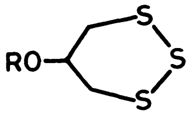
CHEMISTRY LETTERS, pp. 1219-1222, 1978. Published by the Chemical Society of Japan

REACTION AND STEREOCHEMISTRY OF 1,2,3-TRITHIANE RING

Atsushi KATO,* Yohei HASHIMOTO,* Isoji OTSUKA,** and Kazumi NAKATSU**
* Kobe Women's College of Pharmacy, Motoyama-Kitamachi,
Higashinada-Ku, Kobe, Hyogo 658
** Faculty of Science, Kwansei Gakuin University, Uegahara,
Nishinomiya, Hyogo 662

Oxidative desulfurization of 5-hydroxy-1,2,3-trithiane affords *cis*- and *trans*-4-hydroxy-1,2-dithiolane-1-oxide. X-Ray structure determination of 1,2,3-trithian-5-yl N-methylcarbamate reveals that the trithiane ring takes a chair conformation with S-S = 2.040(4) Å(av), S-S-S = 101.5(3)°, and S-S-C = 98.6(3)°(av), and that the side chain places in the equatorial position.

Brugierol and isobrugierol, *cis*- and *trans*-4-hydroxy-1,2-dithiolane-1-oxide, were isolated from a tropical plant, *Bruguiera conjugata* MERR,$^{1)}$ and their structures were established by our spectroscopic and synthetic studies.$^{2)}$ In an attempt to synthesize the brugierols in a different procedure a new compound, 5-hydroxy-1,2,3-trithiane(1), has been obtained. Here we report the reaction concerned with (1) and the X-ray structure of its N-methylcarbamate derivative(2).

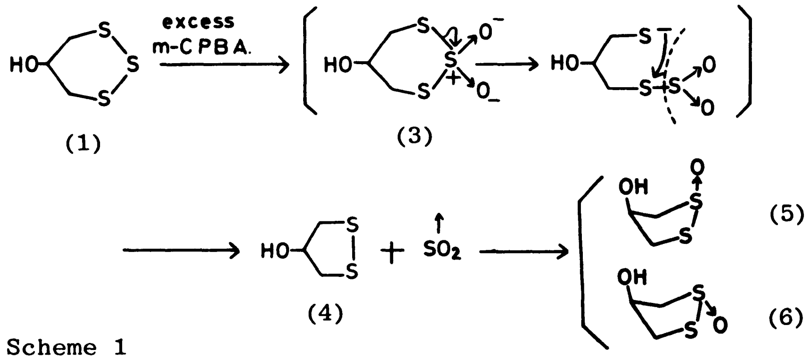


(1) R = H
(2) R = $CONHCH_3$

Glycerol-α,α'-dichlorohydrin, $Cl-CH_2-CH(OH)-CH_2-Cl$(1.6 g, 12 mmol) dissolved in a water-ethanol-chloroform(1:5:6) mixture(30 ml) was poured slowly on sodium tetrasulfide(Na_2S_4)$^{3)}$(2.6 g, 14.7 mmol) at 60 °C. The resulting solution gave pale yellow, needle crystals(1.5 g, 70% yield): mp 60 °C; UV λ_{max}^{MeOH} 263 nm(ε, 3.2);$^{4)}$ IR $\nu_{max}^{CS_2}$ 3595, 3533, 3450 cm^{-1}(OH); Exact MS, M^+ 153.959(153.958 for $C_3H_6OS_3$). These data indicate satisfactorily the presence of *v*-trithiane ring with OH.

Thus three sulfur atoms were introduced simultaneously into glycerol-α,α'-dichlorohydrin to produce (1). The IR spectrum of a CS_2 solution(1 mol dm^{-3}, 0.5 mm path) showed the absorption peaks at 3595, 3533, and 3450 cm^{-1}; these are assignable to the stretching vibrations of the free, the intramolecularly OH...S hydrogen-bonded, and the intermolecularly OH...O hydrogen-bonded OH group, respectively, on the basis of the IR spectra of the solutions with different concentrations.[5)] The IR spectra suggest that the solutions contain several conformers.

In order to synthesize the brugierols from (1) several desulfurizing reagents were examined, in which *m*-chloroperbenzoic acid(*m*-CPBA) was found to be most efficient. The following was a typical reaction: 0.1 g of (1) in 50 ml of chloroform was added dropwise to an excess of *m*-CPBA(0.16 g) in chloroform with stirring. Brugierol(5) and isobrugierol(6) were obtained in a ratio of 5 : 1 (total yield 65%). A possible mechanism of this oxidative desulfurization is illustrated by Scheme 1: the central sulfur atom in the *v*-trithiane ring is oxidized to form sulfone (3), in which an intramolecular nucleophilic rearrangement takes place to give the 1,2-dithiolane ring(4) and SO_2.



Scheme 1

As the crystals of (1) were unsuitable for X-ray work, the structure analysis was carried out on the crystals of 1,2,3-trithian-5-yl N-methylcarbamate(2) to elucidate the stereochemistry of the *v*-trithiane ring. The carbamate derivative (2)(1.0 g) was prepared from (1)(1.0 g) and methylisocyanate(0.6 g) in dry toluene by the usual method. The single crystals were obtained from an acetone solution as colorless transparent plates. Crystal data: orthorhombic; space group $P2_12_12_1$; *a* = 9.089(7), *b* = 21.187(17), *c* = 4.851(4) Å; Z = 4; *D*x = 1.502 g cm^{-3}. A specimen, approximately 0.27 x 0.29 x 0.35 mm^3. was used for X-ray data collection on an automated four-circle diffractometer with graphite-monochromated Mo *K*α radiation (λ = 0.7107 Å). A total of 1287 independent reflections with 2θ less than 50° were measured in the ω-2θ scanning mode, and of these 1116 reflections with $|Fo| > 3\sigma(F)$ were used for the structure determination.

The structure was solved by an application of the symbolic addition method and refined by the block-diagonal least-squares method. Anisotropic thermal vibrations were assumed for the non-hydrogen atoms. All the hydrogen atoms were clearly found from a difference Fourier map and their positional and isotropic thermal parameters were refined. The final conventional *R* index was 0.037. The final atomic coordinates are listed in Table 1. The molecular structure is shown in Fig. 1.

Table 1. Final fractional coordinates with their standard deviations in parentheses.

Atom	*x*	*y*	*z*
S(1)	0.5134(1)	0.39352(5)	0.4262(3)
S(2)	0.3470(1)	0.44968(4)	0.2878(3)
S(3)	0.1663(1)	0.39909(4)	0.4044(2)
C(4)	0.1958(4)	0.3294(2)	0.1911(8)
C(5)	0.3336(4)	0.2928(1)	0.2719(6)
C(6)	0.4794(4)	0.3250(1)	0.2094(9)
O(7)	0.3305(3)	0.2368(1)	0.0962(4)
C(8)	0.3367(3)	0.1797(1)	0.2210(6)
O(9)	0.3438(4)	0.1736(1)	0.4664(5)
N(10)	0.3340(3)	0.1340(1)	0.0365(5)
C(11)	0.3381(4)	0.0670(1)	0.1083(8)

Atom	*x*	*y*	*z*
H^1(C4)	0.210(4)	0.341(1)	-0.010(7)
H^2(C4)	0.106(4)	0.306(1)	0.227(8)
H(C5)	0.327(3)	0.278(1)	0.471(7)
H^1(C6)	0.478(5)	0.338(2)	0.008(9)
H^2(C6)	0.553(4)	0.297(2)	0.254(9)
H(N)	0.342(4)	0.145(2)	-0.095(8)
H^1(C11)	0.243(5)	0.051(2)	0.113(8)
H^2(C11)	0.346(4)	0.057(2)	0.303(8)
H^3(C11)	0.409(4)	0.046(2)	-0.031(9)

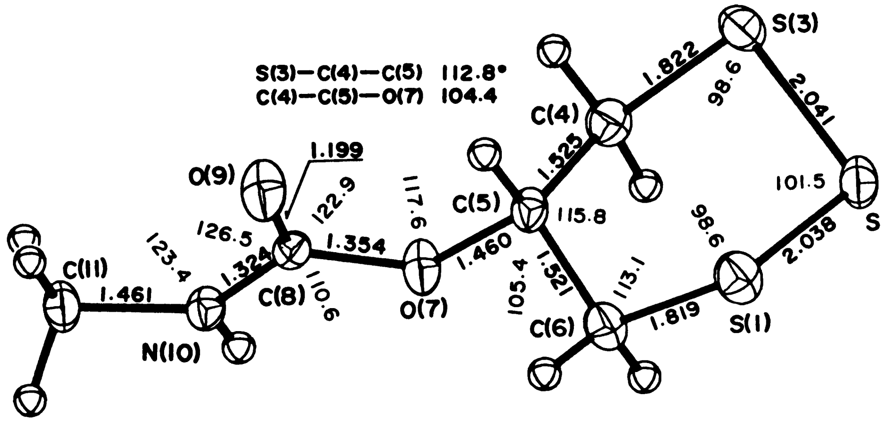


Fig. 1. A perspective view of the molecular structure of 1,2,3-trithian-5-yl N-methylcarbamate with the bond lengths(in Å) and angles(in °). Thermal ellipsoids are drawn at the 20% probability level. The standard deviations are: 0.002 Å for S-S; 0.004 Å for S-C; 0.003-5 Å for C-C, -N, or -O; 0.1° for S-S-S or -C; 0.3° for the other angles. The C-H lengths range between 0.92(3) and 1.03(3) Å, and N(10)-H is 0.68(4) Å.

The molecule has an approximate mirror plane containing S(2), C(5), and non-hydrogen atoms of planar side-chain. The *v*-trithiane ring, having almost strict m(C_s) symmetry, assumes a chair form. The side chain at C(5) is equatorial. The interplanar angle of 64° between the planes S(1)-S(2)-S(3) and S(1)-C(6)... C(4)-S(3) is slightly larger than that of 61° between the latter plane and the plane C(4)-C(5)-C(6). The bond lengths of S-S(av. 2.040 Å) and S-C(av. 1.821 Å) are in close agreement with the values expected for the respective single-bond lengths. The S-S-S angle of 101.5° agrees well with that found in cyclohexasulfur (102°),[6,7] whereas the C(4)-C(5)-C(6) angle of 115.8° is considerably spreaded out from the tetrahedral angle.

The N-methylcarbamate moiety is completely planar, and makes an angle of 87° with the plane S-S-S. The bond lengths and angles in the moiety are in an expected range, except that C(8)-N(10) is somewhat short. The C(5)-H[C(5)] and C(8)-O(9) bonds are in an eclipsed conformation about the C(5)-O(7)-C(8) linkage, the H[C(5)]...O(9) distance of 2.21 Å being considerably shorter than the sum of the van der Waals radii. In the crystals the molecules are linked together by the N(10)-H...O(9) hydrogen bonds[N...O 2.891(4) Å] to form hydrogen-bonded chains along the c axis, the three atoms being almost linear. As far as we know, this is the first structure determination on the compound containing a *v*-trithiane ring.

References and Notes

1) A. Kato and M. Numata, *Tetrahedron Lett.*, 1972, 203.
2) A. Kato and T. Okutani, *Tetrahedron Lett.*, 1972, 2959.
3) Na_2S_4 was prepared from NaSH and sulfur powders.
H. J. Backer and N. Evenhuis, *Recl. Trav. Chim. Pays-Bas*, 56, 174 (1937).
4) The absorption maximum coincides with that ascribed to the *v*-trithiane ring.
L. Schotte, *Ark. Kemi*, 9, 361 (1955).
5) In IR spectra of CS_2 solution at low concentrations(2×10^{-2} mol and 5×10^{-3} mol in 10 mm path), the band at 3450 cm^{-1} disappeared, but two bands at 3595 cm^{-1} and 3533 cm^{-1} remained unchanged.
   a) A. Luttringhaus, S. Kabuss, H. Prinzbach, and F. Langenbucher, *Anal. Chem.*, 653, 195 (1962).
   b) C. H. Eugster and K. Allner, *Helv. Chim Acta.*, 45, 1750 (1962).
6) M. Schmidt, *Angew. Chem.*, 12, 445 (1973).
7) J. Donohue, A. Caron, and E. Goldish, *J. Am. Chem. Soc.*, 83, 3748 (1961).

(Received August 12, 1978)