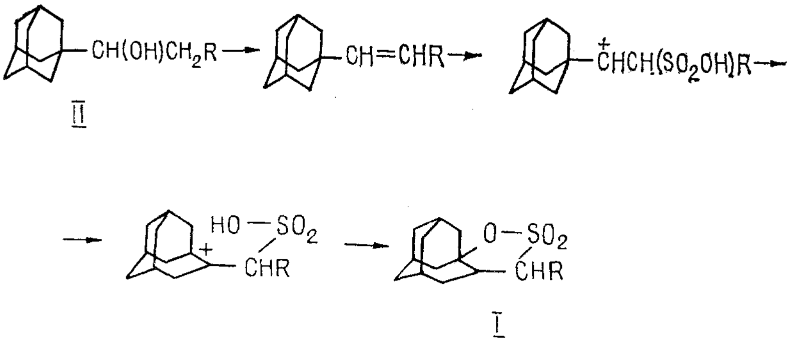
CRYSTAL AND MOLECULAR STRUCTURE OF THE γ-SULTONE OF 1-(3-OXY-4-HOMOADAMANTYL)ETHANE-1-SULFONIC ACID

L. A. Aslanov, V. A. Tafeenko,
V. V. Kovalev, and É. A. Shokova

UDC 548.737:547.77

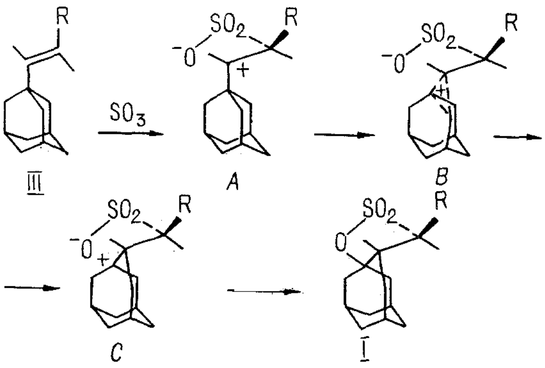
A study was carried out on the crystal and molecular structure of the γ-sultone of 1-(3-oxy-4-homoadamantyl)ethane-1-sulfonic acid. The data obtained supported the general nature of trans cyclization in the synthesis of homoadamantylsultones from 1-(1-adamantyl)-1-alkanols. An interesting feature of this sultone was discovered, namely, the extremely unusual C3,C4,C5,C12,C13 fragment, in which the distance between the electron density maxima of C4 and C12 is only 1.327 Å, while the sum of the bond angles at C4 and C12 is 360°. These features are attributed to the random cocrystallization of different conformers.

In previous work [1], we obtained a new type of framework compounds, namely, the γ-sultones of 1-(3-oxy-4-homoadamantyl)alkane-1-sulfonic acids (I). The starting materials for this synthesis are alkyl(1-adamantyl)carbinols, 1-AdCH(OH)CH_2R (II), which are readily converted in high yield to the indicated sultones by the action of concentrated sulfuric acid in acetic acid or trifluoroacetic acid or their anhydrides. The sultone formation may be represented by the following scheme:



The establishment of the structure of these compounds with a homoadamantane system and a five-membered ring consisting of three carbon atoms, a sulfur atom, and an oxygen atom was unequivocally proven by x-ray diffraction structural analysis [2, 3]. In addition, the x-ray diffraction structural analysis data indicate a stereospecific course for this reaction since only the trans isomer is formed in the case of sultones I (R = isobutyl and neopentyl) (trans position of the hydrogen atoms in the five-membered ring). The mean interatomic distances and bond angles in these sultones have standard values.

The steric specificity of the reaction may be represented as follows:



M. V. Lomonosov Moscow State University. Translated from Zhurnal Strukturnoi Khimii, Vol. 30, No. 6, pp. 79-84, November-December, 1989. Original article submitted August 25, 1987.

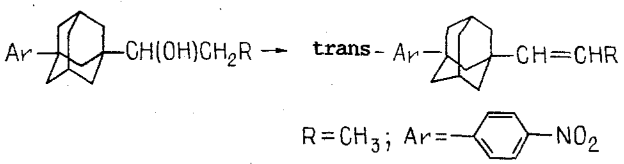
TABLE 1. Positional Parameters of the Atoms in the Structure of the γ-Sultone of 1-(3-Oxy-4-homoadamantyl)ethane-1-sulfonic Acid

Atom	x	y	z	B_j
S1	0,6110(1)	0,0331(1)	0,7213(1)	5,6(3)
O1	0,4805(4)	—0,0294(3)	0,7641(4)	8,2(1)
O2	0,6769(5)	—0,0328(4)	0,6372(4)	9,1(1)
O3	0,6934(6)	0,0683(5)	0,8206(4)	10,5(2)
C1	0,1541(6)	0,0914(5)	0,8909(4)	5,5(1)
C2	0,3084(6)	0,0584(5)	0,8827(5)	5,9(1)
C3	0,3466(5)	0,0351(4)	0,7554(5)	4,6(1)
C4 *	0,3831(6)	0,1368(5)	0,6840(6)	7,3(1)
C5	0,2714(5)	0,2146(4)	0,6531(5)	5,4(1)
C6	0,1230(5)	0,1991(4)	0,6948(5)	5,7(1)
C7	0,0512(6)	0,0998(6)	0,6394(6)	7,1(2)
C8	0,0901(5)	—0,0067(5)	0,7028(5)	5,9(1)
C9	0,2419(6)	—0,0408(5)	0,6898(5)	6,1(1)
C10	0,1168(6)	0,1993(5)	0,8324(6)	6,9(1)
C11	0,0628(5)	0,0008(5)	0,8377(5)	5,9(1)
C12 *	0,5162(6)	0,1448(6)	0,6560(7)	10,5(2)
C13	0,5939(6)	0,2193(5)	0,5845(6)	6,6(2)
H1	0,136(4)	0,107(4)	0,973(4)	5(1)
H2	—0,031(4)	0,017(4)	0,847(4)	6(1)
H3	0,034(5)	—0,070(4)	0,660(4)	7(1)
H4	0,684(4)	0,221(4)	0,583(4)	7(1)
H5	0,034(5)	0,221(4)	0,853(4)	7(1)
H6	0,545(4)	0,280(4)	0,560(5)	7(1)
H7	0,301(4)	0,273(4)	0,561(4)	6(1)
H8	0,186(5)	0,259(5)	0,874(5)	8(1)
H9	0,069(4)	0,096(4)	0,547(5)	7(1)
H10	0,277(5)	0,221(5)	0,564(5)	9(2)
H11	0,078(4)	0,256(4)	0,662(4)	6(1)
H12	0,085(5)	—0,079(4)	0,880(5)	8(1)
H13	0,324(4)	0,002(4)	0,929(4)	6(1)
H14	0,261(5)	—0,053(5)	0,596(5)	9(2)
H15	0,370(5)	0,372(4)	0,423(5)	8(1)
H16	—0,038(5)	0,115(5)	0,630(5)	9(2)
H17	0,572(6)	0,187(5)	0,523(6)	14(2)
H18	0,261(5)	—0,116(5)	0,720(5)	8(1)

---

*The averaged values of the parameters are indicated by an asterisk.

Intermediate olefin (III) in the synthesis of sultones (I) from alcohols (II) should have trans configuration, especially in the case of bulky substituents such as R = isobutyl and neopentyl. Proof for this behavior is found in the exclusive formation of the trans olefin in trifluoroacetic acid at 50°C even when R = CH_3 in the case of a 3-aryl-substituted alcohol:



The structure of the trans isomer was rigorously demonstrated by ^{13}C NMR spectroscopy.

Carbocation (A) formed after the addition of SO_3^+ (or SO_3H^+) to olefin (III) undergoes trans cyclization with rearrangement of the adamantane fragment to give a homoadamantane fragment. The bond in the adamantane fragment in the trans position to the SO_3 (or SO_3H) group is cleaved. This process leads to intermediate (C), in which an oxygen

TABLE 2. Bond Lengths *d* (Å) in the Structure of the γ-Sultone of 1-(3-Oxy-4-homoadamantyl)ethane-1-sulfonic Acid

Bond	*d*	Bond	*d*	Bond	*d*
S1—O1	1,558(4)	C1—C11	1,510(8)	C6—C7	1,509(8)
S1—O2	1,409(5)	C2—C3	1,509(7)	C6—C10	1,536(9)
S1—O3	1,390(5)	C3—C4 *	1,526(8)	C7—C8	1,518(9)
S1—C12	1,772(7)	C3—C9	1,520(7)	C8—C9	1,521(8)
O1—C3	1,500(6)	C4 *—C5	1,455(7)	C8—C11	1,538(8)
C1—C2	1,534(8)	C4 *—C12$^+$	1,327(8)	C12—C13	1,442(9)
C1—C10	1,505(8)	C5—C6	1,526(7)		

*The averaged values of the parameters are indicated by an asterisk.

TABLE 3. Bond Angles ω (deg) in the Structure of the γ-Sultone of 1-(3-Oxy-4-homoadamantyl)ethane-1-sulfonic Acid

Bond angle	ω	Bond angle	ω	Bond angle	ω
O1—S1—O2	108,3(3)	O1—C3—C4 *	104,1(4)	C6—C7—C8	114,0(5)
O1—S1—O3	109,6(3)	O1—C3—C9	104,1(4)	C7—C8—C9	113,6(5)
O1—S1—C12	96,0(3)	C2—C3—C4 *	114,0(4)	C7—C8—C11	110,6(5)
O2—S1—O3	116,8(3)	C2—C3—C9	112,3(4)	C9—C8—C11	108,7(6)
O2—S1—C12	113,9(3)	C4 *—C3—C9	114,2(4)	C3—C9—C8	113,0(5)
O3—S1—C12	109,9(4)	C3—C4 *—C5	118,1(5)	C1—C10—C6	114,0(5)
S1—O1—C3	114,4(4)	C3—C4 *—C12	115,4(5)	C1—C11—C8	107,5(4)
C2—C1—C10	114,2(5)	C5—C4 *—C12	126,4(6)	S1—C12—C4	108,7(5)
C2—C1—C11	108,5(5)	C4 *—C5—C6	121,7(5)	S1—C12—C13	116,5(4)
C10—C1—C11	110,9(5)	C5—C6—C7	112,6(5)	C4—C12—C13	134,6(6)
C1—C2—C3	112,7(5)	C5—C6—C10	112,9(4)		
O1—C3—C2	106,6(4)	C7—C6—C10	111,5(5)		

*The averaged values of the parameters are indicated by an asterisk.

atom of the SO_3 (or SO_3H) group is in the immediate vicinity of the carbocation site as indicated by an examination of models. Such propinquity is favorable for the stabilization of the cation due to its cyclization to exclusively the trans isomer of sultone (I).

In order to determine the scope of this trans cyclization reaction, we studied the crystal and molecular structure of the γ-sultone of 1-(3-oxy-4-homoadamantyl)ethane-1-sulfonic acid (I), which differs from the previously studied by the small size of the radical R. In this case, R = methyl, while R = isobutyl and neopentyl in our previous work [3].

EXPERIMENTAL

A 0.2 × 0.2 × 0.3-mm transparent monocrystal of homoadamantylsultone (I, R = CH_3) was attached to a glass fiber in an arbitrary direction. The preliminary analysis and data collection were carried out on an Enraf-Nonius CAD-4 diffractometer.

The unit cell parameters and orientation matrix for automatic data collection were obtained after least squares refinement of the setting angles of 23 reflections at $15° > \theta > 11°$. The preliminary unit cell parameters were determined by self-induction of 13 reflections for $\theta \sim 8°$.

The refined parameters are as follows: $a = 9.538(2)$, $b = 12.334(2)$, $c = 11.121(2)$ Å, $\beta = 93.13(2)°$, $V = 1295.7$ Å^3, $Z = 4$. The $P2_1/c$ space group was determined from the systematic extinctions $0k0$ ($k = 2n$), $h0l$ ($l = 2n$).

The data collection was carried out at 24 ± 1°C by ω-scanning with a graphite monochromator for $\theta \leq 46°$. A total of 2014 independent reflections were measured, of which 1483 reflections with intensities $\geqslant 3\sigma$ were used for refinement of the positional and temperature parameters of the molecule. The molecular configuration was found by the direct method using the SDP MULTAN program.

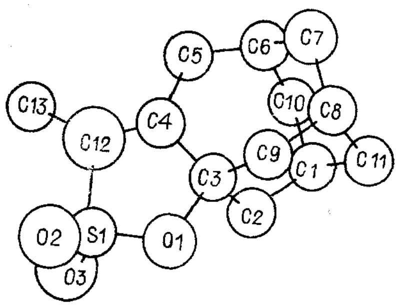


Fig. 1. Numbering of the atoms in the γ-sultone of 1-(3-oxy-4-homoadamantyl)-ethane-1-sulfonic acid.

The nonhydrogen atoms were refined in the isotropic full-matrix approximation to $R = 15.7\%$ and then in the anisotropic approximation to $R = 9.8\%$. Then, the hydrogen atoms were localized in the Fourier difference map and refined isotropically. The final $R_1 = 0.063$ and $R_2 = 0.060$, where

$$R_1 = \sum |F_N - F_H| / \sum F_N, \quad R_2 = \sqrt{\sum (F_N - F_H)^2 / \sum F_N^2}.$$

RESULTS AND DISCUSSION

The numbering of the nonhydrogen atoms is given in Fig. 1. The atomic coordinates are given in Table 1, while the interatomic distances are given in Table 2 and the bond angles are given in Table 3.

The data obtained indicate that this sultone is a trans isomer, i.e., the sultone formation reaction proceeds stereospecifically also when the small methyl substituent (R) is found in the starting alcohol (II).

The product (I, R = CH_3) is a homoadamantane fragment condensed with a five-membered sultone ring fused at the common C3—C4 bond.

Chair conformation is found for both seven-membered rings (*A*: C1, C2, C3, C4, C5, C6, C10 and *B*: C3, C4, C5, C6, C7, C8, C9). The C2, C3, C6, C10 (*1*) and C3, C4, C5, C6 (*2*) fragments are planar in ring *A* (the extrusions of the atoms from the mean-square plane do not exceed 0.01 Å). The C3, C6, C7, C9 (*3*) fragment is planar in ring *C* (the maximum extrusion is 0.003 Å).

The angle between the C1, C2, C10 plane and *1* is 58.7°. The angle between the C1, C2, C10 plane and *2* is 1.9°. The angle between planes *1* and *2* is 56.9°. In ring *B*, the angle between the C7, C8, C9 plane and *3* is 59.03°. The angle between the C7, C8, C9 plane and plane *2* is 2.3°. The angle between planes *2* and *3* is 56.8°.

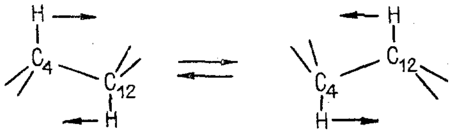
The shortest intermolecular contacts between nonhydrogen atoms do not show anomalies. The coordination unit of the sulfur atom is a somewhat distorted tetrahedron; the largest angle is found for O2—S—O3 (116.8°).

We should note an extremely unusual fragment entailing C3, C4, C5, C12, and C13, in which the distance between the electron density maxima of the C4—C12 bond is very short (1.327 Å) and the sums of the bond angles at C4 and C12 are 360°, i.e., the fragment is planar.

Three alternative explanations are possible for this observation:

1. The C4—C12 is not a single bond but rather a double bond, i.e., an unsaturated sultone is formed. However, this proposal is not in accord with the spectral data. The mass spectrum of (I, R = CH_3) shows a molecular ion peak with m/Z 256, corresponding to a saturated compound. The PMR spectrum has a doublet for the methyl group protons at 1.37 ppm and quartet for the C12H methine group proton at 3.06 ppm. The ^{13}C NMR spectrum lacks signals for double bond carbon atoms.

2. Our experimental data reflect oscillation of the trans hydrogen atoms at C4 and C12. This may be represented schematically as follows:



However, this proposal is rejected as a result of a study of the PMR spectra of sultones deuterated at C4 or C12. Spectra were obtained before and after conversion to the monocrystal. These spectra are invariant while, as a result of the oscillation of the deuterium atoms, they should become identical and correspond to a sultone with an equal deuterium content at C4 and C12.

3. The x-ray diffraction structural analysis data reflect contact conformerism [5] (the coexistence of molecules with two types of conformation of the five-membered ring, namely, C4 and C12 envelopes) such that positions of the atoms of the homoadamantane fragment coincide in the two conformers except for C4 and the methyl group carbon atom C13, while the positions of C4 and C12 and, to some extent, O1, O2, and O3 do not coincide. Thus, the electron density maxima assigned to C4, C12, O1, O2, and O3 have positional parameters, averaged for pairs of these atoms, belonging to two different conformers. This conclusion is indirectly supported by the finding that the major axes of the temperature vibration ellipsoids of the electron density maxima designated C4 and C12 are directed perpendicularly to the plane of the five-membered sultone ring. Thus, the shortened distance between the electron density maxima for C4 and C12 is the result of the low resolution of the electron density maps. Analogous behavior is apparently observed in the case of the complex of cupric chloride with thiophane oxide, in which the length of the C—C single bond in the thiophane ring is 1.317 Å [6]. The crystals studied have domain structure [7] and this explains the doubling of the maxima in the electron density maps.

LITERATURE CITED

1. V. V. Kovalev and É. A. Shokova, Zh. Org. Khim., **24**, No. 4, 738-742 (1988).
2. É. A. Shokova, V. V. Kovalev, L. A. Aslanov, and V. A. Tafeenko, Dokl. Akad. Nauk SSSR, **287**, No. 2, 359-362 (1986).
3. V. A. Tafeenko, L. A. Aslanov, A. E. Prozorovskii, et al., Zh. Strukt. Khim., **28**, No. 2, 107-112 (1987).
4. W. Burkhart and N. Allinger, Molecular Mechanics [Russian translation], Mir, Moscow (1986), pp. 106, 116.
5. P. M. Zorkii and A. E. Razumaeva, Zh. Strukt. Khim., **20**, No. 3, 463-466 (1979).
6. D. D. Swank, C. P. Zandu, and R. D. Willet, Phys. Rev., **B20**, No. 5, 2154-2158 (1979).
7. P. M. Zorkii and Ya. M. Nesterova, Zh. Strukt. Khim., **27**, No. 1, 115-119 (1986).