Structures of the Intermediates of Metal-Ion-Promoted Ring Opening Reactions of 1,3-Dithiolanes and 1,3-Dithianes in Nonaqueous Media

Peter Viski,* David P. Waller, and Michael Zuraw

Polaroid Corporation, 750 Main Street, 2-B,
Cambridge, Massachusetts 02139

Received May 29, 1996

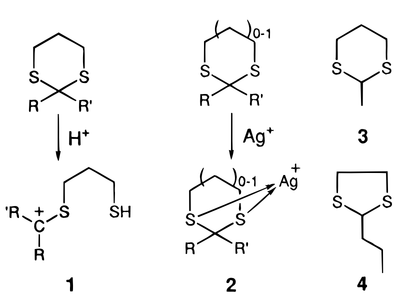

Figure 1. Key intermediates of acid-promoted ring opening reactions of 1,3-dithianes **1** and the proposed structure of intermediates **2** of the silver-assisted reaction of 1,3-dithianes and dithiolanes. **3** and **4** are the model compounds of this study.

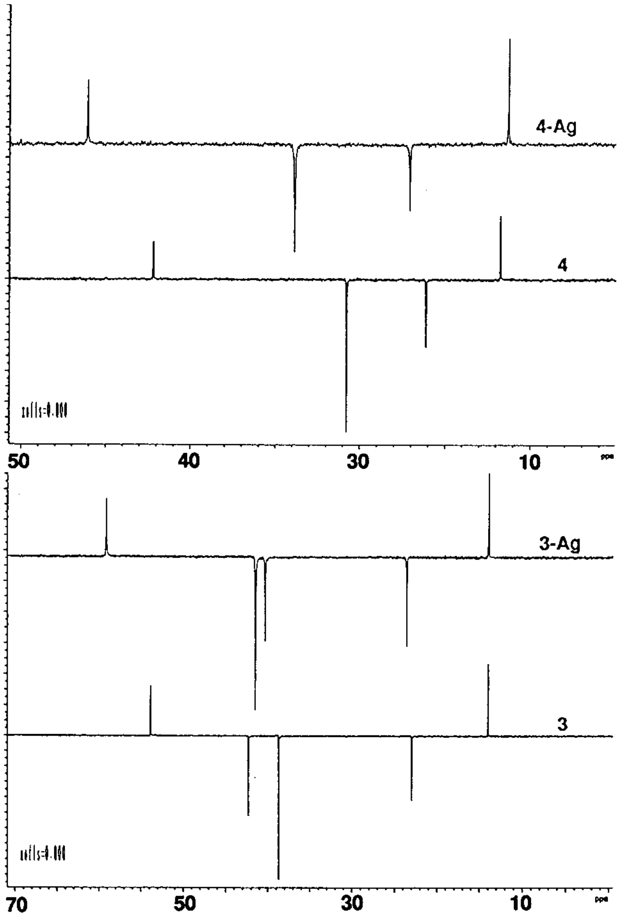

Figure 2. DEPT spectra of **3**, **4**, and their silver nitrate complexes (**3-Ag** and **4-Ag**).

Acid-catalyzed and metal-ion-assisted ring opening reactions of 1,3-heterocycles have been studied extensively in the literature. The intermediate in the generally accepted mechanism for the acid-catalyzed ring opening reactions of five- or six-membered 1,3-heterocycles is an open form “onium” type cation involving one of the heteroatoms.[1−3] In water or aqueous solvents the fast first step is the formation of this species. The rate-determining step is usually the hydrolysis of the already opened “onium” cation. A thio carbocation **1** is suggested for acid-catalyzed hydrolysis 1,3-dithiolanes or 1,3-dithianes[4] (Figure 1).

Less clear is the case of metal-ion-assisted ring openings of the same heterocycles. Satchell and co-workers, based on kinetic studies, suggested a different, closed ring intermediate **2** for analogous, metal-promoted reactions in 10% dioxane/water of 1,3-dithiolanes[6] and 1,3-dithianes[4,7] (Figure 1), but no evidence for such a structure has been presented so far.

The use of silver ions to accelerate the hydrolytic ring opening reactions of 1,3-dithianes and 1,3-dithiolanes in organic solvents containing not significantly more than a stoichiometric amount of water have now been investigated. The model compounds were 2-propyl-1,3-dithiolane (**3**) and 2-methyl-1,3-dithiane (**4**) (Figure 1). The solvent was DMF, and the silver ion source was silver nitrate. The first step in both cases was the rapid formation of a new species, which slowly reacted with the available water leading to butyraldehyde from **3**, and acetaldehyde from **4**. If the solvent was sufficiently dry, the intermediates were stable enough to obtain NMR spectra, and in one case a crystalline product was isolated.

The ^{13}C NMR spectra, after the addition of AgNO$_3$ solution showed the presence of symmetrical molecules in both cases (DEPT spectra shown on Figure 2). The number of signals remained the same as in the parent compounds, but with different chemical shifts. The absorption of the ring CH in **3** shifted from 53.85 ppm to 59.11 ppm in the silver complex. The ring methylenes originally detected at 38.69 ppm in **3** appear at 40.32 ppm in the complex. Similarly the CH signal of **4** shifted from 42.16 ppm to 46.07 ppm by complexation. The signal of ring methylenes next to the sulfur atoms change from 30.77 ppm to 33.66 ppm when complexed. These observations, especially that the methylene groups next to the heteroatoms remained equivalent when complexed, clearly indicate the preservation of symmetry. In a ring-opened structure the symmetry of the parent molecules would be lost. The results strongly suggest the presence of symmetrical silver complexes of the closed rings. After mixing concentrated solutions of **4** and AgNO$_3$ in dry DMF, colorless crystals (**4-Ag**) slowly formed. The determination of the crystal structure[9] clearly shows a closed ring complex, but interestingly the silver ions are bridging two rings instead of being connected to the sulfur atoms of the same ring (Figure 3).

Conclusion

On the basis of our findings, we propose that the metal-promoted hydrolytic reactions of 1,3-dithiolanes and 1,3-dithianes in aprotic organic solvents leading to the parent

---

(1) Fife, T. H.; Natarajan, R.; Shen, C. C.; Bembi, R. *J. Am. Chem. Soc.* **1991**, *113*, 3071, and references therein.

(2) Ali, M.; Satchell, D. P. N. *J. Chem. Soc., Perkin Trans. 2* **1992**, 219.

(3) Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581.

(4) Ali, M.; Satchell, D. P. N.; Le, W. T. *J. Chem. Soc., Perkin Trans. 2* **1993**, 917.

(5) Satchell, D. P. N.; Weil, T. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1191.

(6) Mohiuddin, T. F.; Satchell, D. P. N.; Satchell, R. S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 163.

(7) Penn, D.; Saidi, Z.; Satchell, D. P. N.; Satchell, R. S. *J. Chem. Res.* **1987**, 200.

S0022-3263(96)00993-0 CCC: $12.00

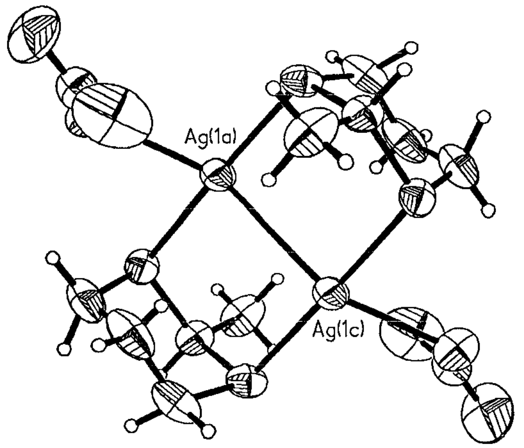

Figure 3. Thermal ellipsoid drawing of **4-Ag**. The Ag−Ag distance is 3.13 Å, the Ag−S distance is 2.69 Å, and the S−Ag−S bond angle is 179°. The Ag−O distance is 2.6 Å when the nitrate anions bridge the Ag atoms between dimers.

carbonyl compounds go through a symmetrical, closed ring/metal ion complex. The subsequent reaction of the complex with water becomes the rate-limiting step in the ring opening process.

Experimental Section

The NMR spectra were recorded on a 300 MHz instrument in DMF-d_7. All chemical shifts are reported in parts per million. DMF and DMF-d_7 were dried over CaO and fractionated. The product aldehydes were identified by GC-MS. **3** (^{13}C NMR 53, 85, 42.30, 38.69, 22.96, 13.94) was prepared according to a known procedure,[8] and **4** (^{13}C NMR 42.18, 30.77, 26.11, 21.73) was purchased from Aldrich.

Preparation of 2-Methyl-1,3-dithiane/AgNO$_3$ Complex (3-Ag). To a solution of 0.0335 g (0.226 mmol) **3** in 0.3 mL of dry DMF-d_7 was added 0.0384 g (0.226 mmol) of AgNO$_3$ dissolved in 0.5 mL of DMF. This product was not isolated (^{13}C NMR 59.10, 41.47, 40.32, 23.55, 13.90).

Preparation of 2-Methyl-1,3-dithiane/AgNO$_3$ complex (4-Ag). To a solution of 0.0228 g (0.17 mmol) of **4** in 0.3 mL of dry DMF was added 0.0229 g (0.17 mmol) of AgNO$_3$ dissolved in 0.5 mL of DMF. The solution was kept at room temperature in darkness overnight. The colorless crystals (**4-Ag**) were filtered and dried (^{13}C NMR 46.07, 33.86, 27.07, 21.28).

Supporting Information Available: DEPT spectra of **3**, **4**, and their silver complexes (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960993C

---

(8) Martinez, A. G.; Alvarez, R. M.; Fraile, A. G.; Subramanian, L. R. *Synthesis* **1987**, *1*, 49.

(9) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.