

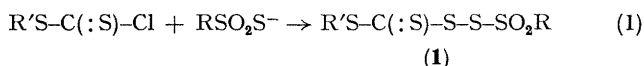
## Reactions of Toluene-*p*-sulphonic Thioanhydride with Sulphur Nucleophiles

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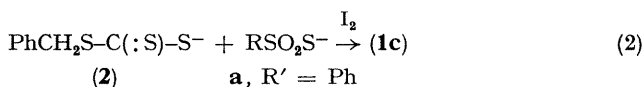
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**Summary** Ethoxythiocarbonyl *p*-tolylsulphonyl disulphide (5), benzylthio(thiocarbonyl) *p*-tolylsulphonyl disulphide (1c), and *NN*-dimethylthiocarbamoyl *p*-tolylsulphonyl disulphide (10) are formed in the reactions of toluene-*p*-sulphonic thioanhydride (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)]<sup>1</sup>



(1)



(2)

a, R' = Ph

b, R' = Me

c, R' = PhCH<sub>2</sub>

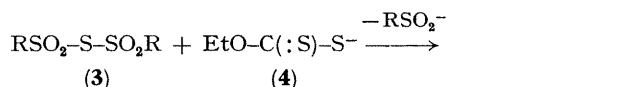
R = *p*-MeC<sub>6</sub>H<sub>4</sub> throughout

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<sup>2</sup>

An ethanolic solution of potassium *O*-ethyl dithiocarbonate (4) was slowly added to toluene-*p*-sulphonic

thioanhydride (3)<sup>3</sup> 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)]

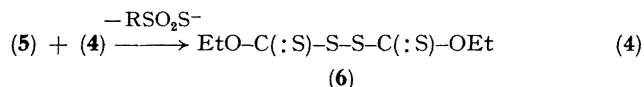


(3)

(4)

EtO-C(:S)-S-S-SO<sub>2</sub>R (3)

(5)



(6)

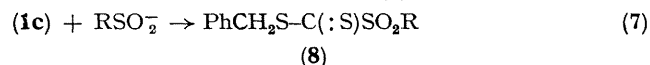
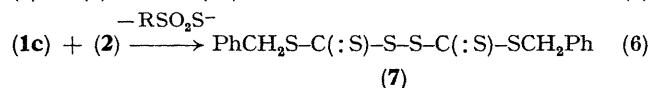
Ethoxythiocarbonyl *p*-tolylsulphonyl disulphide (5) was isolated in 8% yield as a slowly crystallizing oil. Recrystallization gave colourless crystals, m.p. 66–68 °C (from ether), *ν*<sub>r</sub> (KBr), *ν*(SO<sub>2</sub>) 1145 and 1330 cm<sup>-1</sup>, <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>), *δ* 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)

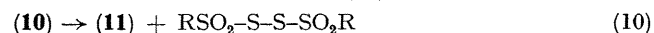
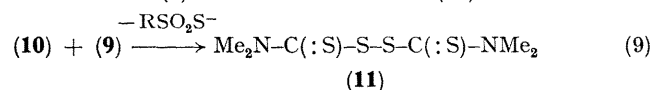
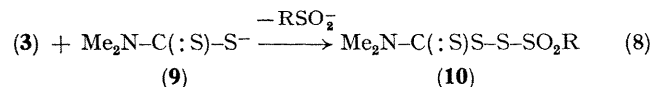
† All novel compounds gave satisfactory elemental analyses. Yields were not optimised.

‡ 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*-sulphonate in ethanol.



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),  $\nu(\text{SO}_2)$  1145 and 1330  $\text{cm}^{-1}$ ,  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  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  $^1\text{H}$  n.m.r. spectroscopy.



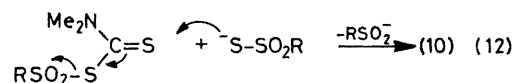
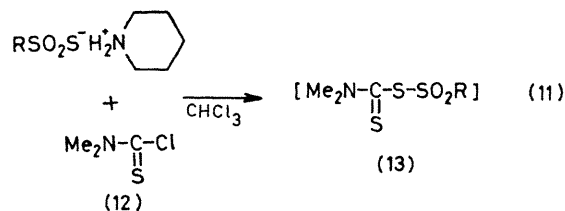
<sup>1</sup> H. C. Hansen and A. Senning, *J. Chem. Soc., Chem. Commun.*, 1979, 1135.

<sup>2</sup> Cf. N. H. Nilsson and A. Senning, *Chem. Ber.*, 1974, **107**, 2345.

<sup>3</sup> 'Beilstein's Handbuch der Organischen Chemie,' Vol. 11, Vierte Auflage, Springer-Verlag, Berlin, 1928, p. 114.

<sup>4</sup> N. H. Nilsson, personal communication.

<sup>5</sup> O. Foss, *Acta Chem. Scand.*, 1947, **1**, 307.



Compound (10) has previously been obtained by Nilsson<sup>4</sup> from piperidinium toluene-*p*-thiosulphonate and *NN*-dimethylthiocarbamoyl chloride (12) [reactions (11) and (12)]. As in the analogous reaction (1),<sup>1</sup> 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,<sup>5</sup> the sulphinate anion  $\text{RSO}_2^-$  would be expected to be a better thiophile than the thiosulphonate anion  $\text{RSO}_2\text{S}^-$ . Therefore, substitution by attack of  $\text{RSO}_2\text{S}^-$  at the sulphenyl sulphur of (13) with  $\text{RSO}_2^-$  as the leaving group seems unlikely and, instead, the proposed pathway [reaction (12)] involves thiophilic attack at the thiocarbonyl group.

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