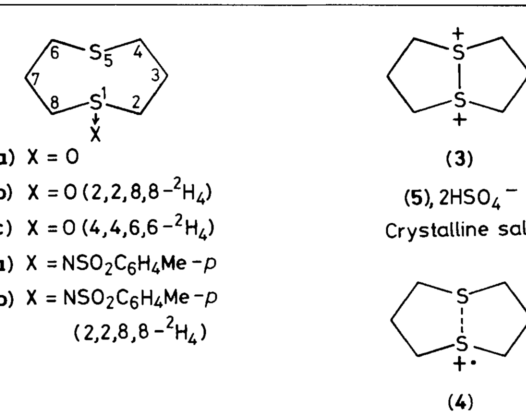
Formation and Isolation of the Disulphide Dication of 1,5-Dithiacyclo-octane in the Reactions of the Corresponding *S*-Oxide and *S*-(*N*-tosylimide) in Concentrated Sulphuric Acid

Naomichi Furukawa,* Akira Kawada, and Tsutomu Kawai

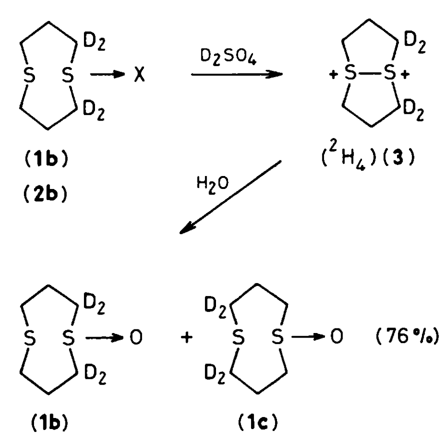
Department of Chemistry, The University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

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_2SO_4 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_2 in acidic aqueous media.[1] They have isolated the dications of several cyclic bis-sulphides by treating the corresponding sulphides with $NOBF_4$ (2 equiv.) in MeCN.[2,3] Numata and Oae have postulated the formation of the dithietanium dication on dissolution of *o*-methylthiophenyl phenyl sulphoxide in conc. H_2SO_4.[4] Treatment of a cyclic bis-sulphide *S*-oxide having a conformationally feasible structure for intramolecular S–S bond interaction with conc. H_2SO_4 should lead to the corresponding dication. We have accordingly dissolved dithiacyclo-octane *S*-oxide (**1a**) or *S*-(*N*-tosylimide) (**2a**) in conc. D_2SO_4, and detected the formation of the corresponding disulphide dication (**3**) by ^1H and ^{13}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_2SO_4 solution showed signals due to the corresponding cation radical (**4**).



(**1a**) X = O
(**1b**) X = O (2,2,8,8-$^2H_4$)
(**1c**) X = O (4,4,6,6-$^2H_4$)
(**2a**) X = $NSO_2C_6H_4Me$-*p*
(**2b**) X = $NSO_2C_6H_4Me$-*p* (2,2,8,8-$^2H_4$)
(**3**)
(**5**), $2HSO_4^-$ Crystalline salt
(**4**)



Scheme 1

1,5-Dithiacyclo-octane *S*-oxide (**1a**), the *S*-(*N*-tosylimide) (sulphilimine) (**2a**),† [m.p. 175—178 °C; $\nu_{max.}$ (KBr) 1270, 1140, 1090, and 1000 cm^{-1}] and the corresponding 2,2,8,8-tetradeuteriated derivatives (**1b**) and (**2b**) were synthesized.‡ When (**1a**) was dissolved in conc. H_2SO_4 (96%), the solution became slightly yellow. The ^1H and ^{13}C n.m.r. spectra of D_2SO_4 (98%) solutions of (**1a**) were recorded immediately; the signals observed in $CDCl_3$ for (**1a**) disappeared and two sets of new peaks appeared in a 2 : 1 ratio.§ 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**).¶ Treatment of the H_2SO_4 solution of (**1a**) with H_2O and work-up led to the starting *S*-oxide (**1a**) in 72% yield. Similar treatment of (**1b**) in D_2SO_4 led to similar changes in the ^1H and ^{13}C n.m.r. spectra, except that the peak ratio was 1 : 1. Hydrolysis of the H_2SO_4 solution of (**1b**) led to 76% recovery of the *S*-oxide, the ^1H 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_2SO_4 took place during the reaction (Scheme 1). The solution of (**3**) in H_2SO_4 was poured into ice-cooled anhydrous diethyl ether and the salt (**5**) was obtained as white hygroscopic crystals, m.p. 66—69 °C.†** Hydrolysis of the salt (**5**) gave the starting *S*-oxide (**1a**).

In general, *N*-tosylsulphilimines (>S=$NSO_2C_6H_4Me$-*p*) undergo cleavage of the N–$SO_2(C_6H_4Me$-*p*) bond to afford the

† Satisfactory elemental analyses were obtained.

‡ Compound (**1a**) did not undergo H–D exchange in NaOD–D_2O–tetrahydrofuran at 50 °C, so it was necessary to heat the solution under reflux for 20 h at 100 °C under N_2. In contrast, H–D exchange of (**2a**) could be carried out at 70 °C for 6 h; deuterium content: (**1a**), 100%; (**2a**), 81%.

§ Musker *et al.*[2] reported that the dication $(BF_4)_2$ salt has broad ^1H n.m.r. signals at δ *ca.* 2—4 in CD_3CN, while the ^{13}C n.m.r. spectra correspond roughly with our results. The broadening of the ^1H n.m.r. spectrum observed by Musker *et al.* is probably due to the MeCN solvent which may interact with the S^+ unit in (**3**), while D_2SO_4 does not lead to such a solvation effect, resulting in sharp ^1H n.m.r. spectra.

¶ The solution of (**1a**) in H_2SO_4 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.

** The salt (**5**) is very hygroscopic, becoming a liquid on exposure to air. The H_2O content thus depends on the conditions employed for the analyses.

Table 1. N.m.r. data for (**1**)—(**3**) (dithiacyclo-octane ring atoms only).[a]

(**1a**)[b]	3.23—3.04 [m, 4H, $-S(O)CH_2-$], 2.76—2.54 (m, 4H, $-SCH_2-$), and 2.43—2.18 (m, 4H, $-CH_2CH_2CH_2-$)
(**1b**)	2.76—2.55 (m, 4H, $-SCH_2-$) and 2.45—2.19 (br. m, 4H, $-CH_2CH_2CH_2-$)
(**2a**)[c]	3.41—3.22 [m, 4H, $-S(NSO_2C_6H_4Me$-*p*$)CH_2-$], 2.78—2.54 (m, 4H, $-SCH_2-$), and 2.39—2.17 (m, 4H, $-CH_2CH_2CH_2-$)
(**2b**)	2.77—2.53 (m, 4H, $-SCH_2-$) and 2.45—2.19 (br. m, 4H, $-CH_2CH_2CH_2-$)
(**3**)[d]	4.32—3.40 (br. m, 8H, $-S^+CH_2-$) and 3.32—2.10 (br. m, 4H, $-CH_2CH_2CH_2-$)

[a] ^1H and ^{13}C data for (**1**) and (**2**) in $CDCl_3$, relative to Me_4Si; data for (**3**) in D_2SO_4 relative to sodium 4,4-dimethyl-4-silapentanesulphonate (DSS). [b] ^{13}C: δ 56.6, 30.2, and 23.7. [c] ^{13}C: δ 50.8, 30.4, and 25.3. [d] ^{13}C: δ 56.3 and 38.6.

corresponding *N*-unsubstituted sulphilimines on treatment with conc. H_2SO_4.[5] However, on dissolution of the sulphilimine (**2a**) in conc. D_2SO_4, the ^1H 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_2SO_4 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.

Received, 12th April 1984; Com. 529

References

1 J. T. Doi and W. K. Musker, *J. Am. Chem. Soc.*, 1981, **103**, 1159, and references cited therein.
2 W. K. Musker, T. L. Wolford, and P. B. Roush, *J. Am. Chem. Soc.*, 1978, **100**, 6416.
3 On treatment with 1 equiv. of $NOBF_4$ the corresponding cation radical was detected by e.s.r. spectroscopy.[2] E.s.r. spectra of disulphide cation radicals have been reported: P. G. Gilbert, D. K. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1748; D. Bahnemann and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.*, 1975, 238; *J. Chem. Soc., Perkin Trans. 2*, 1975, 675; W. K. Musker and P. B. Roush, *J. Am. Chem. Soc.*, 1976, **98**, 6745; S. Oae and N. Kunieda, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 696; H. J. Shine and L. Piette, *J. Am. Chem. Soc.*, 1962, **84**, 4798.
4 T. Numata and S. Oae, *Int. J. Sulfur Chem.*, 1971, **1**, 6.
5 T. Yoshimura, T. Omata, T. Aida, N. Furukawa, and S. Oae, *J. Org. Chem.*, 1976, **41**, 1728. Cleavage of the S–NSO_2 bond has been reported: O. Bohman and S. Allenmark, *Tetrahedron Lett.*, 1973, 405.