products. Therefore, it was most surprising to find (Scheme 1) that treatment of *O,S*-dimethyl dithiocarbonate (Ia) with one equiv. of sulfuryl chloride[4,5] gave directly a relatively *stable* chlorinated adduct[6] best assigned the alkoxydichloromethyldisulfanyl structure IIa. This conclusion was supported by a variety of further transformations of IIa, as generalized for the chlorination products of additional alkoxythiocarbonylsulfenyl substrates (Scheme 2). The present report also argues, on the basis of kinetic measurements and trapping experiments, that the *expected* adduct, as IIIa, does form but then undergoes a *rapid intramolecular rearrangement* that involves a three-membered transition state with two sulfur heteroatoms[7] and a partial positive charge, as IVa.

Scheme 1



Regardless of how made, alkoxydichloromethyldisulfanyl compounds reacted either as "masked" (dithio)carbonyl chlorides (Scheme 2, F and M) or as "masked" sulfenyl chlorides (Scheme 2, H to L). A special case of the latter was the reaction of Ia plus SO_2Cl_2 (2 : 1 molar ratio), which upon distillation[8] led to a 73% yield of pure *S*-methylsulfenyl,*S'*-methyl dithiocarbonate (Va)[3], bp 116 °C (20 mm), along with 8% of bis([methylthio]carbonyl)disulfane (VIa)[9,10], bp 105-107 °C (0.1 mm). Applying the earlier understanding, a general synthesis for mixed sulfenyl dithiocarbonates was devised (Scheme 3), with the fates of the R groups exactly as drawn[11].

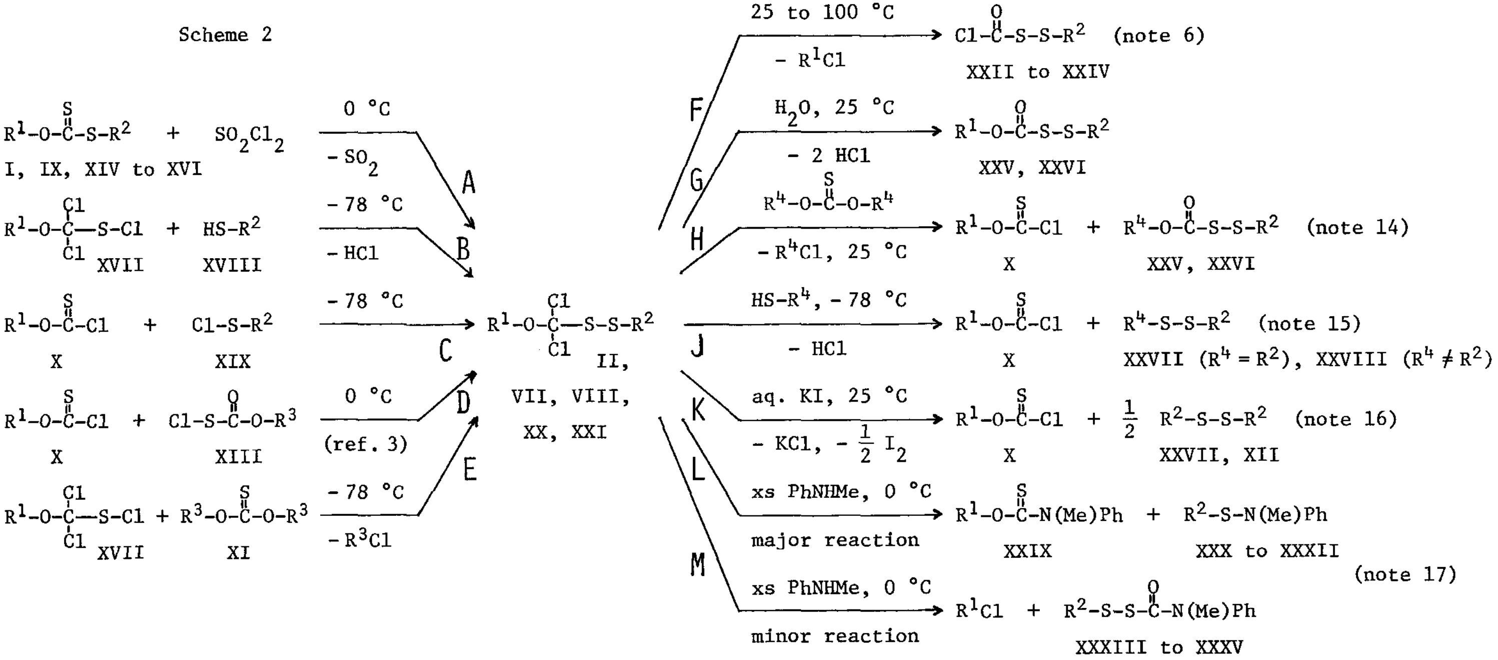
Scheme 3



a with $R^2 = R^4 = CH_3$
others as per this Scheme 3 & note 11

In contrast to the results with dithiocarbonates (Scheme 3), *O,O'*-dimethyl thiocarbonate (XIa) plus SO_2Cl_2 (2 : 1 molar ratio) rapidly gave at 0 °C bis(methoxycarbonyl)disulfane (XIIa)[12] in 85% distilled yield, pure crystals, mp 33 °C (Scheme 4). Methoxycarbonylsulfenyl chloride (XIIIa), separately documented[3] to react with XIa (1 : 1) to yield XIIa, was shown to be[13] an

Scheme 2



For all compounds with *single* radical, **a** = CH_3, **b** = C_2H_5. For remainder, see following numbering scheme.

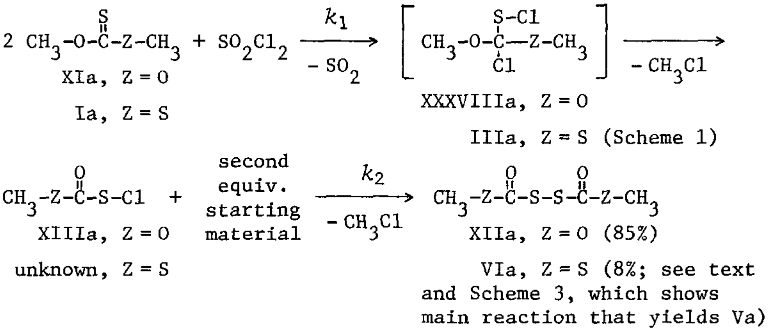
	Substrates	Products	Further Transformations				
			F	G	K	L	M
$R^2 = CH_3$	I	II	XXIIa	XXV	XXVIIa	XXXa	XXXIIIa
$R^2 = C_2H_5$	IX	VII	XXIIb	XXVI	XXVIIb	XXXb	XXXIIIb
$R^2 = (C{=}O)OR$, $R^3 = CH_3$	XIV	VIII	XXIIIa	stable	XIIa	XXXIa	XXXIVa
$R^2 = (C{=}O)OR$, $R^3 = C_2H_5$	XV	XX	XXIIIb	stable	XIIb	XXXIb	XXXIVb
$R^2 = (C{=}S)OCH_3$	XVI	XXI	XXIV	not done	not done	XXXII	XXXV

All starting materials (left of Scheme) described in ref. 3. Among alkoxydichloromethyldisulfanyl compounds (center), VIIIa and XXa were reported in ref. 3, made by route D. All other of these products, and the routes for synthesis, are new. Characterization was by H-NMR, and, if sufficiently stable, by ^{13}C-NMR. The syntheses were carried out neat (except for route B) but also worked well in aprotic solvents as $CDCl_3$ or petroleum ether. Crude yields were in excess of 85% and often nominally quantitative (e.g. with route A, incorporation of theoretical weight of Cl_2). By-products found reflected further reactions of the adduct, either *intramolecular* (*pathway F*) or with one of the starting materials (e.g. pathway J affecting route B, or Scheme 3 which leads to V affecting route A when carried out with starting materials I or IX).

Elucidation of further transformations (right of Scheme) was by methodology outlined in ref. 3, which reports characteristics of all compounds mentioned with the exceptions of XXIV, XXXII, and XXXV *which are all new and to which* note 9 applies.

intermediate which arises by rapid loss of methyl chloride from the presumed chlorination adduct XXXVIIIa that was not observable by H-NMR. Rates of the reactions of SO_2Cl_2 with Ia or XIa were comparable, consistent with initial formation of the highly unstable IIIa or XXXVIIIa.

Scheme 4



$$2\ CH_3\text{-}O\text{-}\overset{S}{\overset{\|}{C}}\text{-}Z\text{-}CH_3 + SO_2Cl_2 \xrightarrow[-\ SO_2]{k_1} \left[CH_3\text{-}O\text{-}\underset{Cl}{\overset{S\text{-}Cl}{C}}\text{-}Z\text{-}CH_3 \right] \xrightarrow[-\ CH_3Cl]{}$$

XIa, Z = O

Ia, Z = S

XXXVIIIa, Z = O

IIIa, Z = S (Scheme 1)

$$CH_3\text{-}Z\text{-}\overset{O}{\overset{\|}{C}}\text{-}S\text{-}Cl + \text{second equiv. starting material} \xrightarrow[-\ CH_3Cl]{k_2} CH_3\text{-}Z\text{-}\overset{O}{\overset{\|}{C}}\text{-}S\text{-}S\text{-}\overset{O}{\overset{\|}{C}}\text{-}Z\text{-}CH_3$$

XIIIa, Z = O

unknown, Z = S

XIIa, Z = O (85%)

VIa, Z = S (8%; see text and Scheme 3, which shows main reaction that yields Va)

	*Rates**	
	k_1	k_2
Z = O	0.1	0.2 (ref. 3)
Z = S	0.4	see text

*measured in $CDCl_3$, at 25 °C

units: L mol^{-1} sec^{-1}

(compare these rates to notes 2c and 18)

Under conditions of Scheme 4, chlorination of XIVa with SO_2Cl_2 to yield VIIIa proceeded at 0.02 L mol^{-1} sec^{-1}, rate and product *unaffected*[19,20] when reaction carried out in presence of one equiv. of an alkoxythiocarbonyl chloride (Xa, Xb). The cited rate was about 70-fold faster than the rate by which Xa plus XIIIa also yield VIIIa. These data appear to be consistent with *intramolecular* processes. Finally, the rearrangement reported herein has been applied[10,21] to bifunctional substrates, including bis(methoxythiocarbonyl) sulfide (XVI) and disulfane (XXXIX). Contrary to literature expectations[4c], linear bis(methoxydichloromethyl) tri- and tetrasulfanes, i.e. $(CH_3OCCl_2)_2S_n$ with $n = 3$ and 4 respectively, formed in excellent yields, and further transformations (comparable to Scheme 2) provided entries to several novel poly-sulfur derivatives.

References and Notes

1. (a) Searle Scholar, 1982; National Institutes of Health Research Career Development Award, AM 01099, 1982-1987; (b) Supported by grants from NIH, GM 28934, Research Corporation Leo H. Baekeland Grant, and Chicago Community Trust, which are all gratefully noted.

2. (a) Reviewed by E. Kühle, "The Chemistry of the Sulfenic Acids", G. Thieme, Stuttgart, 1973, pp. 24-29. For example, $CSCl_2 + Cl_2 \rightarrow CCl_3SCl$; $R\text{-}N{=}C{=}S + Cl_2 \rightarrow R\text{-}N{=}C(Cl)\text{-}SCl$ (see also ref. 2b). (b) G. Ottmann and H. Hooks, J. Org. Chem. 31, 838-841 (1966). (c) Ref. 3 describes the high yield conversion of Xa with SO_2Cl_2 to XVIIa: $CH_3O(C{=}S)Cl + Cl_2 \rightarrow CH_3OCCl_2SCl$. Under conditions of Scheme 4, rate measured (present study) to be 3×10^{-5} L mol^{-1} sec^{-1}.

3. G. Barany, A.L. Schroll, A.W. Mott, and D.A. Halsrud, J. Org. Chem., in press (1983). Consult this manuscript for general procedures of organosulfur chemistry as practiced in this laboratory, including preparations and/or alternate syntheses of all starting materials and all products not specifically identified as new in the present communication, together with spectral (H- and ^{13}C-NMR, MS), analytical, and chromatographic characteristics of reference compounds, and appropriate literature citations. Furthermore, the earlier work describes a quantitative assay for acid chlorides and sulfenyl chlorides by reaction with *N*-methylaniline which was routinely applied in the present study to verify all structural conclusions (Schemes 2 to 4). The reaction of *N*-methylaniline with alkoxydichloromethanesulfenyl compounds is first considered here (Scheme 2, pathways L and M; notes 17 and 21).

4. The general problem of chlorination of alkoxythiocarbonylsulfenyl substrates has been addressed before, in almost all cases using gaseous chlorine at low temperatures. The discoveries of the present paper necessitate reinterpretation of the literature findings and structural assignments. See: (a) I.B. Douglass and C.E. Osborne, J. Am. Chem. Soc. 75, 4582-4583 (1953). (b) K. Sasse, German Pat. 1,018,054 (Dec. 15, 1955), Chem. Abstr. 54, 5480b (1960). (c) B.S. Shasha, W.M. Doane, C.R. Russell, and C.E. Rist, J. Org. Chem. 34, 1642-1645 (1969). (d) H. Böhme, M. Brinkmann, and H.P. Steudel, Liebigs Ann. Chem., pp. 1244-1251 (1981).

5. In contrast to refs. 4, the present study makes use of sulfuryl chloride as a chlorinating agent. It is less reactive than gaseous chlorine, and being a readily measurable liquid, permits setting up precise stoichiometries at 0 to 25 °C.

6. H-NMR ($CDCl_3$): δ 3.76, 2.64; ^{13}C-NMR: δ 119.3, 56.6, 24.1. Also, in $CDCl_3$ at 25 °C, the adduct converted quantitatively to (methyldithio)carbonyl chloride (XXIIa), with $t_{1/2} = 2.4$ hr, $k = 8 \times 10^{-5}$ sec^{-1}; 13-fold faster than rate of conversion of VIIIa to XXIIIa (ref. 3).

7. (a) A. Senning, Angew. Chem. Int. Ed. Engl. 18, 941-942 (1979) attempted to trap hypothetical dithiiranes which ought to be isomers of the unknown thiocarbonyl *S*-sulfides. (b) Compare to L. Carlsen, N. Harrit, and A. Holm, J. Chem. Soc., Perkin Trans. 1, pp. 1404-1407 (1976), who provide evidence for oxathiiranes as intermediates in photolysis of thiocarbonyl *S*-oxides.

8. Both adduct IIa and unreacted starting material Ia were present before starting distillation, but both were fully consumed and transformed to products during distillation.

9. New compound, characterized by H-NMR, IR, elemental analysis, high and low resolution EIMS.

10. Since prepared in good yield by alternate route, A. Mott and G. Barany, presented at 17th Great Lakes Regional Meeting of American Chemical Society, St. Paul, MN, June 1-3, 1983.

11. With I or IX as the limiting reagent (entirely consumed during reaction), the yield of V was 75 to 85% ($R^2 = CH_3$) or 85 to 95% ($R^2 = C_2H_5$). When $R^2 \neq R^4$, product V consisted of 65 to 90% of the correct mixed sulfenyl thiocarbonate, with the symmetrical compounds also formed, total 10 to 35%, scrambling more pronounced for $R^2 = CH_3$. When $R^2 = R^4$ and the reaction was carried out in the presence of $R^5SS(C{=}O)Cl$, R^5 was not incorporated into V. When $R^2 = R^4 \neq R^5$ and the reaction was carried out in the presence of pure $V(R^5)$, some $R^5S(C{=}O)SSR^2$ formed. The scrambling pathway was suggested from the result (driven to completion with excess chlorinated compound): $R^5S(C{=}O)SSR^5 + R^1OCCl_2SSR^2 \longrightarrow R^5S(C{=}O)SSR^2 + R^1OCCl_2SSR^5$.

12. Control: pure XIIa (ref. 3) and SO_2Cl_2, both 1 *M* in $CDCl_3$, no reaction after 24 hr, 25 °C.

13. XIa plus SO_2Cl_2, both 0.5 *M* in $CDCl_3$, gave about equal amounts of XIIa and XIIIa, with the latter demonstrated by conversion (note 3) to its *N*-methylaniline derivative XXXIa.

14. In $CDCl_3$ at 25 °C, IIa plus XIa reacted at 7×10^{-3} L mol^{-1} sec^{-1}. Compare this chemistry to Scheme 3 in text. Also, pathway F rather than H predominated when VIIIa was the substrate.

15. Conditions apply only to II or VII as substrates. In contrast, alkanethiols did not react with (alkyldithio)carbonyl chlorides, both reagents 1 *M* in $CDCl_3$, 25 °C, several days.

16. Solutions of the alkoxydichloromethanedisulfanyl compound in $CDCl_3$ were briefly shaken with saturated aqueous KI to give pathway K (65 to 80%). Pathway G (accounting for remainder) was also followed. Interestingly $CH_3O(C{=}O)SS(C{=}O)OC_2H_5$ (XXXVI) formed when XXa was shaken with aq. KI, but did not form when XXa was shaken with H_2O. Also, XVIIa reacted according to $CH_3OCCl_2SCl + 2\ KI \longrightarrow CH_3O(C{=}S)Cl + 2\ KCl + I_2$, yield 85 to 95%.

17. By comparison, XVIIa with excess *N*-methylaniline gave an 85% yield of *N*,*N*'-dimethyl-*N*,*N*'-diphenylcarbamoylsulfenamide (XXXVII), Ph(Me)N(C=O)SN(Me)Ph, alternatively made (ref. 3) from *N*—methylaniline and Cl(C=O)SCl. Treatment of alkoxydichloromethanedisulfanyl compounds this way never gave any XXXVII. The chemical distinction is significant because H-NMR spectra of alkoxydichloromethyl compounds are essentially superimposable.

18. In reconsideration of the result of ref. 4a, Ia was reacted with 2 equiv. SO_2Cl_2 and shown to give XVIIa plus XIXa (major), along with XXIIa (minor, pathway F). *N*-methylaniline assay (notes 3 and 17): XXXVII, 50 to 60%; XXXIIIa, 25 to 40%. Since Ia plus SO_2Cl_2 quickly gives IIa (Scheme 1), second step: IIa plus SO_2Cl_2 measured $k = 4 \times 10^{-4}$ L mol^{-1} sec^{-1}, $CDCl_3$ at 25 °C.

19. In particular, no VIIIb formed when the synthesis of VIIIa was carried out in the presence of Xb. On the other hand, alkoxydichloromethyl alkyl disulfanes (II, VII) equilibrated rapidly (within 5 min at 25 °C, $K \sim 1$) with alkoxythiocarbonyl chlorides or sulfenyl chlorides, e.g. $CH_3OCCl_2SSCH_3 + C_2H_5O(C{=}S)Cl \rightleftharpoons CH_3O(C{=}S)Cl + C_2H_5OCCl_2SSCH_3$, and $CH_3OCCl_2SSCH_3 + C_2H_5SCl \rightleftharpoons CH_3OCCl_2SSC_2H_5 + CH_3SCl$, and as a control, $C_2H_5SS(C{=}O)Cl + CH_3SCl \rightleftharpoons CH_3SS(C{=}O)Cl + C_2H_5SCl$.

20. The corresponding cross-over experiment in the presence of XIIIb was not feasible because the latter reacted with starting XIVa to yield XXXVI (structure given in note 16).

21. (a) E.A. Larka, A.L. Schroll, and G. Barany, in "Proceedings of 31st Annual Conference on Mass Spectrometry and Allied Topics, Boston, MA", in press, 1983. (b) A.L. Schroll and G. Barany, presented at American Chemical Society meeting mentioned in ref. 10.

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