GEMINAL SYSTEMS. 50.* SOLVOLYSIS OF 1-TOSYLOXY-Δ^2-1,2,3-TRIAZOLINE-5,5-DICARBOXYLATE ESTERS AND THE STRUCTURE OF THE SOLVOLYSIS PRODUCT, O-TOSYL-N-α,α-BIS(ETHOXYCARBONYL)-β-METHOXYETHYL-HYDROXYLAMINE

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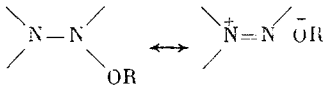
UDC 548.737:543.422.25:542.938:547.791.6:547.238

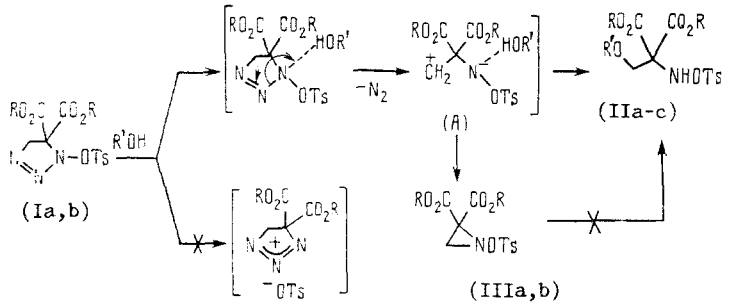
Solvolysis of 1-tosyloxy-Δ^2-1,2,3-triazoline-5,5-dicarboxylic acid esters (1) occurs via elimination of N_2 and leads predominantly to N-β-hydroxylethyl-O-tosylhydroxylamines (II), whose structure was determined unequivocally by x-ray structural analysis. The mechanism of solvolysis of triazolines (I) is discussed, along with the structural characteristics and stabilization factors of the O-tosylhydroxylamine products (II).

Substituted 1-hydroxy-Δ^2-1,2,3-triazoline-5,5-dicarboxylate esters (HTE) under acidolysis, thermolysis, and photolysis conditions in inert solvents are converted primarily into the corresponding N-hydroxyaziridines and isonitrososuccinates via loss of N_2 [2, 3]. On the other hand, the presence of an =N–N–O fragment in these molecules means that HTE can be regarded as unsaturated analogs of N-hydroxyhydrazines, whose most characteristic property is the facility of N–O bond heterolysis, due to weakening of the latter by n–σ*-hyperconjugation [4].



In this regard, therefore, in the present paper we have studied the hydrolysis of HTE (Ia, b), which contains an excellent sulfonyloxy leaving group, in both alcohol and aqueous media, which facilitate bond ionization and also give excellent ion pair solvation.

Methanolysis of HTE (Ia, b) was carried out under mild conditions at 20°C, hydrolysis of (Ib) in a heterophase system (ether/water) in the presence of an acidic additive, BF_3. In all cases N_2 evolution was observed and the corresponding O-tosylhydroxylamines (IIa-c) were formed, along with N-tosyloxyaziridines (IIIa, b), which were also isolated.



R = R′ = Me (a); R = Et, R′ = Me (b); R′ = Et, R′ = H (c).

*For previous communication, see [1].

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1820-1827, August, 1990. Original article submitted October 10, 1989.

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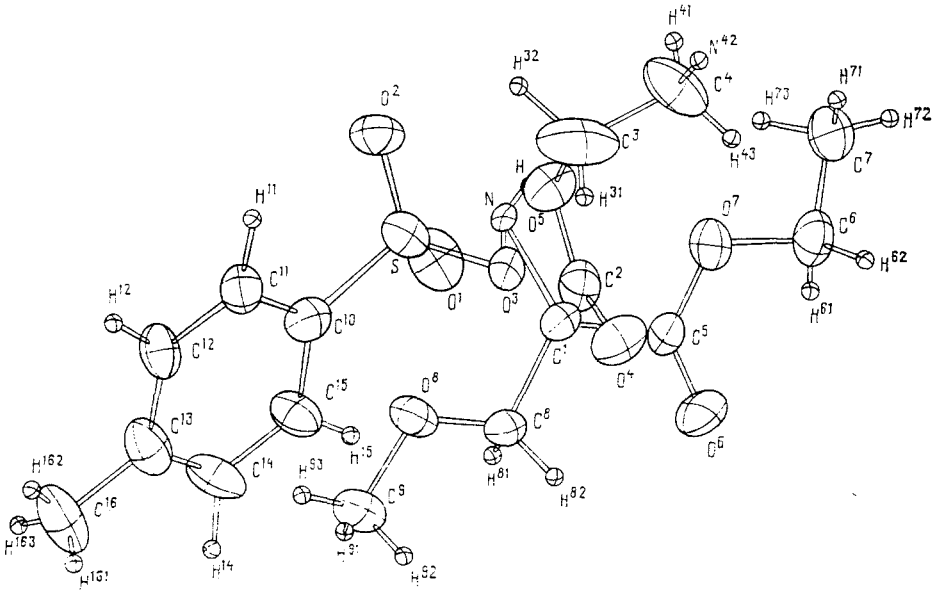


Fig. 1. Overall molecular form of (IIb) with 30% thermal vibration ellipsoids for the nonhydrogen atoms.

Independent experiments revealed that compounds (IIIa, b) were stable under the conditions used for the solvolysis of HTE (Ia, b), and, furthermore, that (IIIa) was not converted to (IIa) even after 24-h reflux in a mixture of MeOH–CF_3CO_2H [at a mole ratio (IIIa)/ MeOH/CF_3CO_2H = 1:10:1]. It followed, therefore, that (IIa-c) are the solvolysis products of (Ia, b), and their formation most probably occurs via reaction of zwitterion (A) with solvent R'OH.

Elimination of N_2 from HTE is thus the most favorable process both in inert as well as protic solvents. The role of protic solvents probably involves acceleration of the elimination process, similar to acid catalysis [2], as well as interception and binding of the intermediate (A). Our results also indicate that the n-donor reactivity of the azo group is insufficient to promote N–O bond cleavage in HTE with a lower activation energy than N_2 elimination. Comparison of the first ionization potentials of the compounds listed below also demonstrates the lower n-donor activity of an azo group compared to amino and hydrazo groups: 3,3,5,5-tetramethyl-1-pyrazoline 8.63; trimethylamine 8.12; 1,2-dimethylpyrazolidine 7.78 eV [5].

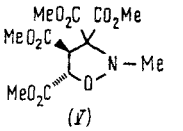
Compounds (IIa-c) are stable at 20°C in the crystallization state and in solution, in contrast to the behavior of previously described O-sulfonylhydroxylamines and their N-alkyl derivatives, whose instability can be attributed to the high anionic activity of the sulfonyloxy group [6]. For this reason, isomeric structures can be proposed for (IIa-c), corresponding to the well known and more stable N-tosylhydroxylamines (IVa-c) (see below). Formation of the latter can be postulated in terms of O → N migration of the tosyl group in the HTE starting materials (Ia, b) or their products (IIa-c), similar to the rearrangement of 1-acyloxybenztriazoles or O-acylhydroxylamines [7]. The IR and PMR spectral data (cf. Experimental Section) for these compounds, however, do not allow us to distinguish or select between these alternative structures (IIa-c) versus (IVa-c). Using dynamic ^{13}C NMR spectroscopy in CD_2Cl_2 solution based on the coalescence temperature (T_c) for the signals due to the nonequivalent carbonyl group ^{13}C nuclei, we were able to measure the barrier to topomerization of (IIc), $\Delta G^{\neq}$ = 11.3 kcal/mole, T_c = 217 K, $\Delta\nu_c$ = 7.3 Hz. This energy barrier is, however, similar in value to the energy barrier for N atom inversion in hydroxylamines, which do not contain π-acceptor substituents, as well as to the rotation barrier for the N–O bond in hydroxylamines containing these types of substituents [8].

Assignment of the structures of the solvolysis products of HTE (Ia, b) as O-tosylhydroxylamines (IIa-c) was therefore established unequivocally via x-ray structural analysis of (IIb) (Figs. 1, 2; Table 1). Some interesting structural properties of the hydroxylamine fragment were discovered: The degree of pyramidality* of the N atom was found to be maximum

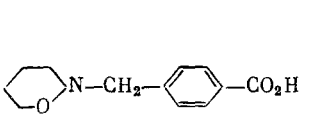
*The degree of pyramidality of the N atom can be conveniently expressed in terms of the sum of the bond angles around the N atom ($\Sigma\theta_i$); the lower $\Sigma\theta_i$, the greater the degree of pyramidality.

compared against other known cyclic and acyclic hydroxylamines (excluding three- and four-membered rings) and the N–O bond length was found to be significantly elongated (Table 2).

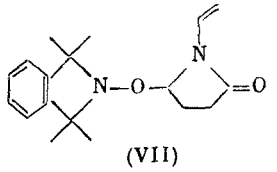
This first property can be explained in terms of reduced steric interaction between the H atom and the other substituents attached to the N atom. In fact, although the O^3NC^1 bond angle in (IIb) is similar to the ONC angles in isoxazolidine (V) and perhydrooxazine (VI), the O^3NH and C^1NH angles in (IIb) are substantially smaller than the other angles around the N atom in (V) or (VI). In the sterically hindered N-hydroxypyrrolidine (VII), on the other hand, the pyramid associated with the hydroxylamine N atom exhibits the greatest degree of planarity (Table 2). Furthermore, the increase in the degree of pyramidality around the N atom in (IIb) can also be attributed to enhanced s-character for the nonbonding n orbital on the N atom, due to the greater electronegativity of the TsO tosyloxy group compared to RO and OH in the other hydroxylamines.



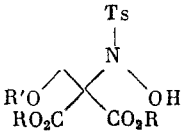
(I)



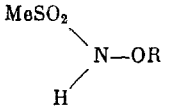
(VI)



(VII)



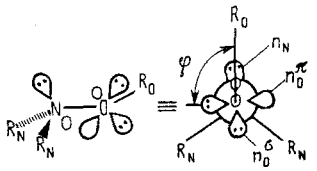
(IVa-c)



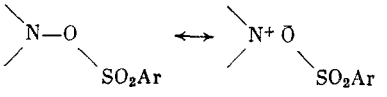
(VIIIa, b)

R = H (a), Me (b).

As can be seen from the data in Table 2, the N–O bond length in hydroxylamines (V)-(VIIIa, b) can be considered as a function of the torsional angle (φ) between the n orbital on the N atom and the n^{π} orbitals on the O atom. Apparently, the greater the shielding (eclipsing) of these n-orbitals (lower φ angle), the greater their destabilizing effect, and the longer the corresponding N–O bond length will be.



The O-tosylhydroxylamine derivative (IIb) does not follow this general trend however. The factor responsible for this (aberration) is that in the case of (IIb) the n_N–n_O interaction is not the decisive or determining influence on the N–O bond length; instead, it is the presence on the O atom of the strongly electron withdrawing SO_2Ar group, which extends or weakens the N–O bond [13].



We should point out also the unusually short distance between the N and O^5 atoms, 2.526(2) Å, which is significantly smaller than the sum of the van der Waals radii for these atoms (2.8 Å [14]). The distances between the N atom and the other atoms, however, are not shorter than the sums of the corresponding radii. The orientation of the N–O bond is close to the plane of the ester group $O^4C^2O^5$ (Figs. 1, 2), which leads us to conclude the presence of intramolecular donor–acceptor interaction between n_O and σ* (N–O); this may also contribute to the observed elongation of the N–O bond.

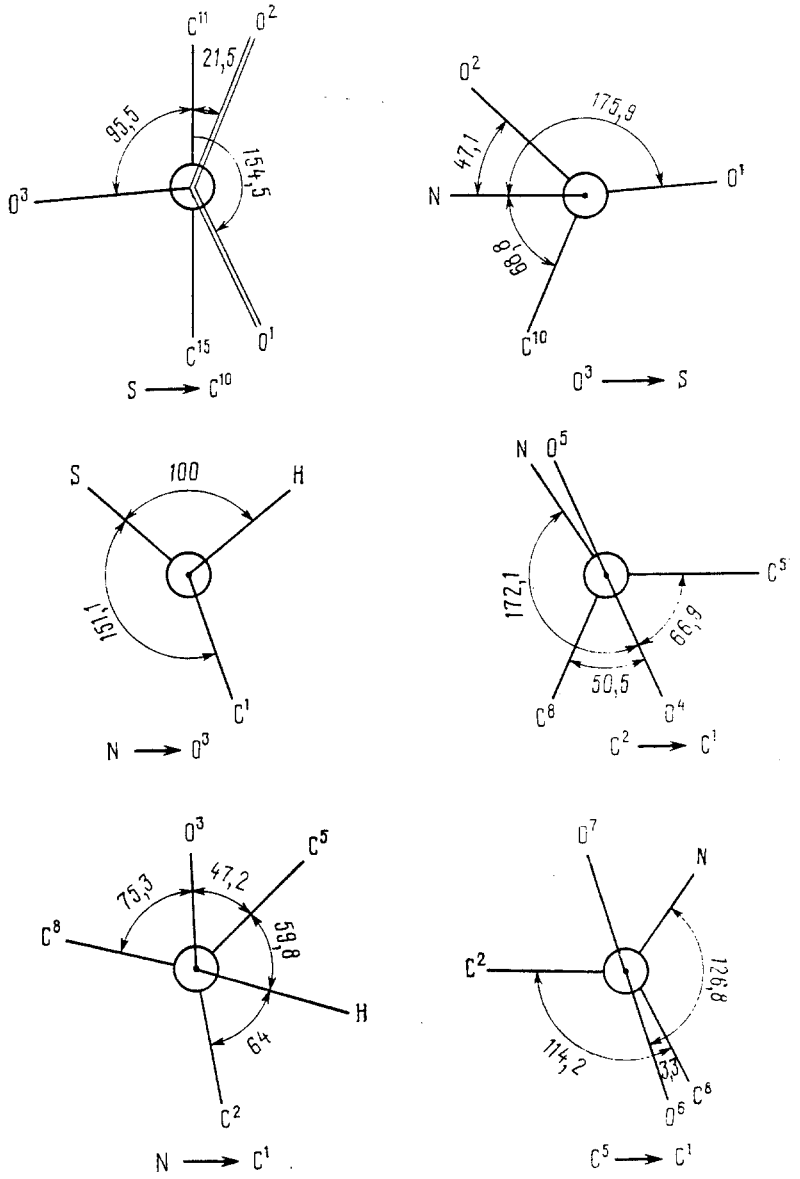
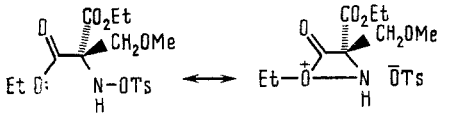


Fig. 2. Principal torsional angles in molecule (IIb) in the crystalline state.



The existence of attraction between the N and O^5 atoms is also supported qualitatively by the inequality of $\angle NC^1C^2 = 109.2(1)° < \angle NC^1C^5 = 112.5(1)°$; this would be expected to be reversed in the case of repulsion between $N...O^5$.

The bond lengths (±0.002 Å) and bond angles (±0.2°) in the O-tosyl group and ester functional group are as follows: $S{=}O_{av}$ 1.42, $S{-}O^1$ 1.596, S–C 1.750, $>C{=}O_{av}$ 1.19, $O{-}C_{sp^2}$ 1.315, $O{-}C_{sp^3av}$ 1.41 Å, ∠O–S=O 110.5, ∠O=S=O 120.7, ∠O–S–C 106.1, ∠O–S=O 125.0°. In the crystalline state in (IIb) the sulfonyl and ester groups are arranged in a trans orientation relative to the $N{-}C^1$ bond. This conformation, in all probability, reflects the propensity or driving force to reduce the overall dipole moment of the molecule (IIb), which is composed primarily of the vectors for the SO_2 and CO_2Et groups.*

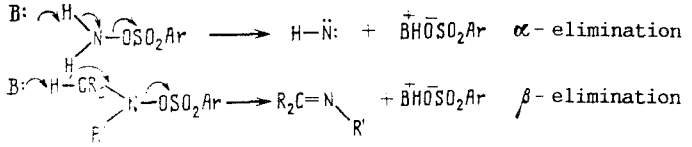
*According to the data in [15] the dipole moment vector for cis-HCOOH forms an angle of ≈15° with the >C=O bond; in the SO_2 group the direction of $\vec{\mu}$ bisects the OSO angle.

TABLE 1. Atomic Coordinates (×10⁴) in the Molecular Structure of (IIb)

Atom	X	Y	Z
S	7710(1)	4872(6)	307(1)
N	8619(1)	3993(1)	298(2)
O^1	7075(2)	5132(1)	−899(3)
O^2	8890(1)	5205(1)	982(3)
O^3	7885(1)	4307(1)	−705(2)
O^4	8892(2)	2505(1)	151(3)
O^5	10152(1)	3398(1)	884(2)
O^6	7193(2)	3041(1)	−2985(2)
O^7	9180(1)	3589(1)	−2899(2)
O^8	7013(1)	3061(1)	2260(2)
C^1	8169(2)	3367(1)	−264(3)
C^2	9100(2)	3033(1)	296(3)
C^3	11188(2)	3144(1)	1249(4)
C^4	12009(3)	3209(2)	−243(5)
C^5	8098(2)	3308(1)	−2208(3)
C^6	9278(3)	3601(1)	−4756(3)
C^7	10327(3)	4112(2)	−5223(4)
C^8	6887(2)	3064(1)	491(3)
C^9	5860(2)	2783(1)	3076(3)
C^{10}	6718(2)	4583(1)	2018(3)
C^{11}	7214(2)	4540(1)	3583(3)
C^{12}	6420(3)	4348(1)	4951(4)
C^{13}	5132(3)	4192(1)	4748(4)
C^{14}	4661(2)	4239(1)	3168(4)
C^{15}	5430(2)	4432(1)	1778(4)
C^{16}	4249(4)	3984(2)	6218(5)
H	9343(20)	4123(9)	−140(18)
H^{11}	8158(28)	4663(13)	3711(40)
H^{12}	6857(33)	4314(15)	6127(41)
H^{14}	3709(28)	4086(13)	2969(42)
H^{15}	5079(24)	4478(12)	544(37)
H^{31}	10820(28)	2734(13)	1527(40)
H^{32}	11673(28)	3421(13)	2222(44)
H^{41}	12267(32)	3591(15)	−602(37)
H^{42}	12649(34)	2988(15)	−45(44)
H^{43}	11525(49)	2927(22)	−1103(63)
H^{61}	9460(27)	3198(12)	−5085(36)
H^{62}	8465(26)	3656(12)	−5145(36)
H^{71}	10099(43)	4481(21)	−4570(65)
H^{72}	10477(34)	4230(16)	−6429(53)
H^{73}	11022(27)	3956(13)	−4781(46)
H^{81}	6226(22)	3279(10)	124(30)
H^{82}	6635(19)	2635(9)	37(26)
H^{91}	5270(27)	3026(13)	2748(41)
H^{92}	5671(24)	2356(11)	2761(35)
H^{93}	6055(29)	2775(14)	4288(44)
H^{161}	3997(40)	3614(20)	6369(40)
H^{162}	4690(28)	3968(13)	7071(44)
H^{163}	3780(31)	4280(14)	6424(36)

Intermolecular H-bonding of the type N–H...O^2 was also detected for (IIb) in the crystalline state, with the following parameters N...O 3.043, H...O 2.24 Å, ∠N–H...O 124°, ∠S=O...H 140°.

Decomposition of O-sulfonylhydroxylamines can occur via either an α- or β-elimination mechanism* [6].

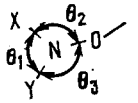


The greater stability of (IIa-c) compared to other O-sulfonylhydroxylamines can therefore be attributed to the absence of an α-proton in the N-alkyl substituent and to steric hindrance and electrostatic "shielding"† of the N atom, which prevent attack by base at the proton attached to the N atom.

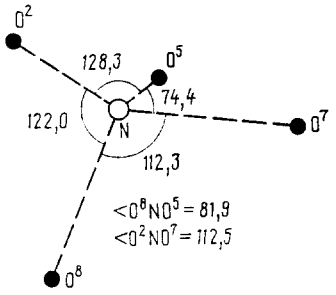
*The role of the base is generally fulfilled by a second hydroxylamine molecule.

†In the crystalline state the N atom is surrounded by a "coat" of negative charged O atoms: the N...O^2, O^8, and O^7 distances are 2.806, 2.845, and 2.816(2) Å, respectively.

TABLE 2. Structural Parameters of Hydroxylamines (IIb), (III), (V), (VI), (VIIa, b)



Compound	θ1	θ2	θ3	∑θi	rN–O, Å	∠φ, deg
	deg					
X=H, Y=C< (II b)	105(1)	102(1)	104,5(2)	311,5	1,471	65.5
X=CH3, Y=C< (V) [9]	115,1(2)	103,7(2)	103,3(2)	322,9	1,466(3)	16,5
X=CH2Ar, Y=CH2 (VI) [10]	113,7(3)	104,8(3)	108,0(3)	327	1,456(6)	37,6
X=Y=CMe2 (VII) [11]	110(1)	109,9(3)	108,8(3)	328,9	1,439(3)	77,5
X=H, Y=SO2Me (VIIIa) [12]	109(3)	101(3)	109,8(2)	319,8	1,437(3)	74,7
X=H, Y=SO2Me (VIIIb) [12]	108(2)	108(2)	108,9(1)	324,9	1,432(2)	81



EXPERIMENTAL

NMR spectra were measured on a Jeol JNN-C-60HL (^{1}H, 60 MHz) spectrometer and on a Bruker WH-80 SY spectrometer (^{1}H, 80 MHz; ^{13}C, 20.15 MHz) versus TMS; IR spectra were recorded on a UR-20 spectrophotometer using KBr pellets. HTE were prepared by reactions of O-tosyloximamesoxalic acid with CH_2N_2 according to [2].

1-Tosyloxy-5,5-bis(ethoxycarbonyl)-Δ^2-1,2,3-triazoline (Ib). Yield 97%, mp 54°C (dec). Found, %: C 46.80; H 4.97; N 10.84. $C_{15}H_{19}N_3O_7$. Calculated, %: C 46.85; H 4.97; N 10.90. PMR spectrum (80 MHz, Freon-21, δ, ppm): 1.21 t ($MeCH_2$, ^3J = 7 Hz), 2.35 (MeC), 4.17 q ($MeCH_2$), 4.71 (CH_2).

Methanolysis of (Ia, b) (general method). A solution of 10 mmoles HTE in 50 ml absolute MeOH was stirred for 5 h at 20°C. After solvent removal the solvolysis products were separated by chromatography in silica gel (λ 40/100 μ, eluent $CHCl_3$, MeOH) and recrystallized.

O-Tosyl-N-α,α-bis(methoxycarbonyl)-β-methoxyethylhydroxylamine (IIa). Eluted with MeOH, 56% yield, mp 109-110°C (from ether). Found, %: C 46.64; H 5.44; N 3.92. $C_{14}H_{19}NO_8S$. Calculated, %: C 46.53; H 5.30; N 3.88. PMR spectrum (60 MHz, $CDCl_3$, δ, ppm): 2.35 (MeC), 3.15 (MeO), 3.41 (MeO_2C), 3.65 (CH_2), 6.78 (NH), 7.43 d and 7.71 d (C_6H_4, J_{AB} = 8.1 Hz). IR spectrum (ν, cm^{-1}): 1720, 1740 (C=O), 3260 (NH).

O-Tosyl-N-α,α-bis(ethoxycarbonyl)-β-methoxyethylhydroxylamine (IIb). Eluted with MeOH, yield 61%, mp 73-74°C (EtOH). Found, %: C 49.23; H 5.59; N 3.83. $C_{16}H_{23}NO_8S$. Calculated, %: C 49.34; H 5.96; N 3.60. PMR spectrum (60 MHz, CD_3OD, δ, ppm): 1.14 t ($MeCH_2$, ^3J = 7

Hz), 2.40 (MeC), 3.10 (MeO), 3.65 (CH_2), 4.09 q ($MeCH_2$), 7.39 d and 7.81 d (C_6H_4, J = 8 Hz). IR spectrum (ν, cm^{-1}): 1720, 1745 (C=O), 3260 (NH).

X-Ray Structural Analysis. Colorless transparent crystals of (IIb) were obtained from ethanol, exhibited monoclinic syngony. Principal crystallographic data: $C_{16}H_{23}NO_8S$, M = 389.477, a = 11.132(2), b = 23.297(4), c = 7.865(1) Å, γ = 106.4(1)°, V = 1956.64 $Å^3$, Z = 4, d_{calc} = 1.33 g/cm^3, $P2_1/b$ space group. The intensities of 2811 reflections with $I \geq 2\sigma(I)$ were measured using a DAR-UM diffractometer. The structure was solved by direct methods using the "Roentgen-75" program and was refined by least squares with anisotropic approximations for the nonhydrogen atoms and isotropic approximations for the H atoms, to a final R value of 0.049. The molecular projection or figure was obtained using the ELLIDS program (for references to the program, see [9]). The atomic coordinates are listed in Table 1.

1-Tosyloxy-2,2-bis(methoxycarbonyl)aziridine (IIIa). Eluted with $CHCl_3$, yield 24%, mp 90-91°C (from i-PrOH) (Cf. [2]).

1-Tosyloxy-2,2-bis(ethoxycarbonyl)aziridine (IIIb). Eluted with $CHCl_3$, 21% yield, mp 71°C (from i-PrOH). Found, %: C 50.64; H 5.12; N 4.08. $C_{15}H_{19}NO_7S$. Calculated, %: C 50.41; H 5.35; N 3.92. PMR spectrum (80 MHz, C_6D_6, δ, ppm): 0.73 t and 0.93 t ($MeCH_2$, ^3J = 7 Hz), 2.04 d and 2.74 d (CH_2, J_{AB} = 4.0 Hz), 1.80 (MeC), 3.71 q and 3.95 q ($MeCH_2$). IR spectrum: ν 1729 cm^{-1} (C=O).

Hydrolysis of (Ib). To a solution of 7.7 g (20 mmoles) (Ib) in 50 ml ether with stirring was added 20 ml water and 5 drops $BF_3 \cdot Et_2O$; stirring was continued for 3 h at 20°C. After 24 h the resulting precipitate was removed by filtration, washed with ether, and recrystallized from i-PrOH. Yield 3.15 g (42%) of O-tosyl-N-α,α-bis(ethoxycarbonyl)-β-hydroxyethylhydroxylamine (IIc), mp 92°C. Found, %: C 48.12; H 5.77; N 3.70. $C_{15}H_{21}NO_8S$. Calculated, %: C 47.99; H 5.64; N 3.73. NMR spectrum (CD_2Cl_2, δ, ppm): ^1H, 80 MHz, 1.20 t ($MeCH_2$, ^3J = 7 Hz), 2.40 (MePh), 2.71 (OH), 4.03 (CH_2), 4.11 q ($MeCH_2$), 7.10 (NH), 7.25 d and 7.68 d (C_6H_4, J_{AB} = 8.0 Hz). $^{13}C\{H\}$, 14 ($MeCH_2$), 21.8 (MePh), 60.7 (CH_2), 74.7 (C_α), 129.4, 130.4, 131.6, 146.7 (C_6H_4), 165.7 (C=O). IR spectrum (ν, cm^{-1}): 1750, 1760 (C=O), 3200 (NH), 3560 (OH).

The ether layer was separated, dried over $MgSO_4$, and the ether evaporated under vacuum. After recrystallization of the residue from i-PrOH, 1.36 g (19%) of N-tosyloxyaziridine (IIIb) was obtained, which was identical to an authentic sample with respect to its mp and PMR spectrum.

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