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Formation of Chlorosulfonium Salt of 1,5-Dithiacyclooctane and Transannular Sulfur-Sulfur Interaction in Hydrolysis of Its Salt

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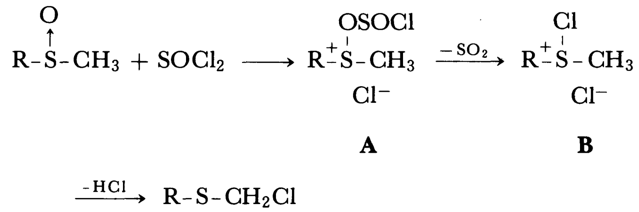
Synopsis. The reaction of 1,5-dithiacyclooctane 1-oxide (**2**) with thionyl chloride afforded the corresponding chlorosulfonium chloride as a stable salt and an evidence for the intermediary formation of the bis-sulfide dication with an equilibrium mixture of the chlorosulfonium salt was found. In contrast to **2**, 1,4-dithiacyclohexane 1-oxide (**6**) reacts with thionyl chloride like a simple sulfoxide.

Normally, the sulfoxides bearing α-protons react with thionyl chloride ($SOCl_2$) to form initially a (chlorosulfinyloxy)sulfonium cation (**A**) which then decomposes to give a chlorosulfonium chloride (**B**) and sulfur dioxide.1a,b) Finally chlorosulfonium salts generated are easily converted to α-chloro sulfides1c) as shown below.

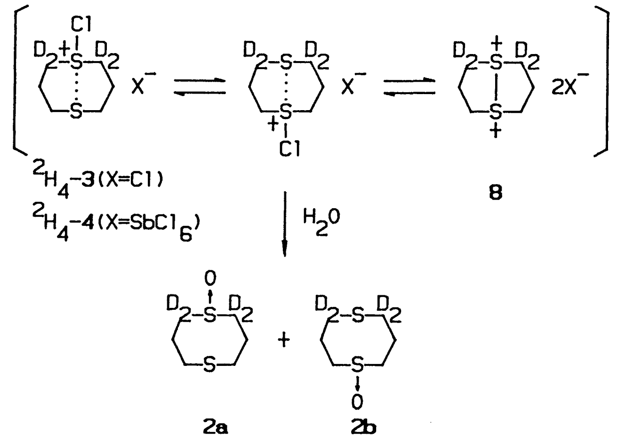


$$R\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}CH_3 + SOCl_2 \longrightarrow \underset{\mathbf{A}}{R\text{-}\overset{+}{\overset{OSOCl}{S}}\text{-}CH_3\ Cl^-} \xrightarrow{-SO_2} \underset{\mathbf{B}}{R\text{-}\overset{+}{\overset{Cl}{S}}\text{-}CH_3\ Cl^-} \xrightarrow{-HCl} R\text{-}S\text{-}CH_2Cl$$

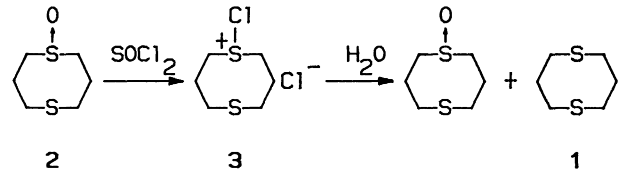
An intermediacy of the bis-sulfide dication of 1,5-dithiacyclooctane (**1**) has been confirmed kinetically by Musker et al. in the reduction of the corresponding sulfoxide with HI.2) Recently, we reported that the bis-sulfide dication of **1** is formed in either the reaction of the corresponding sulfoxide with concd H_2SO_4 or the Pummerer reaction with acetic anhydride.3,4) These results indicate that when a positive charge is induced on the one sulfur atom in the cyclic bis-sulfide, the remote second sulfur atom participates transannularly to stabilize the charge via formation of the S–S bond. We present here the formation of chlorosulfonium salt of **1** and the transannular sulfur-sulfur interaction in the hydrolysis of its salt, and the distinct difference between **1** and 1,4-dithiacyclohexane (**5**) in the reaction mode of the corresponding sulfoxides with thionyl chloride.

The reaction of 1,5-dithiacyclooctane 1-oxide (**2**) with thionyl chloride in anhydrous dichloromethane at 0°C gave the corresponding chlorosulfonium chloride **3** as a stable salt in 74% isolated yield. Secondary ion mass spectrum (SIMS) of **3** indicates the peaks at *m/z* 185 and 183 (base peak) which correspond to $C_6H_{12}S_2Cl^+$. This salt could be stabilized by transannular interaction of the second sulfur atom even in the absence of antimony pentachloride ($SbCl_5$). Treatment of **3** with H_2O and work-up led to sulfoxide **2** in 70% yield and sulfide **1** in 15% yield (Scheme 1). The sulfide was presumably formed by reduction of the halosulfonium ion by the second halide ion as a counterpart of the cation. 2,2,8,8-Tetradeuterated 1,5-dithiacyclooctane 1-oxide (**2a**) was treated similarly with thionyl chloride to afford the chlorosulfonium salt [$^2H_4$]-**3** in 75% yield. Hydrolysis of the salt [$^2H_4$]-**3** led to the sulfoxide in 69% yield and the tetradeuterated sulfide **1a** in 17% yield. The ^1H NMR spectra of the recovered sulfoxide indicate that it is a 1:1 mixture of 2,2,8,8- and 4,4,6,6-tetradeuterated sulfoxides (**2a**) and (**2b**) (Scheme 2). Furthermore, sulfoxide **2** was treated with thionyl chloride in the presence of antimony pentachloride in anhydrous dichloromethane to give 1-chloro-5-thia-1-thioniacyclooctane hexachloroantimonate (**4**) in 75% yield. The ^1H NMR spectrum of salt **4** in CD_3CN showed signals at δ 4.16—3.58 [m, 4H, $S(Cl)CH_2$], 3.52—2.71 (m, 4H, SCH_2), and 2.60—2.32 (m, 4H, CH_2). Hydrolysis of salt **4** gave only sulfoxide **2** in 67% yield. The tetradeuterated hexachloroantimonate salt [$^2H_4$]-**4**5) gave a similar result to [$^2H_4$]-**3**. These results suggest the intermediary formation of bis-sulfide dication **8** with an equilibrium mixture of the chlorosulfonium salt ([$^2H_4$]-**3** or **4**) (Scheme 2).

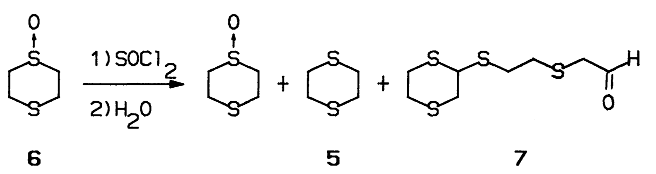
Meanwhile, 1,4-dithiacyclohexane 1-oxide (**6**) in which transannular interaction of the sulfur atoms is



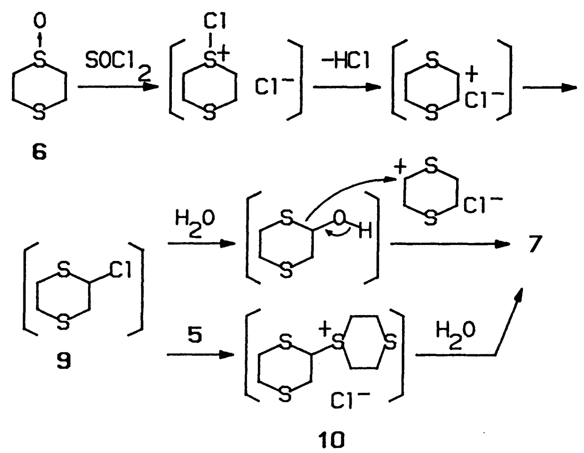
Scheme 2.



Scheme 1.



Scheme 3.



Scheme 4.

minimal, was treated similarly with thionyl chloride as described in **2**. The chlorosulfonium chloride of **5** could not be isolated as a salt in the reaction of **6** with thionyl chloride in the absence of antimony pentachloride. Hydrolysis of the reaction mixture in situ gave sulfoxide **6** in 9%, sulfide **5** in 20%, and aldehyde **7** in 41% yields (Scheme 3). This reaction may have proceeded through the formation of the Pummerer product such as α-chloro sulfide **9** which subsequently is converted into **7** by hydrolysis of **9** as illustrated in Scheme 4. However, an alternative process involving the formation of the sulfonium salt **10** by the reaction of **9** with **5** cannot be excluded (Scheme 4). The structure of **7** was confirmed by the formation of 2,4-dinitrophenyl hydrazone **11**. Thus, this distinct difference of reactivity between **2** and **6** should depend on the degree of the transannular S-S interaction in the six- and eight-membered rings.

Experimental

^{1}H NMR spectra were measured on a Hitachi R-600 FT-NMR spectrometer. The IR spectra were obtained on JASCO A-3 spectrometer. Secondary ion mass spectra were taken by Hitachi M-80B mass spectrometer. Elemental analyses were carried out by the Chemical Analytical Center at this University.

1,5-Dithiacyclooctane was synthesized by a modification of the method of Meadow and Reid.[6] 1,4-Dithiacyclohexane was obtained from Wako Pure Chemical Industries, Ltd.

Cyclic Bis-Sulfide Monosulfoxides. The monosulfoxides were obtained by general oxidation using *m*-chloroperbenzoic acid.

1,5-Dithiacyclooctane 1-Oxide (2): Yield 76%; mp 27—29 °C; IR (neat) 1010 cm^{-1} (S=O); ^{1}H NMR (CDCl$_3$) δ=2.18—2.43 (m, 4H, CH$_2$), 2.54—2.76 (m, 4H, SCH$_2$), and 3.04—3.23 [m, 4H, S(O)CH$_2$].

1,4-Dithiacyclohexane 1-Oxide (6): Yield 36%; mp 125.5—127.0 °C; IR (KBr) 1020 cm^{-1} (S=O); ^{1}H NMR (CDCl$_3$) δ=2.40—2.70 (m, 2H, SCH$_2$-*e*), 2.91—3.22 [m, 4H, S(O)CH$_2$], and 3.43—3.77 (m, 2H, SCH$_2$-*a*).

Preparation of 2,2,8,8-Tetradeuterated 1,5-Dithiacyclooctane 1-Oxide (2a). Deuteration of sulfoixde **2** was carried out in NaOD-D$_2$O under nitrogen atmosphere at 100 °C for 24 h. After usual work-up the tetradeuterated sulfoxide **2a** was obtained in 91% yield; the deuterium content of **2a** was more than 95 atom% by ^{1}H NMR spectroscopy.

Isolation of Chlorosulfonium Chloride 3. Addition of pure thionyl chloride (1 mmol) in anhydrous dichloromethane (1 ml) to a solution of 1,5-dithiacyclooctane 1-oxide (**2**) (1 mmol) in anhydrous dichloromethane (1 ml) under N$_2$ atmosphere at 0 °C resulted in a white crystalline precipitate. Upon filtration in a dry box under rigorously anhydrous conditions, 1-chloro-5-thia-1-thioniacyclooctane chloride (**3**) was obtained in 74% yield as stable hygroscopic crystalline salt: Mp 80°C; SIMS *m/z* (rel intensity) 185(42), 183(100) 151(17), 107(44), and 73(23).

Reactions of Sulfoxide 2 with Thionyl Chloride in the Presence of Antimony Pentachloride. To a stirred solution of sulfoxide **2** (1 mmol) and antimony pentachloride (1 mmol) in anhydrous dichloromethane (1 ml) was added thionyl chloride (1 mmol) in anhydrous dichloromethane under nitrogen at 0 °C. 1-Chloro-5-thia-1-thioniacyclooctane hexachloroantimonate (**4**) was obtained in 75% yield as stable hygroscopic crystalline salt: Mp 106—107 °C (decomp); ^{1}H NMR (CD$_3$CN) δ=2.32—2.60 (m, 4H, CH$_2$), 2.71—3.52 (m, 4H, SCH$_2$), and 3.58—4.16 [m, 4H, S(Cl)CH$_2$]; MS *m/z* 183 (M$^+$−SbCl$_6$).

Hydrolysis of Chlorosulfonium Salt 3. The salt **3** was treated with aqueous NaHCO$_3$ on ice bath. The mixture was extracted with dichloromethane. The combined organic phase was dried over MgSO$_4$, filtered, and concentrated under vacuum to give sulfoxide **2** in 70% and sulfide **1** in 15% yields. The salt **4** was hydrolyzed by the same procedure as **3**.

Reaction of Sulfoxide 6 with Thionyl Chloride. To a stirred solution of 1,4-dithiacyclohexane 1-oxide (**6**) (1 mmol) in anhydrous dichloromethane (1 ml) was added thionyl chloride (1 mmol) in anhydrous dichloromethane (1 ml) under nitrogen at 0 °C. Then the reaction mixture was treated with aqueous NaHCO$_3$ to afford sulfide **5** in 20%, sulfoxide **6** in 9%, and aldehyde **7** in 41% yields. The hydrazone of **7** was prepared as follows. To a solution of aldehyde **7** (19 mg) in ethanol (3 ml) was added 2,4-dinitrophenylhydrazine (50 mg, 0.1%-HCl solution). The reaction mixture was stirred at room temperature for 2 h. The solution was extracted with carbon tetrachloride, and the extract was dried over Na$_2$SO$_4$. After removal of the solvent, hydrazone **11** was purified by silica-gel column chromatography. **11**: Mp 125—126 °C; IR (KBr) 1610 (C=N), 1504 and 1321 cm^{-1} (NO$_2$); ^{1}H NMR (CDCl$_3$) δ=2.70—3.19 (m, 10H), 3.47 (d, *J*=6Hz, 2H, SCH$_2$CH=N), 4.10 (m, 1H, SCHS), 7.47 (t, *J*=6 Hz, 1H, CH=N), 7.92 (d, *J*=9 Hz, 1H, ArH), 8.36 (dd, *J*=9, 3 Hz, 1H, ArH), 9.13 (d, *J*=3 Hz, 1H, ArH), and 11.11 (br s, 1H, NH). Found: C, 38.69; H, 4.17; N, 12.89%. Calcd for C$_{14}$H$_{18}$N$_4$O$_4$S$_4$: C, 38.38; H, 4.14; N, 12.85%.

References

1) a) F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955); b) W. E. Truce, G. Birum, and E. T. McBee, *J. Am. Chem. Soc.*, **74**, 3594 (1952); c) H. Böhme and H. J. Gran, *Justus Liebigs Ann. Chem.*, **577**, 68 (1952).

2) J. T. Doi and W. K. Musker, *J. Am. Chem. Soc.*, **100**, 3533 (1978); W. K. Musker, *Acc. Chem. Res.*, **13**, 200 (1980).

3) N. Furukawa, A. Kawada, and T. Kawai, *J. Chem. Soc., Chem. Commun.*, **1984**, 1151.

4) N. Furukawa, A. Kawada, T. Kawai, and H. Fujihara, *J. Chem. Soc., Chem. Commun.*, **1985**, 1266.

5) In the ^{1}H NMR spectrum of [^{2}H$_4$]-**4** in CD$_3$CN, the splitting pattern is complicated and could not be resolved.

6) J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.*, **56**, 2177 (1934).