Preparation and Properties of Trithiocarbonate *SS*-Dioxides

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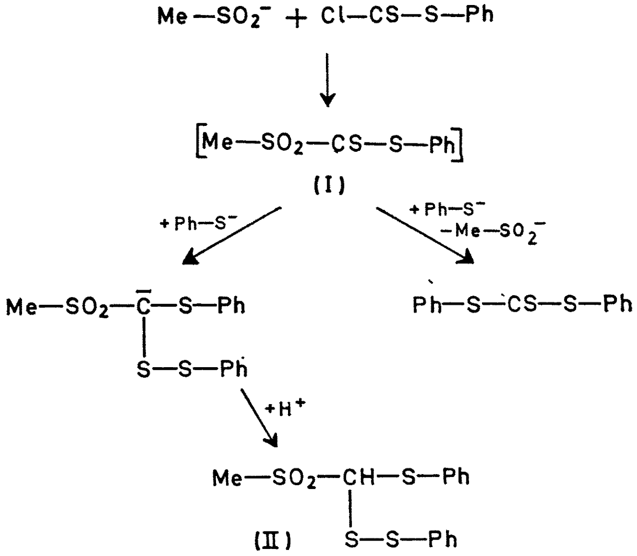
Summary Dithiochloroformates react with metal sulphinates to give trithiocarbonate *SS*-dioxides (I), and phenyl dithiochloroformate and sodium methanesulphinate give phenyl (phenylthio)(methylsulphonyl)methyl disulphide (II); towards nucleophiles, the dioxides (I) behave as thioacylating agents.

DURING our studies of compounds containing electron-depleted thiocarbonyl groups [1,2] we also investigated the *reaction* between dithiochloroformates and metal sulphinates. By carrying out the reaction in water–benzene at

$$R^1\text{-}SO_2^- + Cl\text{-}CS\text{-}S\text{-}R^2 \rightarrow \underset{(I)}{R^1SO_2\text{-}CS\text{-}S\text{-}R^2} + Cl^- \qquad (1)$$

room temperature or slightly above and monitoring the (slow) reaction by t.l.c. we prepared (Ia; $R^1 = Ph, R^2 = Me$),† purified by digestion with cold ethanol, as deep-red crystals, m.p. 86—87°; ν_{max} (KBr) 1107 (C=S), 1145 (SO_2), and 1320 (SO_2) cm^{-1}; λ_{max} (EtOH) 214, 255, and 329 nm and (Ib; $R^1 = p\text{-}MeC_6H_4$, $R^2 = Ph$), as violet crystals (from cold ethanol), m.p. 74°; ν_{max} (KBr) 1107 (C=S), 1140 (SO_2), and 1310 (SO_2) cm^{-1}; λ_{max} (EtOH) 218, 290, and 336 nm, in 45 and 26% yield, respectively.‡

A similar run with phenyl dithiochloroformate and sodium methanesulphinate gave diphenyl trithiocarbonate and a small amount of the disulphide (II), m.p. 98—101°, (from carbon tetrachloride). The benzenethiolate ion (Scheme) is probably derived from partial hydrolysis of the



SCHEME

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† Satisfactory elemental analyses and n.m.r. spectra were obtained for all new compounds mentioned.

‡ (Ib) was prepared independently in the same manner in 65% yield at the University of Groningen. Reaction of (Ib) with ethanethiol gave two products, ethyl (phenylthio)(toluene-*p*-sulphonyl)methyl disulphide [35%, *cf.* (II)] and ethyl phenyl trithiocarbonate (35%); B. Zwanenberg, L. Thijs, and G. E. Veenstra, personal communication.

chlorodithioformate. The direction of the addition to the thione group is in keeping with our observations on similar thione systems.[2] A transient t.l.c. spot with an appropriate R_F value was evidence for the intermediate (I).

An alternative synthesis of (I) would have required the addition of sulphinate anion to carbon disulphide (reaction 2), a reaction which failed.

$$\text{R-SO}_2^- + \text{CS}_2 \rightarrow \text{R-SO}_2\text{-CS-S}^- \qquad (2)$$

Oxidation of trithiocarbonates as a source of (I) is ruled out by the fact that the monoco-ordinated thione sulphur atom is more readily oxidised than adjacent dico-ordinated sulphur atoms.[3]

With amines, the dioxides (I) afford dithiocarbamates whereas attack of azide ion upon (I) leads to 5-alkylthio- or 5-arylthio-1,2,3,4-thiatriazoles. This behaviour towards nucleophiles is analogous to that of the related *C*-sulphonylthioformamides.[1,4] Because of their strongly thioacylating properties, the dioxides (I) cannot be recrystallised from boiling protic solvents.

The pyrolytic decomposition of (Ia) (at 200°) exhibits a rather complicated pattern with up to fifteen products being observed in the gas chromatogram. So far, among these, only dimethyl sulphide, dimethyl disulphide, and diphenyl disulphide have been positively identified.

(*Received, December* 7th, 1970; *Com.* 2118.)

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[2] N. H. Nilsson, C. Jacobsen, and A. Senning, *Chem. Comm.*, 1970, 658.
[3] B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.*, 1970, **5**, 79.
[4] N. H. Nilsson and A. Senning, unpublished observations.