CHEMICAL COMMUNICATIONS, 1971

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 electrondepleted thiocarbonyl groups 1,2 we also investigated the reaction between dithiochloroformates and metal sulphinates. By carrying out the reaction in water-benzene at

$$R^{1}-SO_{2}^{-} + Cl-CS-S-R^{2} \rightarrow R^{1}SO_{2}-CS-S-R^{2} + Cl^{-}$$
(1)
(I)

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 (SO₂), and 1320 (SO₂) cm⁻¹; λ_{max} (EtOH) 214, 255, and 329 nm and (Ib; $R^1 = p$ -MeC₆H₄, $R^2 = Ph$), as violet crystals (from cold ethanol), m.p. 74° ; ν_{max} (KBr) 1107 (C=S), 1140 (SO₂), and 1310 (SO₂) 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



[†] 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 trithio-carbonate (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 $R_{\mathbf{F}}$ 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.

$$R-SO_2^- + CS_2 \rightarrow R-SO_2^-CS^-$$
(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.8

¹ A. Senning, O. Nørgaard Sørensen, and C. Jacobsen, Angew. Chem., 1968, 80, 704.
⁸ N. H. Nilsson, C. Jacobsen, and A. Senning, Chem. Comm., 1970, 658.
⁸ B. Zwanenburg and J. Strating, Quart. Rep. Sulfur Chem., 1970, 5, 79.
⁴ N. H. Nilsson and A. Senning, unpublished observations.

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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