Reactions of Toluene-*p*-sulphonic Thioanhydride with Sulphur Nucleophiles

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Summary Ethoxythiocarbonyl *p*-tolylsulphonyl disulphide (**5**), benzylthio(thiocarbonyl) *p*-tolylsulphonyl disulphide (**1c**), and *NN*-dimethylthiocarbamoyl *p*-tolylsulphonyl disulphide (**10**) are formed in the reactions of toluene-*p*-sulphonic thioanhydride (**3**) with *O*-ethyl dithiocarbonate (**4**), benzyl trithiocarbonate (**2**), and *NN*-dimethyl dithiocarbamate (**9**) ions, respectively.

IN our work with thiocarbonyl compounds we have prepared the novel alkylthio-(or arylthio-)thiocarbonyl *p*-tolylsulphonyl disulphides (**1**) by the reaction of alkyl (or aryl) chlorodithioformates with potassium toluene-*p*-thiosulphonate [reaction (1)], and by the co-oxidation of trithiocarbonate and thiosulphonate ions with iodine [reaction (2)].[1]

$$\mathrm{R'S{-}C({:}S){-}Cl} + \mathrm{RSO_2S^-} \rightarrow \underset{(\mathbf{1})}{\mathrm{R'S{-}C({:}S){-}S{-}S{-}SO_2R}} \qquad (1)$$

$$\underset{(\mathbf{2})}{\mathrm{PhCH_2S{-}C({:}S){-}S^-}} + \mathrm{RSO_2S^-} \xrightarrow{\mathrm{I_2}} (\mathbf{1c}) \qquad (2)$$

a, R′ = Ph
b; R′ = Me
c, R′ = PhCH$_2$
R = *p*-MeC$_6$H$_4$ throughout

We now report an alternative method for the synthesis of (**1**), the novel related ethoxythiocarbonyl *p*-tolylsulphonyl disulphide (**5**), and *NN*-dimethylthiocarbamoyl *p*-tolylsulphonyl disulphide (**10**) using toluene-*p*-sulphonic thioanhydride (toluene-*p*-thiosulphonic acid anhydrosulphide) (**3**) as the 'sulphonylsulphenylating' agent.† A trithiocarbonate *SS*-dioxide (**8**) is a byproduct in the reaction of (**3**) with (**2**). An advantage of this new synthetic route to (**1**) and (**8**) is the avoidance of thiophosgene as starting material.[2]

An ethanolic solution of potassium *O*-ethyl dithiocarbonate (**4**) was slowly added to toluene-*p*-sulphonic thioanhydride (**3**)[3] in ethanol at 0—5 °C and allowed to react for 0.5 h. The reactions of (**3**) with potassium benzyl trithiocarbonate (**2**) and with sodium *NN*-dimethyldithiocarbamate (**9**) were carried out in a similar way. The products were separated by column chromatography and/or recrystallisation.

In agreement with the HSAB principle,‡ (**3**) reacts readily with the soft bases employed. It seems reasonable to assume that in the first step the thioanion attacks (**3**) at the sulphenyl sulphur [reactions (3), (5), and (8)] liberating toluene-*p*-sulphinate anions, but the desired disulphides thus formed are susceptible toward attack by the nucleophiles present and are partially degraded. A common feature is the reaction of the disulphide with the added thioanions with formation of what amounts to the oxidation product of the starting anion [reactions (4), (6), and (9)].

$$\underset{(\mathbf{3})}{\mathrm{RSO_2{-}S{-}SO_2R}} + \underset{(\mathbf{4})}{\mathrm{EtO{-}C({:}S){-}S^-}} \xrightarrow{-\mathrm{RSO_2}^-} \underset{(\mathbf{5})}{\mathrm{EtO{-}C({:}S){-}S{-}S{-}SO_2R}} \qquad (3)$$

$$(\mathbf{5}) + (\mathbf{4}) \xrightarrow{-\mathrm{RSO_2S}^-} \underset{(\mathbf{6})}{\mathrm{EtO{-}C({:}S){-}S{-}S{-}C({:}S){-}OEt}} \qquad (4)$$

Ethoxythiocarbonyl *p*-tolylsulphonyl disulphide (**5**) was isolated in 8% yield as a slowly crystallizing oil. Recrystallization gave colourless crystals, m.p. 66—68 °C (from ether), i.r. (KBr), ν(SO$_2$) 1145 and 1330 cm^{-1}, ^{13}C n.m.r. (CDCl$_3$), δ 208.2 p.p.m. (C=S).

The formation of the trithiocarbonate *SS*-dioxide (**8**) [yield 8%, purple crystals, m.p. 94—96 °C (from acetonitrile)] according to reaction (7) was confirmed in an independent experiment starting with pure (**1c**). Thus (**8**) was obtained in 15% yield [based on (**1c**)] when (**1c**)

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† All novel compounds gave satisfactory elemental analyses. Yields were not optimised.

‡ HSAB = Hard and Soft Acids and Bases, see R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, 1967, **89**, 1827.

was allowed to react with an excess of sodium toluene-*p*-sulphinate in ethanol.

$$(\mathbf{3}) + (\mathbf{2}) \xrightarrow{-\mathrm{RSO_2^-}} (\mathbf{1c}) \qquad (5)$$

$$(\mathbf{1c}) + (\mathbf{2}) \xrightarrow{-\mathrm{RSO_2S^-}} \underset{(\mathbf{7})}{\mathrm{PhCH_2S{-}C(:S){-}S{-}S{-}C(:S){-}SCH_2Ph}} \qquad (6)$$

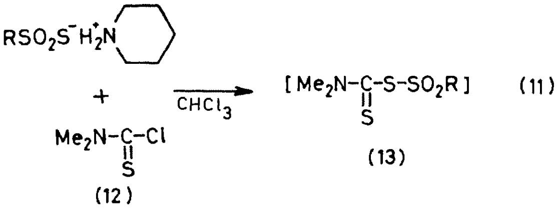
$$(\mathbf{1c}) + \mathrm{RSO_2^-} \rightarrow \underset{(\mathbf{8})}{\mathrm{PhCH_2S{-}C(:S)SO_2R}} \qquad (7)$$

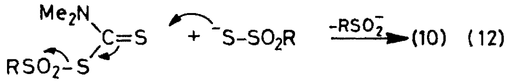
The *NN*-dimethyldithiocarbamate ion (**9**) gave, with (**3**), the expected products (**10**) and (**11**) [reactions (8) and (9)]. *NN*-Dimethylthiocarbamoyl *p*-tolylsulphonyl disulphide (**10**) (crude yield 25%) forms pale yellow crystals, m.p. 91—93 °C (from ether); i.r. (KBr), ν(SO_2) 1145 and 1330 cm^{-1}, ^{13}C n.m.r. ($CDCl_3$), δ 199·0 p.p.m. (C=S). The isolation of pure (**10**) presented some difficulties because (**10**) slowly decomposes, probably by disproportionation [reaction (10)] as indicated by t.l.c. and ^1H n.m.r. spectroscopy.

$$(\mathbf{3}) + \underset{(\mathbf{9})}{\mathrm{Me_2N{-}C(:S){-}S^-}} \xrightarrow{-\mathrm{RSO_2^-}} \underset{(\mathbf{10})}{\mathrm{Me_2N{-}C(:S)S{-}S{-}SO_2R}} \qquad (8)$$

$$(\mathbf{10}) + (\mathbf{9}) \xrightarrow{-\mathrm{RSO_2S^-}} \underset{(\mathbf{11})}{\mathrm{Me_2N{-}C(:S){-}S{-}S{-}C(:S){-}NMe_2}} \qquad (9)$$

$$(\mathbf{10}) \rightarrow (\mathbf{11}) + \mathrm{RSO_2{-}S{-}S{-}SO_2R} \qquad (10)$$





Compound (**10**) has previously been obtained by Nilsson[4] from piperidinium toluene-*p*-thiosulphonate and *NN*-dimethylthiocarbamoyl chloride (**12**) [reactions (11) and (12)]. As in the analogous reaction (1),[1] no simple substitution product could be isolated. To explain the formation of (**10**) we propose the mixed acid thioanhydride (**13**) as an intermediate.

According to Foss's rule,[5] the sulphinate anion RSO_2^- would be expected to be a better thiophile than the thiosulphonate anion RSO_2S^-. Therefore, substitution by attack of RSO_2S^- at the sulphenyl sulphur of (**13**) with RSO_2^- as the leaving group seems unlikely and, instead, the proposed pathway [reaction (12)] involves thiophilic attack at the thiocarbonyl group.

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[1] H. C. Hansen and A. Senning, *J. Chem. Soc., Chem. Commun.*, 1979, 1135.

[2] *Cf.* N. H. Nilsson and A. Senning, *Chem. Ber.*, 1974, **107**, 2345.

[3] 'Beilstein's Handbuch der Organischen Chemie,' Vol. 11, Vierte Auflage, Springer-Verlag, Berlin, 1928, p. 114.

[4] N. H. Nilsson, personal communcation.

[5] O. Foss, *Acta Chem. Scand.*, 1947, **1**, 307.