Reactions of Chlorodithioformates and Thiophosgene with Metal Thiosulphonates

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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] thiocarbamoyl 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^+ $-\mathrm{CS_2}$), 217 (M^+ $-\mathrm{C_7H_7SO_2}$), i.r. (KBr): ν(CS) 1075, $\nu(\mathrm{SO_2})$ 1145 and 1337 cm^{-1}, u.v. (cyclohexane), $\lambda_{\max}$ (log ϵ): 249 (4·23) and 304 nm (3·91), ^{13}C n.m.r. ($\mathrm{CDCl_3}$): 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).

$$\underset{\mathbf{(1)}}{\mathrm{RS{-}C({:}S){-}Cl}} + \underset{\mathbf{(2)}}{\mathrm{TsS^-}} \xrightarrow{-\mathrm{Cl^-}} \underset{\mathbf{(3)}}{[\mathrm{RS{-}C({:}S){-}S{-}Ts}]} \qquad (1)$$

$$\mathbf{(3)} \xrightarrow{+\mathbf{(2)},\ -\mathrm{Ts^-}} \underset{\mathbf{(4)}}{\mathrm{RS{-}C({:}S){-}S{-}S{-}Ts}} \qquad (2)$$

$$\mathbf{(1)} \xrightarrow{+\mathrm{Ts^-},\ -\mathrm{Cl^-}} \underset{\mathbf{(5)}}{\mathrm{RS{-}C({:}S){-}Ts}} \qquad (3)$$

$$\mathbf{(3)} \xrightarrow{\qquad} \underset{\mathbf{(6)}}{\mathrm{RS{-}C({:}S){-}S{-}S{-}C({:}S){-}SR}} \qquad (4)$$

$$\mathbf{(3a)} \xrightarrow{-\mathrm{CS_2}} \underset{\mathbf{(7a)}}{\mathrm{Ph{-}S{-}Ts}} \qquad (5)$$

a; R = Ph
b; R = Me
c; R = $\mathrm{PhCH_2}$

Ts = *p*-$\mathrm{MeC_6H_4SO_2}$ throughout.

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

$$\mathrm{RS{-}C({:}S){-}S^-} + \mathbf{(2)} \xrightarrow{+\mathrm{I_2},\ -2\mathrm{I^-}} \mathbf{(4)} + \mathbf{(6)} + \mathrm{Ts{-}S{-}S{-}Ts} \qquad (6)$$

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-thiatriazole with sodium azide, and 1-phenylthiothiocarbonyl morpholine and morpholinium toluene-*p*-thiosulphonate with morpholine. Cyanide ion replaces toluene-*p*-sulphinate 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

$$\begin{tikzcd}
\mathbf{(2)} + \mathrm{CS_2} \arrow[r, "//"] & \mathrm{Ts{-}S{-}C({:}S){-}S^-} \arrow[d, "+\mathrm{RX}"', "-\mathrm{X^-}"] \\
& \mathbf{(3)}
\end{tikzcd} \qquad (7)$$

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

$$\begin{tikzcd} \mathrm{PhCH_2{-}S{-}C(:S){-}S^-} + \mathrm{TsCl} \arrow[r, "-\mathrm{Cl}^-"] & {[(\mathbf{3c})]} \arrow[d, "+\mathrm{PhCH_2SC(:S)S^-}"', "-\mathrm{Ts}^-"] \\ & (\mathbf{6c}) \end{tikzcd} \tag{8}$$

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]

$$\mathrm{CSCl_2} + (\mathbf{2}) \xrightarrow{-\mathrm{Cl}^-} \underset{(\mathbf{8})}{\mathrm{Ts{-}S{-}C(:S){-}Cl}} \tag{9}$$

$$\begin{tikzcd} (\mathbf{8}) \arrow[r, "+(\mathbf{2}),\ -\mathrm{Cl}^-"] \arrow[d, "-\mathrm{CS_2}"] & \underset{(\mathbf{9})}{[\mathrm{Ts{-}S{-}C(:S){-}S{-}Ts}]} \arrow[d] \\ \underset{(\mathbf{10})}{[\mathrm{TsCl}]} \arrow[r, "+(\mathbf{2}),\ -\mathrm{Cl}^-"] & \underset{(\mathbf{11})}{\mathrm{Ts{-}S{-}Ts}} \end{tikzcd} \tag{10}$$

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**) → (**11**) *via* the intermediates (**9**) and (**10**) is known,[7] but (**11**) could also be formed directly from (**8**) and (**2**), with CS_2 and Cl^- being lost simultaneously.

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