New Evidence for Intramolecular Sulphur–Sulphur Interaction in 2,6-Bis(methylthiomethyl)phenyl Phenyl Sulphide

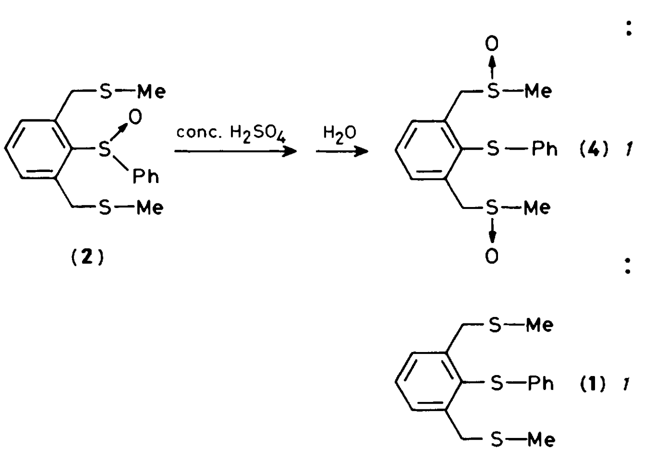
Hisashi Fujihara, Jer-Jye Chiu, and Naomichi Furukawa*

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

Evidence for intramolecular sulphur–sulphur interaction between the three sulphur atoms of 2,6-bis(methylthiomethyl)phenyl phenyl sulphide was found in the reactions of the corresponding sulphoxides with conc. H_2SO_4 and in electrochemical oxidation.

Recently, results have accumulated indicating the presence of transannular sulphur–sulphur interactions in the reactions of 1,5-dithiacyclo-octane and related derivatives.[1–4] However, no clear cut example of transannular interactions between the three sulphur atoms in trithia compounds has been reported. We now report evidence for S–S interactions between the three sulphur atoms of the 2,6-bis(methylthiomethyl)phenyl phenyl sulphide system (**1**) in the reaction of the corresponding sulphoxides with conc. H_2SO_4. The electrochemical oxidation of (**1**) is also of interest.

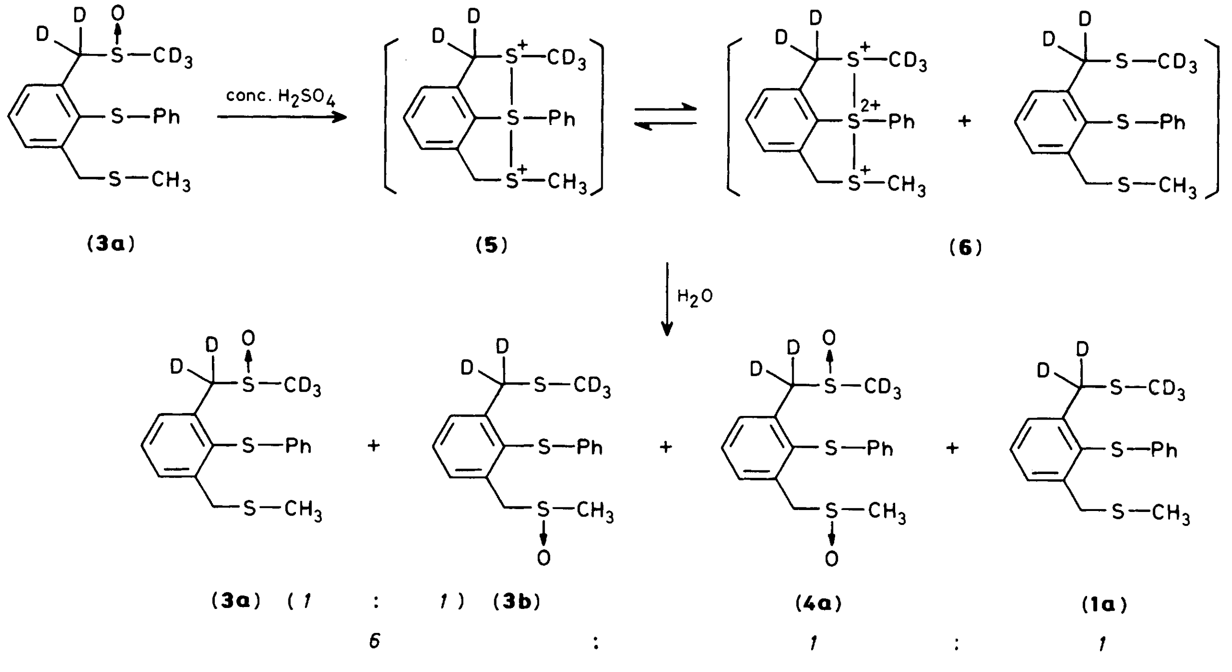
The tris-sulphide (**1**),[†] the bis-sulphide–sulphoxides (**2**)[†] and (**3**),[†] and the corresponding deuteriated compound (**3a**)[†] were synthesized. When (**2**) was dissolved in conc. D_2SO_4 (98%) at room temperature, the solution became yellow. The ^1H n.m.r. spectrum of this solution showed signals at δ 7.70—6.80 (m, 8H, Ph), 4.30—4.07 (br. m, 4H, SCH_2), and 2.90—2.30 (br. m, 6H, SMe). Treatment of the D_2SO_4 solution of (**2**) with ice-H_2O and work-up afforded only three products in 80% isolated yield which were separated by preparative liquid chromatography to give compounds (**3**), (**1**), and (**4**)[‡] in a 6 : 1 : 1 ratio (Scheme 1). Although sulphide derivatives such as 2-methylthiomethylphenyl phenyl sulphoxide and 1-methylsulphinylmethyl-3-methylthiomethylben-



Scheme 1

[†] Compound (**1**) was synthesized by the reaction of 2,6-bis(bromomethyl)phenyl phenyl sulphide with sodium methanethiolate under phase transfer conditions. 2,6-Bis(bromomethyl)phenyl phenyl sulphide was prepared by a modification of the method of F. Vögtle, J. Grütze, R. Nätscher, W. Wieder, E. Weber, and R. Grün, *Chem. Ber.*, 1975, **108**, 1694: ^1H n.m.r. δ ($CDCl_3$) 1.99 (s, 6H, Me), 3.88 (s, 4H, CH_2), and 6.83—7.50 (m, 8H, ArH); m/z 306 (M^+). Compound (**2**) was prepared by the reaction with sodium methanethiolate of 2,6-bis(bromomethyl)phenyl phenyl sulphoxide, which was obtained by oxidation using *m*-chloroperbenzoic acid of 2,6-bis(bromomethyl)phenyl phenyl sulphide: m.p. 78—78.5 °C; i.r.(KBr) 1030 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 1.94 (s, 6H, Me), 3.71, 4.18 (ABq, J 14 Hz, 4H, CH_2), and 7.30—7.73 (m, 8H, ArH). Compound (**3**) was prepared by oxidation using sodium metaperiodate of the sulphide (**1**): i.r.(neat) 1040 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 2.00 (s, 3H, Me), 2.46 (s, 3H, Me), 3.89 (s, 2H, CH_2), 4.08, 4.34 (ABq, J 13 Hz, 2H, CH_2), and 6.78—7.62 (m, 8H, ArH). Compound (**3**) was deuteriated by heating with NaOD–D_2O–tetrahydrofuran in a sealed tube at 85 °C for 10 h; deuterium content of (**3a**): >95 atom%. Satisfactory elemental analyses were obtained for (**1**) and (**2**).

[‡] I.r. (neat) 1040 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 2.49 (d, 6H, Me), 4.23 (m, 4H, CH_2), and 6.78—7.62 (m, 8H, ArH).



Scheme 2

zene were decomposed by conc. H_2SO_4,§ the H_2SO_4 solutions of either (**2**) or (**3**) were strongly stabilized by introduction of the third sulphur atom. These findings strongly suggest that the charge developed on one sulphur atom is delocalized over the three sulphur atoms in the trithia compound (**2**).

On dissolution of (**3**) in conc. D_2SO_4, the ^1H n.m.r. chemical shifts observed were consistent with those of the D_2SO_4 solution of (**2**). Hydrolysis of the D_2SO_4 solution of (**3**) led to 82% recovery of a mixture of (**3**), (**1**), and (**4**) in a 6 : 1 : 1 ratio. Similar treatment of (**3a**) in D_2SO_4 led to analogous changes in the ^1H n.m.r. spectra and a mixture of monosulphoxide, disulphoxide, and sulphide in a 6:1:1 ratio was obtained by hydrolysis of the D_2SO_4 solution. The ^1H n.m.r. spectrum of the mono-sulphoxide obtained indicated that it was a 1:1 mixture of (**3a**) and the pentadeuteriated isotopomer (**3b**) and also that no H–D exchange with the solvent H_2SO_4 took place during the reaction (Scheme 2). These results demonstrate that the three sulphur atoms in (**3**) participate in the stabilization of a positive charge developed on one sulphur atom, and hence indicate that (**2**) and (**3**) are converted initially into a dication such as (**5**). The mechanism for formation of the disulphoxide (**4**) and sulphide (**1**) is not unambiguous (intermolecular S–S interaction cannot be excluded); however, formation and hydrolysis of the tetracation (**6**) which is formed by disproportionation of the dication (**5**) are the probable processes.

In order to confirm the existence of S–S interactions in (**1**), the electrochemical oxidation of (**1**) was studied by cyclic voltammetry.¶ The peak potentials (E_p) for (**1**) and other sulphides showed the following values: (**1**), 1.15 V; 2-methylthiomethylphenyl phenyl sulphide, 1.34 V; 1,3-bis(methylthiomethyl)benzene, 1.82 V; and diphenyl sulphide, 1.55 V. Comparison of the trithia compound (**1**) with a monothia compound such as diphenyl sulphide shows a peak potential 400 mV more cathodic for the former, so that (**1**) should be oxidised more readily. Thus, the trithia compound (**1**) exhibits large negative potential shifts which are undoubtedly related to neighbouring-group interactions.[5]

Received, 1st May 1986; Com. 584

References

1 N. Furukawa, A. Kawada, and T. Kawai, *J. Chem. Soc., Chem. Commun.*, 1984, 1151.
2 H. Fujihara, A. Kawada, and N. Furukawa, *Heterocycles*, 1986, **24**, 17.
3 N. Furukawa, A. Kawada, T. Kawai, and H. Fujihara, *J. Chem. Soc., Chem. Commun.*, 1985, 1266.
4 G. S. Wilson, D. D. Swanson, J. T. Klug, R. S. Glass, M. D. Ryan, and W. K. Musker, *J. Am. Chem. Soc.*, 1979, **101**, 1040.
5 The importance of neighbouring group participation in electrochemical oxidation of sulphides has been demonstrated: R. S. Glass, M. Hojjatie, A. Petsom, G. S. Wilson, M. Göbl, S. Mahling, and K.-D. Asmus, *Phosphorus Sulfur*, 1985, **23**, 143; R. S. Glass, J. R. Duchek, J. T. Klug, and G. S. Wilson, *J. Am. Chem. Soc.*, 1977, **99**, 7349 (see ref. 4 therein).

---

§ 1,5,9-Trithiacyclododecane 1-oxide, a tris-sulphide analogue of 1,5-dithiacyclo-octane 1-oxide, was also decomposed in conc. H_2SO_4.

¶ Peak potentials of first oxidation peak determined at a Pt electrode, 200 mV/s scan rate, in acetonitrile–0.1 M $Bu^n{}_4NClO_4$ *vs.* saturated calomel electrode.