Transformation of Thiosulphonates into α-Sulphonyldisulphides, a New Class of Thioaldehyde Precursors

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Toluene-*p*-thiosulphonates, RCH_2SSO_2Tol (**1**) where R is an electron-withdrawing group, are transformed readily into α-sulphonyldisulphides (**2**) which, with triethylamine, undergo fragmentation–elimination to give 2 moles of thioaldehydes, RCHS.

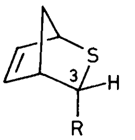
We reported[1] recently that 'Bunte salts', RCH_2SSO_3Na where R is an electron-withdrawing group, react with triethylamine to give transient, dienophilic thioaldehydes, RCHS, with expulsion of sulphite (SO_3^{2-}). We expected that the corresponding thiotosylates (**1**; Tol = 4-MeC_6H_4) would behave similarly [equation (1)] and that the singly charged leaving group, $TolSO_2^-$, would be expelled more readily. We find, unexpectedly, that the thiotosylates (**1**) are transformed readily [equation (2)] into the α-sulphonyldisulphides (**2**), which afford thioaldehydes by fragmentation–elimination [equation (3)].

Treatment of the thiotosylate (**1a**)[2] (2 mmol) with triethylamine or, better, ethyldi-isopropylamine (1 mmol) for 3 h in benzene (10 ml) at room temperature gave the disulphide (**2a**), m.p. 155—159 °C (95%). Similarly, (**1b**)[3] with triethylamine in chloroform for 4 days gave (**2b**), m.p. 148—149 °C (78%). The corresponding transformations of (**1c**)[2] to give (**2c**), m.p. 160—183 °C (*ca.* 100%) and of (**1d**)† to give the oily (**2d**) (*ca.* 100%) were best effected by prolonged contact with silica gel (chromatographic grade) in chloroform–light petroleum.

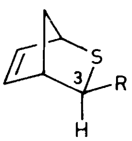
$$\underset{(\mathbf{1})}{RCH_2SSO_2Tol} + Et_3N \rightarrow [RCHS] + Et_3\overset{+}{N}H + TolSO_2^- \qquad (1)$$

$$2RCH_2SSO_2Tol \rightarrow \underset{(\mathbf{2})}{RCH_2SSCH(SO_2Tol)R} + TolSO_2H \qquad (2)$$

$$\underset{(\mathbf{2})}{RCH_2SSCH(SO_2Tol)R} + Et_3N \rightarrow 2[RCHS] + Et_3\overset{+}{N}H + TolSO_2^- \qquad (3)$$



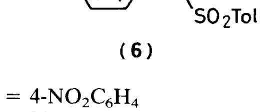
(**3**)



(**4**)

RCH₂SCH(SSO₂Tol)R

(**5**)



(**6**)

a; R = 4-$NO_2C_6H_4$
b; R = Ph
c; R = 4-BrC_6H_4CO
d; R = EtO_2C

Tol = 4-MeC_6H_4

The disulphides (**2a**), (**2c**), and (**2d**) (each 0.2 mmol) reacted with triethylamine (0.2 mmol) in benzene (5 ml) containing cyclopentadiene (0.4 mmol) at room temperature for 1 h [for (**2c**) and (**2d**)] or 12 h [for (**2a**)] to give, respectively, the thioaldehyde adducts (**3a**) and (**4a**)[1] (*endo* : *exo* ratio 7 : 1; combined yield 0.30 mmol), (**3c**)‡ and (**4c**)‡ (7 : 4; 0.37 mmol), and (**3d**) and (**4d**)[1] (7 : 3; 0.31 mmol). Clearly, efficient fragmentation of the disulphides had occurred to give 2 mol. equiv. of the corresponding thioaldehydes [equation (3)]. The benzyl derivative (**2b**) was much less reactive; nevertheless, with triethylamine and cyclopentadiene in acetonitrile it gave the adducts (**3b**)‡ and (**4b**)‡ (4 : 1). We believe that this new fragmentation–elimination reaction is concerted, at least for (**2a**), since bis-4-nitrobenzyl disulphide was recovered in high yield (98%), and free from deuterium, after exposure to triethylamine and cyclopentadiene in benzene containing tetradeuteriomethanol at room temperature for 24 h.

Two, alternative structures, (**2**) and (**5**), were considered for the transformation products of the thiotosylates (**1**). Both might, in principle, fragment to give 2 moles of thioaldehyde. A decision, in favour of (**2**), was made on the following grounds. Bis-4-nitrobenzyl sulphide was converted[5] into the benzylic chloro-derivative[6] which was treated in benzene with Amberlyst A-26 resin charged with toluene-*p*-thiosulphonate[4] to give the sulphide (**5a**) (43%), m.p. 148—151 °C. Significantly, (**5a**) reacted rapidly with triethylamine in benzene to give the known[6] dithioester, 4-$NO_2C_6H_4CH_2SCS$(4-$NO_2C_6H_4$), in high yield (94%). Further, in the ^{13}C n.m.r. spectrum of (**5a**) the methine (CH) carbon (δ 55.6) absorbed at higher field (Δδ 23.5) than the corresponding carbon (δ 79.1) in (**2a**). A closely similar chemical shift difference (Δδ 23.1) was observed for the methylene carbons in the model compounds (**1a**) and 4-$NO_2C_6H_4CH_2SO_2Tol$. Comparison of the ^{13}C n.m.r. spectra (Table 1) for compounds within the series (**2**) leaves no doubt that they must all have analogous, disulphide structures.

The foregoing observations lead us to revise two structural assignments in the literature. Hayashi *et al.*[3] treated (**1b**) with sodium ethoxide in ethanol and obtained a product, m.p. 147—148.5 °C, to which they ascribed the structure (**5b**). In our hands, the product of this reaction was identical with that obtained using triethylamine, namely (**2b**). Similarly,

Table 1. ^{13}C N.m.r. spectra of disulphides (**2**) and sulphide (**5a**) (δ, p.p.m., in $CDCl_3$).

	(**2a**)	(**2b**)	(**2c**)	(**2d**)	(**5a**)
CH	79.1	79.2	78.9	77.7	55.6
CH_2	42.4	43.8	46.9	41.8	36.9

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† (**1d**) was prepared in chloroform from ethyl bromoacetate and Amberlyst A-26 resin charged with toluene-*p*-thiosulphonate.[4]

‡ Selected physical data for new cycloadducts: M.p.s., b.p.s. (Kugelrohr distillation), and diagnostic ^1H n.m.r. ($CDCl_3$) signals were as follows: (**3b**) + (**4b**), b.p. 115 °C (0.03 mbar); (**3b**), δ 4.38 (d, *J* 4 Hz, 3-H); (**4b**), δ 3.99 (br. s, 3-H); (**3c**), m.p. 108—110 °C (decomp.), δ 5.01 (d, *J* 4 Hz, 3-H); (**4c**), m.p. 122—123 °C, δ 3.98 (br. s, 3-H).

Weidner and Block[2] heated (**1c**) in ethanol and obtained a product, m.p. 182—183 °C, assigned the structure (**5c**). Again, in our hands, the product was identical with that obtained by rearrangement on silica, namely (**2c**).

The mechanism of the transformation of (**1a**) into (**2a**) has been studied briefly. It seemed likely that the first step would be the expected elimination [equation (1)] to produce 4-nitrothiobenzaldehyde. Reversible attack by toluene-*p*-sulphinate on the thioaldehyde would form the powerful nucleophile (**6**) which could undergo sulphenylation by (**1a**) to give (**2a**). To test this idea, (**1a**) (1 mmol) was treated with triethylamine (1 mmol) in benzene (8 ml) and ethanol (2 ml) containing cyclopentadiene (1.2 mmol) and calcium chloride dihydrate[1] (1 mmol). After 3 h at room temperature the cycloadducts (**3a**) and (**4a**) were obtained (82%) accompanied by only a trace (*ca.* 5%) of the disulphide (**2a**). In the absence of calcium chloride the disulphide was the major product and the cycloadducts were formed in only trace amounts. It appears therefore that toluene-*p*-sulphinate is removed by Ca^{2+}, by either precipitation or ion-pairing, thus allowing the thioaldehyde to be captured by cyclopentadiene. The same thiolate (**6**) may also be formed reversibly during fragmentation of (**2a**) [equation (3)]. However, there is then no effective sulphenylating agent present and capture of the thioaldehyde by cyclopentadiene may proceed to completion.

We thank the S.E.R.C. for financial support and Dr D. S. Rycroft for n.m.r. spectra.

Received, 3rd August 1984; Com. 1141

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