A New Preparative Method, Characterization, and Reactivity of Disulphide Dication Salts of Cyclic Bis-sulphides: $R_2\overset{+}{S}-\overset{+}{S}R_2\cdot 2CF_3SO_3^-$

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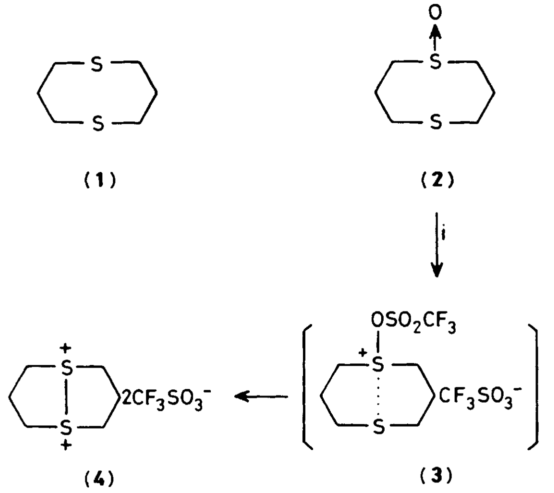
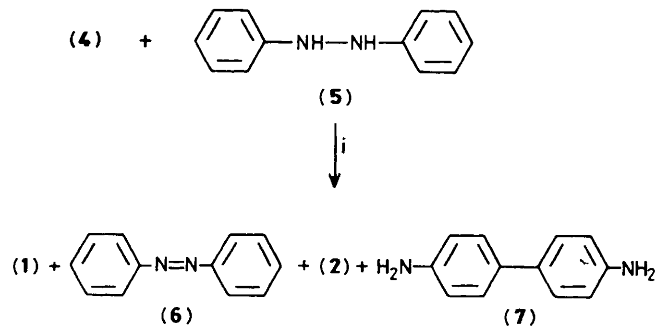
The reaction of 1,5-dithiacyclo-octane 1-oxide with trifluoromethanesulphonic anhydride affords the corresponding disulphide dication as a stable crystalline salt which serves as an oxidizing agent in the oxidation of 1,2-diphenylhydrazine; the disulphide dication of 1,4-dithiane has also been isolated.

The disulphide dication of 1,5-dithiacyclo-octane (**1**) has been prepared by either the two-electron oxidation of (**1**) using $NOBF_4$[1] or the reaction of the corresponding sulphoxide with conc. H_2SO_4.[2] However, these two procedures have the following disadvantages, namely that nitrosonium salts (*e.g.*, $NO^+BF_4^-$) are often accompanied by nitrosation and even nitration,[3] and that the bis(hydrogen sulphate)salt of the dication of (**1**) cannot be dissolved in general organic solvents. Recently, we found that the Pummerer reaction of 1,5-dithiacyclo-octane 1-oxide (**2**) with acetic anhydride proceeds *via* the formation of the disulphide dication as an intermediate.[4] We now report a new method for the preparation of



Scheme 1. i, $(CF_3SO_2)_2O$, CH_2Cl_2, −20 °C.

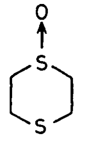


Scheme 2. i, MeCN, Ar, 0 °C, 30 min.

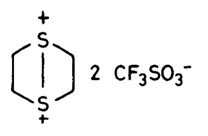
the disulphide dication salt of (**1**) in good yield, by the reaction of (**2**) with trifluoromethanesulphonic anhydride, together with its reactivity for oxidation of 1,2-diphenylhydrazine and the preparation of the analogous dication of 1,4-dithiane.

Typically, addition of 1.3 mmol of pure trifluoromethanesulphonic anhydride $[(CF_3SO_2)_2O]$ in 50 ml of anhydrous methylene chloride to a stirred solution of 1.3 mmol of (**2**)[2] in 10 ml of anhydrous methylene chloride under an Ar atmosphere at −20 °C resulted in a colourless crystalline precipitate. Upon filtration in a dry box under rigorously anhydrous conditions and recrystallization from anhydrous acetonitrile–methylene chloride the dication (**4**) was obtained in 85% yield as a remarkably stable crystalline salt, m.p. 100—102 °C (decomp.).[†] This reaction should proceed *via* the initial formation of the trifluoromethylsulphonyloxy sulphonium salt (**3**) which subsequently should be converted into the disulphide dication (**4**) by a nucleophilic displacement of the trifluoromethanesulphonate ion ($CF_3SO_3^-$) by the second sulphur atom as shown in Scheme 1. The Pummerer rearranged products were not obtained at all.

The dication salt (**4**) was characterized by spectroscopic and chemical means. The ^1H n.m.r. spectrum of dication (**4**) in CD_3CN shows somewhat broad singlet peaks at δ 3.6—2.9 and 2.7—2.2 with a ratio of 2 : 1 and its u.v. spectrum exhibits $\lambda_{max.}$ 231 nm in acetonitrile.[‡] Hydrolysis of the salt (**4**) gave the starting *S*-oxide (**2**) in quantitative yield. 2,2,8,8-Tetradeuteriated 1,5-dithiacyclo-octane *S*-oxide[2] was treated in a similar way with trifluoromethanesulphonic anhydride in methylene chloride to afford the dication $[^2H_4]$(**4**). Hydrolysis of the salt $[^2H_4]$(**4**) led to 93% recovery of the *S*-oxide, the ^1H n.m.r. spectrum of which indicates that it is a 1 : 1 mixture of the 2,2,8,8- and 4,4,6,6-tetradeuteriated *S*-oxides. This result indicates clearly the structure of $[^2H_4]$(**4**). Meanwhile, the reaction of the dication salt (**4**) (1 equiv.) with 1,2-diphenylhydrazine (**5**) (1 equiv.) was carried out in acetonitrile under an Ar atmosphere at 0 °C for 30 min. Then the reaction mixture was treated with aqueous sodium hydrogen carbonate solution to give azobenzene (**6**) as the oxidation product in 35% yield, sulphide (**1**) as the reduction product (33%), and sulphoxide (**2**) in 47% yield. Furthermore, 4,4′-diaminobiphenyl (benzidine) (**7**)[§] was obtained in 52% yield by acid-catalysed rearrangement of (**5**) (Scheme 2). When 1,4-diazabicyclo[2.2.2]octane (DABCO) (1 equiv.)[¶] as a base was added to the above reaction system, the yields of the redox products were increased. Hence, we obtained the compounds (**6**) in 71%, (**1**) in 73%, (**7**) in 22%, and (**2**) in 10% yields, respectively (Scheme 2). This result indicates that the dication (**4**) serves as oxidizing agent.



(**8**)



(**9**)

The six-membered cyclic bis-sulphide in which transannular interaction of the sulphur atoms is minimal, 1,4-dithiane 1-oxide (**8**) also reacts with trifluoromethanesulphonic anhydride in anhydrous methylene chloride to give the disulphide dication salt (**9**) in 41% yield, m.p. 135 °C (decomp.), although the dication·$(BF_4)_2$ salt could not be isolated by treatment of 1,4-dithiane with $NOBF_4$.[1] The ^1H n.m.r. spectrum of the salt (**9**) in CD_3CN shows a singlet peak at δ 3.80. 2,2,6,6-Tetradeuteriated 1,4-dithiane 1-oxide gave similar results to the dithiacyclo-octane analogue.

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[†] Satisfactory elemental (C,H) analyses were obtained. An *X*-ray diffraction analysis of (**4**) is underway in this laboratory.

[‡] Musker *et al.*[1] found complex ^1H signals at δ *ca.* 2—4 in CD_3CN for the dication·$(BF_4)_2$ salt which could not be resolved. We found that $\lambda_{max.}$ of the dication·$(CF_3SO_3)_2$ was in fair agreement with that of the dication salt reported by Musker *et al.*[1]

[§] The benzidine rearrangement should occur by the acid liberated in the redox reaction. 2,4′-Diaminobiphenyl and other isomers were not obtained at all.

[¶] The dication (**4**) did not react with DABCO under our experimental conditions.