Tetrahedron Letters,Vol.30,No.33,pp 4399-4402,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

TRANSANNULAR SULFUR-SULFUR INTERACTION IN 3,7,9-TRITHIABICYCLO[3.3.1]NONANE AS A NEW CYCLIC TRIS-SULFIDE: QUEST FOR THE INTRABRIDGED DITHIA DICATION

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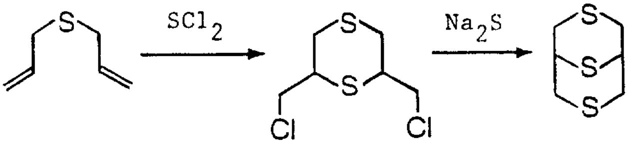
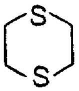
Abstract: A new cyclic tris-sulfide, 3,7,9-trithiabicyclo[3.3.1]nonane (1) has been synthesized. Transannular S-S interaction in 1 was found in the reactions of 1 and its sulfoxide with concd H_2SO_4 and in electrochemical oxidation.

Currently, there is considerable interest in the study of the transannular interaction or bond formation between the sulfur atoms in cyclic bis-sulfides.[1-4] This aspect is of particular interest for dications of multithia compounds where more than two sulfur atoms are involved in the stabilization of the cationic species of sulfur atom. However, no such example has been reported, except for our recent result.[5] This paper describes the transannular S-S interaction of 3,7,9-trithiabicyclo[3.3.1]nonane (**1**) as a new saturated aliphatic cyclic tris-sulfide in the reactions of **1** and the corresponding sulfoxide with concd H_2SO_4, and in electrochemical oxidation of **1**.

The title compound **1** was synthesized as follows. 2,6-Dichloromethyl-1,4-dithiane[6] (5) (45.5 g, 0.21 mol) was treated with Na_2S (18.0 g, 0.23 mol) in dimethylformamide (1 L) using a high dilution technique at room temperature. The whole mixture was stirred at 150 °C for 12 h. After usual work-up, the crude products were purified by silica-gel column chromatography (eluent: hexane) to afford the compound 1 (Scheme 1). The tris-sulfide 1 was further purified by preparative liquid chromatography.[7] The 500-MHz ^1H NMR spectrum (Table 1 and Figure 1) of **1** in $CDCl_3$ is assigned to the twin-chair form.[8]



Scheme 1 5 1



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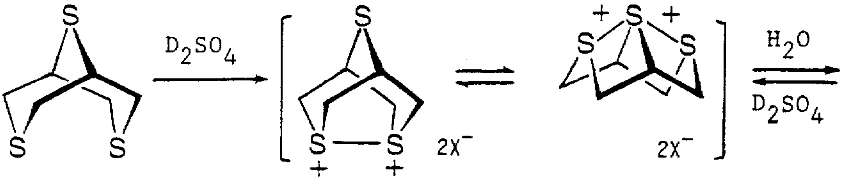
In order to verify the existence of S-S interaction in the tris-sulfide **1**, the electrochemical oxidation of **1** was studied by cyclic voltammetry.[9] The peak potentials (Ep) for **1** and cyclic bis-sulfide, 1,4-dithiane (**4**) showed the following values: **1**, 0.53 V and **4**, 1.32 V vs Ag/0.1M $AgNO_3$. Simple sulfides normally exhibit a peak potential of ca. 1.2 to 1.5 V (Ag/Ag^+). Interestingly, comparison of the tris-sulfide **1** with the bis-sulfide **4** shows a peak potential 800 mV more cathodic for the former, so that **1** should be oxidized more readily. Thus, the trithia compound **1** exhibits large negative potential shifts which are undoubtedly related to transannular S-S interactions.[10]



1 **2a** **2b** **3**

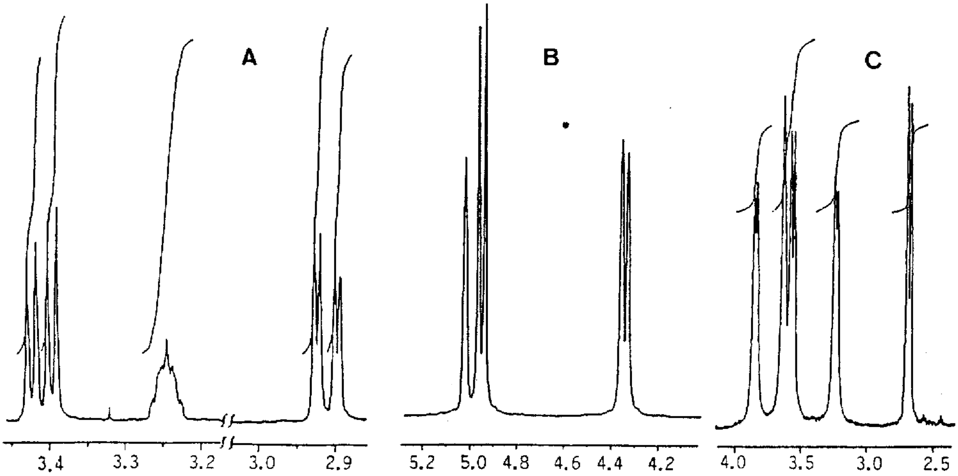


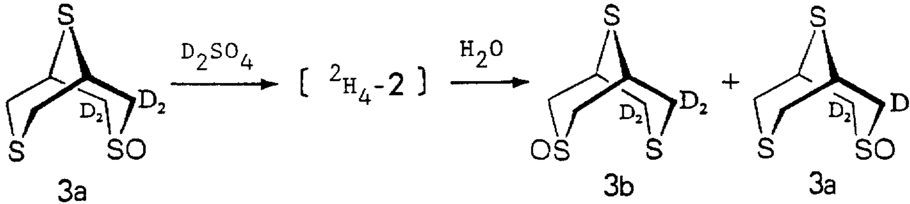
Figure 1. 500-MHz ^1H NMR Spectra. (A) **1** in $CDCl_3$; (B) **1** and **3** in D_2SO_4; (C) **3** in $CDCl_3$.

Table 1. ^1H and ^{13}C NMR Spectroscopic Data for **1**, **2**, and **3**.

	^1H, δ	^{13}C, δ
1^a	3.41 (dd, Je-a=12.4 Hz, Ja-x=5.9 Hz, 4H), 3.26-3.23 (m, 2H), 2.91 (dd, Je-a=12.4 Hz, Je-x=3.6 Hz, 4H)	31.9 (d), 29.8 (t)
2^b	5.03 (s, 2H), 4.96 (d, J=13 Hz, 4H), 4.35 (d, J=13 Hz, 4H)	52.9 (t), 48.6 (d)
3^a	3.83 (d, J=11 Hz, 2H), 3.62 (s, 2H), 3.55 (d, J=14 Hz, 2H), 3.22 (d,J=11 Hz,2H), 2.67 (d,J=14 Hz, 2H)	58.9 (t), 36.6 (d), 33.5 (t)

a) In $CDCl_3$ solution at 25 °C. b) In D_2SO_4 solution at 25 °C.

Dissolution of tris-sulfide **1** in concd D_2SO_4 (98%) at room temperature resulted in an orange colored solution. The 500-MHz ^1H NMR spectrum of the D_2SO_4 solution of **1** showed at δ 5.03 (s, 2H), 4.96 (d, 4H), and 4.35 (d, 4H), while the 125-MHz ^{13}C NMR spectrum of the solution showed two absorptions at δ 52.9 and 48.6 (see Table 1 and Figure 1). Both the ^1H and ^{13}C NMR spectra show significant downfield shifts for the D_2SO_4 solution of **1** compared to its starting sulfide **1**. These results clearly indicate that **1** is converted into the dithia dication **2**. The ^1H NMR spectrum of the D_2SO_4 solution of **1** suggests a rapidly equilibrating mixture of **2a** and **2b**, since the methine proton appeared as singlet. This behavior can be explained as follows; the difference between the energies of the twin-chair and chair-boat conformations in bicyclo[3.3.1]nonanes was estimated to be 2.7 to 3.7 kcal/mole.[11] This is significantly lower than the ΔH value, 6.9 kcal/mole, associated with the chair-boat conversion in cyclohexane. On treatment of the D_2SO_4 solution of **1** with ice-H_2O, the sulfoxide **3** was obtained in 83% isolated yield, and none of the sulfide **1** or 3,7,9-trithiabicyclo[3.3.1]nonane 9-oxide was obtained.[12] Meanwhile, two-electron oxidation of **1** with $NOPF_6$ (2 equiv) in CH_3CN-CH_2Cl_2 also gave the dication $(PF_6)_2$ salt, which on treatment with H_2O again resulted in the formation of sulfoxide **3**. This result suggests that the reaction of **1** with concd H_2SO_4 may proceed via a two-electron-transfer process.[13] In contrast, bis-sulfide **4** did not react with concd H_2SO_4. Thus, the tris-sulfide **1** is easily oxidized to the dication **2** which is remarkably stabilized by transannular S-S interaction.



Scheme 2

On dissolution of the sulfoxide **3** in concd D_2SO_4, the ^1H and ^{13}C NMR chemical shifts observed were found to be analogous to those of the D_2SO_4 solution of **1**. Similar treatment of the tetradeuteriated monosulfoxide **3a**,[14] in D_2SO_4 gave the analogous ^1H NMR spectrum and the sulfoxide was obtained by hydrolysis of the D_2SO_4 solution of **3a**. The ^1H NMR spectrum of the monosulfoxide obtained indicated that it was a 1:1 mixture of **3a** and the tetradeuteriated isotopemer **3b** and also that no H-D exchange with the solvent H_2SO_4 took place during the reaction (Scheme 2).

These findings obviously demonstrate that the three sulfur atoms in the trithia compound participate transannularly in the stabilization of a positive charge developed on the one sulfur atom, and hence indicate that **1** and **3** are converted into a common dication such as **2**, namely the formation of the intrabridged dithia dication **2a**.[15]

References and Notes

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7) **1**: Mp 220 °C; MS (m/z) 178 (M^+). Anal. Calcd for $C_6H_{10}S_3$: C, 40.41; H, 5.65; S, 53.94%. Found: C, 40.30; H, 5.67; S, 53.95%.
8) The details of the conformational analysis and the X-ray structure of **1** will be reported in a separate paper.
9) Peak potentials of first oxidation peak determined at a glassy carbon electrode, 300 mV/s scan rate, in CH_3CN-0.1 M $NaClO_4$ vs. Ag/0.1 M $AgNO_3$.
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12) **3**: Mp 202 °C; FT-IR (KBr, cm^{-1}) 1024 and 993 (SO). Anal. Calcd for $C_6H_{10}OS_3$: C, 37.09; H, 5.19%. Found: C, 37.20; H, 5.22%. This sulfoxide **3** was obtained also by the oxidation of **1** using m-chloroperbenzoic acid.
13) Concd H_2SO_4 also acts as an oxidizing agent: A. J. Bard, A. Ledwith, and H. J. Shine, Adv. Phys. Org. Chem., **12**, 155 (1976).
14) Compound **3** was deuteriated by heating with NaOD-D_2O-tetrahydrofuran in a sealed tube at 90 °C for 8 h; deuterium content of **3a**: >95 atom%.
15) Other aliphatic cyclic tris-sulfides such as 1,3,5-trithiane and 1,5,9-trithiacyclododecane did not show the formation of dications. These results indicate that the geometry of sulfur atoms in space is important for the stabilization of positively charged species.

(Received in Japan 5 June 1989)