

# Formation and Isolation of the Disulphide Dication of 1,5-Dithiacyclo-octane in the Reactions of the Corresponding S-Oxide and S-(*N*-tosylimide) in Concentrated Sulphuric Acid

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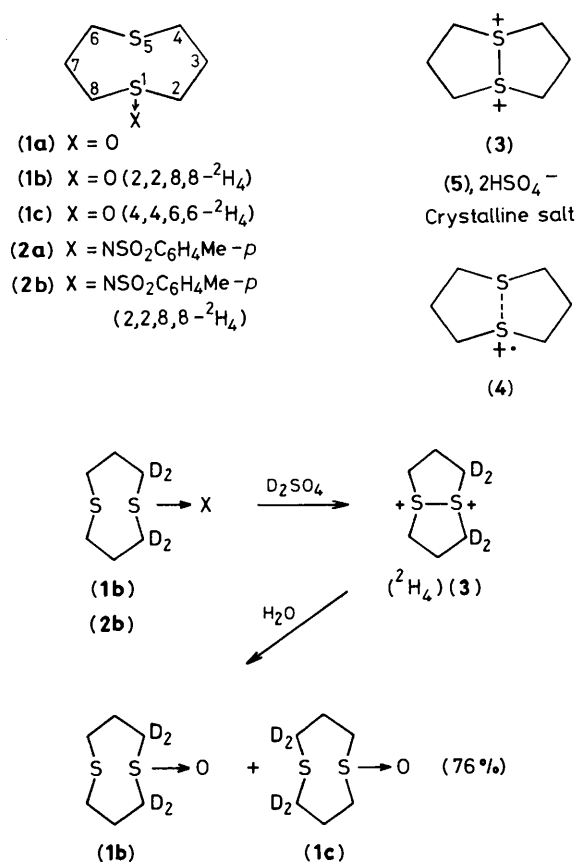
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The disulphide dication of 1,5-dithiacyclo-octane was generated in the reaction of the corresponding S-oxide and S-(*N*-tosylimide) with conc. H<sub>2</sub>SO<sub>4</sub> and isolated in crystalline form.

The intermediacy of cyclic disulphide dications has been confirmed kinetically by Musker *et al.* in either the reduction of the corresponding S-oxide with HI or the oxidation of the bis-sulphide with I<sub>2</sub> in acidic aqueous media.<sup>1</sup> They have isolated the dications of several cyclic bis-sulphides by treating the corresponding sulphides with NOBF<sub>4</sub> (2 equiv.) in MeCN.<sup>2,3</sup> Numata and Oae have postulated the formation of the dithietanium dication on dissolution of *o*-methylthiophenyl phenyl sulphoxide in conc. H<sub>2</sub>SO<sub>4</sub>.<sup>4</sup> Treatment of a cyclic bis-sulphide S-oxide having a conformationally feasible structure for intramolecular S-S bond interaction with conc. H<sub>2</sub>SO<sub>4</sub> should lead to the corresponding dication. We have accordingly dissolved dithiacyclo-octane S-oxide (**1a**) or S-(*N*-tosylimide) (**2a**) in conc. D<sub>2</sub>SO<sub>4</sub>, and detected the formation of the corresponding disulphide dication (**3**) by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy; the bis(hydrogensulphate) salt (**5**) of this dication could actually be isolated. The e.s.r. spectrum of the S-oxide in conc. H<sub>2</sub>SO<sub>4</sub> solution showed signals due to the corresponding cation radical (**4**).

1,5-Dithiacyclo-octane S-oxide (**1a**), the S-(*N*-tosylimide) (sulphilimine) (**2a**),<sup>†</sup> [m.p. 175–178 °C; ν<sub>max</sub>. (KBr) 1270, 1140, 1090, and 1000 cm<sup>-1</sup>] and the corresponding 2,2,8,8-tetradeuteriated derivatives (**1b**) and (**2b**) were synthesized.<sup>‡</sup> When (**1a**) was dissolved in conc. H<sub>2</sub>SO<sub>4</sub> (96%), the solution became slightly yellow. The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of D<sub>2</sub>SO<sub>4</sub> (98%) solutions of (**1a**) were recorded immediately; the signals observed in CDCl<sub>3</sub> for (**1a**) disappeared and two sets of new peaks appeared in a 2 : 1 ratio.<sup>§</sup> These spectra did not change for 24 h at room temperature; the data are in Table 1.

These results indicate that (**1a**) is converted into the symmetrical intermediate dication (**3**).<sup>¶</sup> Treatment of the H<sub>2</sub>SO<sub>4</sub> solution of (**1a**) with H<sub>2</sub>O and work-up led to the starting S-oxide (**1a**) in 72% yield. Similar treatment of (**1b**) in D<sub>2</sub>SO<sub>4</sub> led to similar changes in the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra,



Scheme 1

<sup>†</sup> Satisfactory elemental analyses were obtained.

<sup>‡</sup> Compound (**1a**) did not undergo H-D exchange in NaOD-D<sub>2</sub>O-tetrahydrofuran at 50 °C, so it was necessary to heat the solution under reflux for 20 h at 100 °C under N<sub>2</sub>. In contrast, H-D exchange of (**2a**) could be carried out at 70 °C for 6 h; deuterium content: (**1a**), 100%; (**2a**), 81%.

<sup>§</sup> Musker *et al.*<sup>2</sup> reported that the dication (BF<sub>4</sub>)<sub>2</sub> salt has broad <sup>1</sup>H n.m.r. signals at δ ca. 2–4 in CD<sub>3</sub>CN, while the <sup>13</sup>C n.m.r. spectra correspond roughly with our results. The broadening of the <sup>1</sup>H n.m.r. spectrum observed by Musker *et al.* is probably due to the MeCN solvent which may interact with the S<sup>+</sup> unit in (**3**), while D<sub>2</sub>SO<sub>4</sub> does not lead to such a solvation effect, resulting in sharp <sup>1</sup>H n.m.r. spectra.

<sup>¶</sup> The solution of (**1a**) in H<sub>2</sub>SO<sub>4</sub> showed similar e.s.r. spectra to those reported by Musker (*Acc. Chem. Res.*, 1982, **13**, 200). We assume that the intermediate in this reaction is the dication (**3**) with equilibrium formation of the cation radical (**4**) in low concentration. This may explain the n.m.r. spectra.

except that the peak ratio was 1 : 1. Hydrolysis of the H<sub>2</sub>SO<sub>4</sub> solution of (**1b**) led to 76% recovery of the S-oxide, the <sup>1</sup>H n.m.r. spectra of which indicate that it is a 1 : 1 mixture of the 2,2,8,8- and 4,4,6,6-tetradeuteriated S-oxides (**1b**) and (**1c**) and also that no H-D exchange with the solvent H<sub>2</sub>SO<sub>4</sub> took place during the reaction (Scheme 1). The solution of (**3**) in H<sub>2</sub>SO<sub>4</sub> was poured into ice-cooled anhydrous diethyl ether and the salt (**5**) was obtained as white hygroscopic crystals, m.p. 66–69 °C.<sup>\*\*\*</sup> Hydrolysis of the salt (**5**) gave the starting S-oxide (**1a**).

In general, *N*-tosylsulphilimines (>S=NSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-*p*) undergo cleavage of the N-SO<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me-*p*) bond to afford the

<sup>\*\*\*</sup> The salt (**5**) is very hygroscopic, becoming a liquid on exposure to air. The H<sub>2</sub>O content thus depends on the conditions employed for the analyses.

**Table 1.** N.m.r. data for (1)–(3) (dithiacyclo-octane ring atoms only).<sup>a</sup>

(1a) <sup>b</sup>	3.23–3.04 [m, 4H, –S(O)CH <sub>2</sub> –], 2.76–2.54 (m, 4H, –SCH <sub>2</sub> –), and 2.43–2.18 (m, 4H, –CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –)
(1b)	2.76–2.55 (m, 4H, –SCH <sub>2</sub> –) and 2.45–2.19 (br. m, 4H, –CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –)
(2a) <sup>c</sup>	3.41–3.22 [m, 4H, –S(NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Me- <i>p</i> )CH <sub>2</sub> –], 2.78–2.54 (m, 4H, –SCH <sub>2</sub> –), and 2.39–2.17 (m, 4H, –CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –)
(2b)	2.77–2.53 (m, 4H, –SCH <sub>2</sub> –) and 2.45–2.19 (br. m, 4H, –CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –)
(3) <sup>d</sup>	4.32–3.40 (br. m, 8H, –S <sup>+</sup> CH <sub>2</sub> –) and 3.32–2.10 (br. m, 4H, –CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –)

<sup>a</sup> <sup>1</sup>H and <sup>13</sup>C data for (1) and (2) in CDCl<sub>3</sub>, relative to Me<sub>4</sub>Si; data for (3) in D<sub>2</sub>SO<sub>4</sub> relative to sodium 4,4-dimethyl-4-silapentanesulphonate (DSS).<sup>b</sup> <sup>13</sup>C: δ 56.6, 30.2, and 23.7. <sup>c</sup> <sup>13</sup>C: δ 50.8, 30.4, and 25.3. <sup>d</sup> <sup>13</sup>C: δ 56.3 and 38.6.

corresponding *N*-unsubstituted sulphilimines on treatment with conc. H<sub>2</sub>SO<sub>4</sub>.<sup>5</sup> However, on dissolution of the sulphilimine (2a) in conc. D<sub>2</sub>SO<sub>4</sub>, the <sup>1</sup>H n.m.r. chemical shifts observed agreed well with those expected for a 1 : 1 mixture of (3) and toluene-*p*-sulphonamide. When this H<sub>2</sub>SO<sub>4</sub> solution was treated in the same way as the solution of (1a), the salt (5) was obtained; treatment of (5) with aqueous alkali solution

gave (1a) quantitatively. The tetradeuteriated compound (2b) gave similar results to (1b).

The present results thus provide a simple and convenient method of preparation of a new class of organosulphur compound.

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