

Reactions of Chlorodithioformates and Thiophosgene with Metal Thiosulphonates

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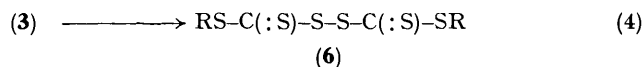
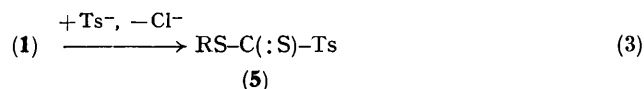
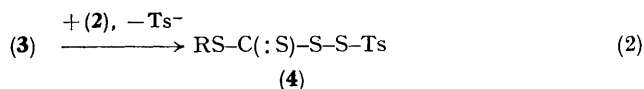
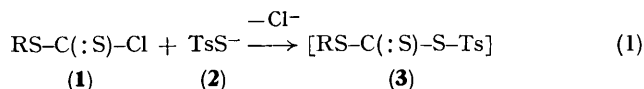
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Summary Alkyl (aryl) chlorodithioformates (**1**) react with potassium toluene-*p*-thiosulphonate (**2**) to give alkylthio- (arylthio-) thiocarbonyl *p*-tolylsulphonyl disulphides (**4**), trithiocarbonate SS-dioxides (**5**), and hexathioperoxydicarbonates (**6**); in the reaction of thiophosgene with (**2**), toluene-*p*-thiosulphonic acid anhydrosulphide (**11**) is formed.

RECENTLY we have described the thioacylation of metal sulphinates with thiophosgene,¹ thiocarbonyl chlorides,² and chlorodithioformates,³ and we have also developed an interest in the corresponding reactions of metal thiosulphonates. Equimolar amounts of (**1**) and (**2**) were allowed to react in acetonitrile at 0–5 °C. Contrary to

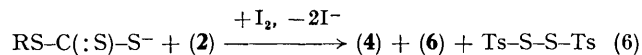
our expectations none of the primary product (**3**) [reaction (1)] could be isolated; instead, the secondary product (**4**) was found together with (**5**), (**6**) and, in the case of R = Ph, (**7a**) [reactions (2)–(5)]. Experimental data: † (**4a**), yield 30% [based on (**1**)], yellow crystals, m.p. 103 °C (from ether), *m/e* 372 (*M*⁺), 328 (*M*⁺ – CS), 296 (*M*⁺ – CS₂), 217 (*M*⁺ – C₇H₇SO₂), i.r. (KBr): ν(CS) 1075, ν(SO₂) 1145 and 1337 cm⁻¹, u.v. (cyclohexane), λ_{max} (log ε): 249 (4.23) and 304 nm (3.91), ¹³C n.m.r. (CDCl₃): δ 220.5 p.p.m. (C=S); (**4b**), yield 21%, m.p. 70 °C (from ether); (**4c**), yield 22%, m.p. 65 °C (from ether).

Compounds (**4**) were synthesised independently by co-oxidation of thioxanthates and (**2**) with iodine but yields were low [13% for (**4c**)] [reaction (6)].

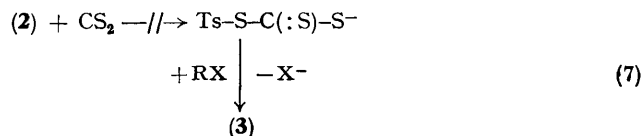


a; R = Ph
b; R = Me
c; R = PhCH₂

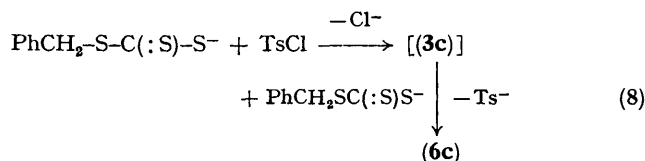
Ts = *p*-MeC₆H₄SO₂ throughout.



The polyfunctionality of (**4**) is interesting since the compounds can be regarded as trithiocarbonates, disulphides, thiosulphonates, and mixed thioacid anhydrosulphides. Preliminary tests have shown that (**4a**) gives 5-phenylthio-1,2,3,4-thiaziazole with sodium azide, and 1-phenylthiothiocarbonyl morpholine and morpholinium toluene-*p*-thiosulphonate with morpholine. Cyanide ion replaces toluene-*p*-sulphinat ion in its reaction with (**4a**). When (**4a**) is treated with an equimolar amount of sulphuryl chloride, (**1a**) and di-*p*-tolylsulphonyl trisulphide are obtained. Finally, owing to the dienophilicity of the thiocarbonyl group of (**4a**), a ready Diels–Alder reaction is observed between (**4a**) and cyclopenta-1,3-diene. Attempts to synthesise (**3**) according to reactions (7) and (8) were unsuccessful. Nevertheless, it is likely that (**3**) is the

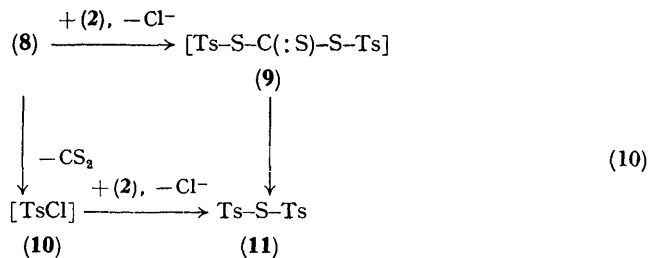
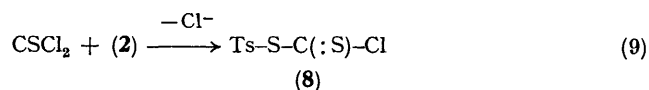


† All compounds exhibited spectroscopic and analytical data consistent with the proposed structure. Yields were not optimised.



primary product of the reaction sequences (2), (4), (5), and (8) but immediately suffers degradation by nucleophiles [reactions (2) and (8)], disproportionation [reaction (4)], or loss of carbon disulphide [reaction (5)]. The existence of compound (3) has also been assumed in a different type of reaction, in which it is postulated as a reactive intermediate.⁴ The mechanism of formation of (6) *via* (3) is analogous to that proposed for the reactions of arenesulphonyl chlorides with metal ethyl xanthates,⁵ and with dithio acid salts.⁶

When (2) (2 mol. equiv.) reacted with thiophosgene in acetonitrile, (11) was formed [crude yield 79% based on (2)]. No other product was observed and the use of equimolar amounts gave the same product. Of the possible



mechanistic pathways in reaction (10) step (10) \rightarrow (11) *via* the intermediates (9) and (10) is known,⁷ but (11) could also be formed directly from (8) and (2), with CS₂ and Cl⁻ being lost simultaneously.

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