Specord UV-vis spectrophotometer at 20°C over the range 330-760 nm. The concentration of the solutions was ~10^{-5} M. The specific electrical conductivities were determined from data obtained from measurements made with direct current. The measurements were made with pellets pressed under a pressure of 10^8 Pa, to which silver electrodes were applied by vacuum deposition. The configuration of the electrodes and the methods used for the measurements provided for the elimination of surface currents [6]. Prior to the measurements, the samples were heat treated at 420°K in vacuo (10^{-3} Pa) for 4 h.

Compounds I-XVII were obtained by the methods in [1]. Dichlorozirconium phthalocyanine was synthesized by a known method [8].

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SYNTHESIS, STRUCTURE, AND TRANSFORMATIONS OF 1-AZA-3-OXA-7-THIABICYCLO[3.4.0]NONAN-2-ONE

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UDC 547.869.2:548.312.5:
542.942

1-Aza-3-oxa-7-thiabicyclo[3.4.0]nonan-2-one was obtained by reduction of 3,4-dimethoxycarbonyltetrahydro-1,4-thiazine. The reduction of this product with lithium aluminum hydride led to 3-hydroxymethyl-4-methyltetrahydro-1,4-thiazine. The molecular and crystal structures of 1-aza-3-oxa-7-thiabicyclo[3.4.0]nonan-2-one were investigated by x-ray diffraction analysis.

It has been previously shown that the reduction with sodium borohydride of diesters I and II, obtained by alkylation of methyl tetrahydro-1,4-thiazine-3-carboxylate with methyl chloroacetate and methyl acrylate, leads to the formation of the corresponding diols III and IV [1] (see scheme on following page).

However, the reduction of diester V, obtained from methyl tetrahydro-1,4-thiazine-3-carboxylate and methyl chlorocarbonate, with sodium borohydride under similar conditions did not lead to the formation of the corresponding diol. The PMR spectrum of the only product (VIII) did not contain the broad singlets that are characteristic for the protons of hydroxy groups. In addition, the IR spectrum of VIII does not contain bands of stretching vibrations

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1280-1285, September, 1986. Original article submitted July 3, 1985.

0009-3122/86/2209-1039$12.50

TABLE 1. PMR Spectra of the Synthesized Compounds

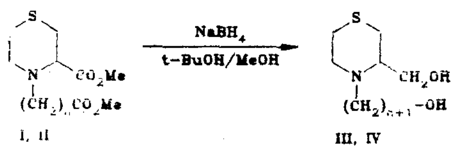
Compound	Chemical shifts, δ, ppm							Remaining singnals
	2-H (*a*)	2-H (*e*)	3-H	5-H (*a*)	5-H (*e*)	6-H (*a*)	6-H (*e*)	
VI	2,92	2,64	4,19 (*e*)	3,20 (br)	4,51 (br)	2,72	2,44	2,20 (OH); 3,72 (OCH_3); 3,98 (**CH_2**OH)
VIII	2,65	2,56	3,89 (*a*)	3,13	4,15	2,73	2,48	3,94 ($H_a—CH_2O$); 4,45 ($H_e—CH_2O$)
XI	2,69	2,54	2,75 (*a*)	2,73	3,16	2,72	2,51	2,30 (OH); 2,38 ($N—CH_3$); 3,55 ($H_e—CH_2O$); 3,85 ($H_a—CH_2O$)

TABLE 2. Spin-Spin Coupling Constants (J, Hz) of the Synthesized Compounds

Compound	*2a2e*	*3a2a*	*3e2a*	*5a5e*	*6a6e*	*6a5a*	*6a5e*	*6e5a*	*6e5e*	*7a7e*
VI	14,0	4,0	3,0		13,3	12,5		3,0	2,3	—
VIII	13,0	10,1	3,7	13,3	13,5	12,1	3,1	3,5	2,4	10,2
XI	12,5	10,3	4,2	12,7	13,8	11,2	2,6	3,2	3,0	—

TABLE 3. ^{13}C NMR Spectra of the Synthesized Compounds

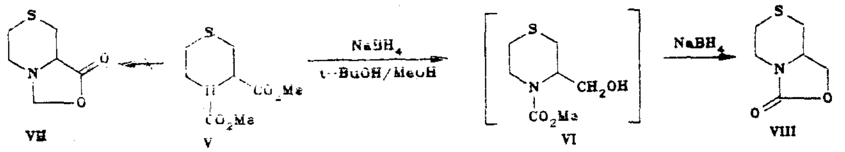
Compound	Chemical shifts, δ, ppm					
	$C_{(2)}$	$C_{(3)}$	$C_{(5)}$	$C_{(6)}$	C=O	remaining signals
VI	26,8	40,5	51,6	27,1	156,4	52,5 (OCH_3); 59,5 (OCH_2)
VIII	25,9	54,2	42,3	30,5	155,9	67,2 (OCH_2)
XI	25,9	63,6	55,7	28,2	—	42,4 ($N—CH_3$); 62,5 (OCH_2)



I, III n=1; II, IV n=2

of hydroxy groups (3200-3300 cm^{-1}). The mass spectrum of VIII is characterized by the presence of a most intense molecular ion with mass 159; this indicates that the reaction product has a cyclic structure.

The presence of a band at 1735 cm^{-1} in the IR spectrum and a signal of protons of a CH_2 group, which resonates in the form of a doublet of doublets with a constant of spin-spin coupling with the proton of the tetrahydrothiazine ring of 10.7 Hz, made it possible to choose in favor of bicyclic urethane VIII rather than the isomeric lactone VII.



The different pathways in the reduction of I and II as compared with V can evidently be explained as follows: the ester group attached to the nitrogen atom has reduced reactivity as compared with the ester group attached to the carbon atom. One may therefore assume the formation of intermediate VI, which, under the reduction conditions, tends to undergo intramolecular cyclization to give bicyclic VIII. Since we were unable to detect the formation of intermediate VI in the reaction, this compound was synthesized from 3-hydroxymethyltetrahydro-1,4-thiazine (IX) [2] and methyl chlorocarbonate.

The experiment showed that VI readily undergoes cyclization to bicyclic urethane VIII under the conditions of reduction with sodium borohydride.

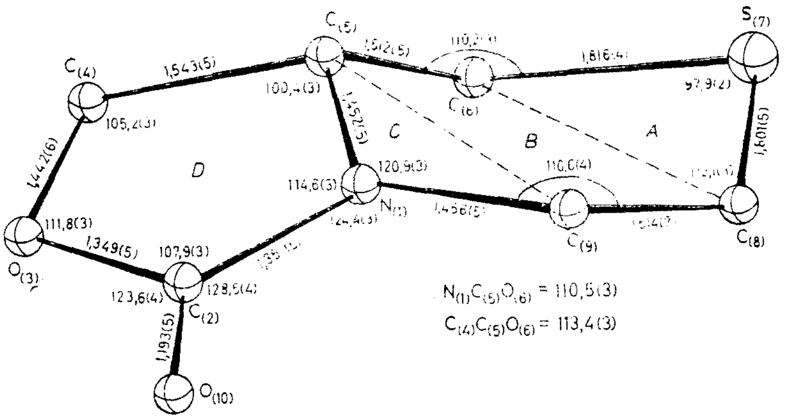


Fig. 1. Designations of the atoms and geometry of the VIII molecule.

TABLE 4. Equations of the Root-Mean-Square (rms) Planes of the Planar Fragments of the VIII Molecule and Deviations of the Atoms from Them

Plane	Atoms of the plane	Deviation of the atoms from the plane, Å	Normal Eq. of the plane Ax + By + Cz − D = 0			
			A	B	C	D
A	$S_{(7)}$ $C_{(8)}$ $C_{(6)}$	— — —	−0,1322	0,6854	−0,7160	1,6245
B	$C_{(5)}$ $C_{(6)}$ $C_{(8)}$ $C_{(9)}$ $S_{(7)}$* $N_{(1)}$*	−0,014(4) 0,013(4) −0,013(5) 0,014(5) −0,926(1) 0,574(3)	0,5316	0.2031	−0,7875	0,0368
C	$C_{(5)}$ $N_{(1)}$ $C_{(9)}$	— — —	−0,1556	0,7031	−0,6938	2,8034
D	$N_{(1)}$ $C_{(2)}$ $O_{(3)}$ $C_{(4)}$ $C_{(5)}$ $O_{(10)}$*	−0,001(3) 0,010(4) −0,015(3) 0,012(5) −0,007(4) 0,010(3)	−0,1447	0,7014	−0,6979	2,7576

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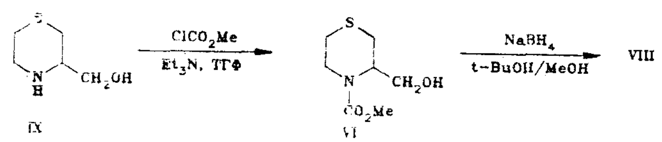
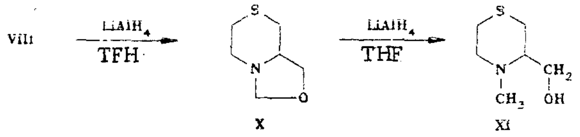
*These atoms were not taken into account in the calculation of the rms planes.



As we assumed, bicyclic VIII does not undergo further reduction by sodium borohydride. An investigation of its chemical properties showed that it is stable in both acidic and alkaline media, as well as under the influence of amines. Prolonged refluxing of VIII with 1,1-dimethylhydrazine does not give rise to any changes in the starting bicyclic compound. Further investigation of its reactivity showed that under the influence of lithium aluminum hydride the urethane ring opens to give 3-hydroxymethyl-4-methyltetrahydro-1,4-thiazine (XI). A compound, which was isolated from the reaction mixture by preparative gas chromatography and was identified as 1-aza-3-oxa-7-thiabicyclo[3.3.0]nonane (X), is formed along with ring-opening product XI when a twofold excess of lithium aluminum hydride is used in the reduction. It was demonstrated that the physicochemical characteristics of X coincide completely with the constants presented in [2].

TABLE 5. Coordinates of the Atoms [$\cdot 10^4$ ($\cdot 10^3$ for the H Atoms)] in the VII Structure

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
$N_{(1)}$	8320(4)	1237(3)	3962(3)	$H_{(1)}C_{(4)}$	1074(5)	377(4)	471(4)
$C_{(2)}$	9771(5)	940(4)	3411(4)	$H_{(2)}C_{(4)}$	1124(7)	255(5)	596(5)
$C_{(3)}$	11104(3)	1755(3)	4031(3)	$H_{(5)}$	852(5)	189(4)	609(4)
$C_{(4)}$	10532(5)	2691(5)	5010(6)	$H_{(1)}C_{(6)}$	767(5)	407(4)	365(4)
$C_{(5)}$	8573(5)	2322(4)	5000(4)	$H_{(2)}C_{(6)}$	759(5)	429(4)	539(4)
$C_{(6)}$	7340(5)	3558(4)	4609(5)	$H_{(1)}C_{(8)}$	537(6)	223(4)	218(4)
$S_{(7)}$	5063(1)	2965(1)	4390(1)	$H_{(2)}C_{(8)}$	413(5)	121(4)	289(4)
$C_{(8)}$	5194(6)	1635(6)	3124(5)	$H_{(1)}C_{(9)}$	663(6)	−18(5)	288(4)
$C_{(9)}$	6617(5)	548(5)	3581(5)	$H_{(2)}C_{(9)}$	617(6)	−3(5)	440(4)
$O_{(10)}$	9932(4)	98(3)	2553(3)				



The only reaction product is XI when a fourfold or greater excess of $LiAlH_4$ is used. Compound X is evidently an intermediate in the reduction of bicyclic urethane VIII. This is confirmed by the fact that the reduction of X led to XI in quantitative yield.

The structures of VI, VIII, and XI were proved by ^{13}C and ^1H NMR spectroscopy. The spectral parameters are presented in Tables 1-3. The chemical shifts (CS) of the ^{13}C atoms can be assigned unambiguously on the basis of a study of the ^{13}C NMR spectra under conditions of complete spin decoupling and without suppression of spin-spin coupling with the protons, as well as by comparison of the experimental data with the values calculated via an additive scheme. Thus, the appearance of a signal corresponding to the $C_{(3)}$ atom in the form of a doublet due to coupling with the 3-H proton and NCH_3 and OCH_3 signals in the form of quartets is characteristic.

The structures and conformations of the compounds obtained can also be established on the basis of a study of the chemical shifts and spin-spin coupling constants (SSCC) in the PMR spectra (Tables 1 and 2). In the case of VIII we were able to perform a complete analysis of the spectrum and measure all of the SSCC. The SSCC of the ring protons [$J_{2,3}$ = 10.1 Hz (aa)] in VIII corresponds to a ring conformation in which the 3-H proton is axially oriented, whereas in the PMR spectrum of VI the 3-H proton appears in the form of a broad multiplet with characteristic SSCC $J_{2,3}$ = 4.0 Hz (ae), which corresponds to an equatorial orientation of the 3-H proton and an axial orientation of the CH_2OH substituent. Broadening of the signals in the PMR spectrum corresponding to the protons in the 3 and 5 positions is characteristic for VI; this is probably due to retarded rotation of the $COOCH_3$ group about the N—C bond. Broadening of the signals hindered an accurate analysis of all of the SSCC for this compound.

To establish the molecular-crystal structure of VIII we subjected it to an x-ray diffraction study. The geometry of the molecule with designation of the atoms and planes is presented in Fig. 1.

The molecule is a condensed bicyclic system consisting of a six-membered tetrahydrothiazine ring with a chair form (see planes A, B, and C in Fig. 1) and a planar (±0.014 Å) oxazole ring D. The coefficients of the equations of the root-mean-square (rms) planes of the planar fragments of the molecule and the deviations of the atoms from them are presented in Table 4.

The $N_{(1)}$ and $S_{(7)}$ atoms deviate 0.574(3) Å and 0.925(1) Å, respectively, to opposite sides from plane B. The dihedral angles between plane A and plane B and between plane C and plane B are 51.2° and 53.2°, respectively. Within the limits of the experimental error, plane C is coplanar with plane D.

The average lengths of the C—S bonds in the tetrahydrothiazine ring [1.809(5) Å] and the C—C bonds [1.523(6) Å] are close to their standard values [3]. Due to conjugation, the $C_{(2)}$—$N_{(1)}$ bond [1.351(5) Å] is shortened as compared with a single bond; the other two C—N bonds have the standard values. There are three types of C—O bonds in the molecule: the

$C_{(4)}—O_{(3)}$ bond [1.442(6) Å] is a single bond, the $C_{(2)}—O_{(3)}$ bond [1.349(5) Å] is a sesquibond, and the $C_{(2)}—O_{(10)}$ bond [1.193(5) Å] is a double bond.

The molecules are packed in the crystal at distances no less than the sums of the van der Waals radii of the corresponding atoms [4].

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were obtained with Bruker WH-90 (90 MHz) and Bruker WM-360 (360 MHz) spectrometers with tetramethylsilane (^1H NMR) and cyclohexane (^{13}C NMR) as the internal standards. The mass spectra were recorded with an MS-50 AEI spectrometer (at an ionizing voltage of 70 eV). The IR spectra of the pure compounds or suspensions in mineral oil were obtained with UR-20 spectrometer. The x-ray diffraction analysis was performed with a Syntex diffractometer. Preparative gas chromatography was carried out with a Pye-Unicam 105 chromatograph with columns packed with an SE-30 stationary phase. The course of the reactions was monitored by means of gas-liquid chromatography (GLC); with a CHROM-5 chromatograph with 2.5-m and 1.5-m columns packed with an SE-30 stationary phase (10%) applied to Chromaton AW; and thin-layer chromatography (TLC) (with Silufol UV-254 plates, hexane—ethyl acetate (2:1) as the eluent, and detection in UV light or by development in iodine vapors).

X-Ray Diffraction Analysis of 1-Aza-3-oxa-7-thiabicyclo[3.4.0]nonan-2-one (VIII). Single crystals of VIII were grown from ethyl acetate, had the composition $C_6H_9NO_2S$, were monoclinic, and had the following parameters: a = 7.682(4) Å, b = 9.423(5) Å, c = 10.054(3) Å, $\beta = 99.24(3)°$, V = 718.3 Å^3, M = 159.2, $d_{calc} = 1.47$ g-cm^{-3}, $\mu(CuK_\alpha) = 33.9$ cm^{-1}, Z = 4, space group $P2_1/c$, and $F_{000} = 336$. The intensities of 1203 independent reflections were measured with a Syntex $P2_1$ four-circle diffractometer (CuK_α emission, graphite monochromator) by the $\theta/2\theta$ scanning method up to $2\theta_{max} = 150°$. In the calculation we used 957 reflections with $J > 2\sigma_J$. The structure was decoded by the direct method by means of the MULTAN program of the XTL system and was refined by the method of least squares within a total-matrix anisotropic approximation. Absorption was disregarded. The hydrogen atoms, the coordinates of which were calculated geometrically, were refined isotropically. The maximum standard deviations of the angular and linear characteristics were, respectively, 0.4° and 0.007 Å (disregarding the hydrogen atoms). The final value of the divergence factor was 0.041. The coordinates of the atoms are presented in Table 5.*

3-Hydroxymethyl-4-methoxycarbonyltetrahydro-1,4-thiazine (VI). A 1.2-g (12 mmole) sample of methyl chlorocarbonate was added with stirring at 20°C to a solution of 1.33 g (10 mmole) of IX and 2.1 ml (15 mmole) of triethylamine in 40 ml of dry tetrahydrofuran (THF), after which the mixture was stirred for 1 h, the resulting precipitate was removed by filtration, and the filtrate was evaporated at reduced pressure. The residue was distilled under a high vacuum [120°C (10^{-2} mm Hg)] to give 1.6 g (84% of the theoretical yield) of a viscous oil. Found, %: C 43.9, H 6.9, N 7.4. $C_{17}H_{13}NO_3S$. Calculated, %: C 44.0, H 6.8, N 7.3. IR spectrum: $\nu_{C=O}$ 1750, ν_{OH} 3220-3300 cm^{-1}. Mass spectrum, m/z (relative intensity), %: 174 (M − OH) (3.3), 160 (M−OMe) (20), (M−MeOH) (53.3), 144 (15.2), 130 (9.5), 128 (7.6), 126 (12.4), 118 (5.7), 117 (9.5), 116 (100), 115 (5.7), 114 (7.6), 113 (26.6), 112 (13.3), 103 (5.7), 102 (13.6), 101 (16.7), 100 (16.7).

1-Aza-3-oxa-7-thiabicyclo[3.4.0]nonan-2-one (VIII). A 20-ml sample of methanol was added with stirring in the course of 30 min to a solution of 5.47 g (25 mmole) of 3,4-dimethoxycarbonyltetrahydro-1,4-thiazine and 3.8 g (100 mmole) of sodium borohydride in 100 ml of tert-butyl alcohol, after which the mixture was refluxed for 3 h and then cooled to 20°C. The excess sodium borohydride was decomposed with 5 ml of water, the solvent was removed in vacuo, and the residue was treated with chloroform. The chloroform solution was dried over anhydrous sodium sulfate, after which the chloroform was evaporated. The residue was recrystallized from ethyl acetate to give 2.8 g (70%) of colorless crystals with mp 96-97°C (from ethyl acetate).

An identical compound was obtained in 97% yield by reduction of 1.91 g (10 mmole) of VI with 0.95 g (25 mmole) of sodium borohydride under the conditions presented above. IR spectrum (Nujol): $\nu_{C=O}$ 1735, ν_{OH} 3200-3300 cm^{-1}. Mass spectrum, m/z (relative intensity), %: 159 (M, 100), 144 (20), 126 (23.1), 113 (46.2), 101 (23.1), 100 (15.4). Found, %: C 45.2, H 5.6, N 9.0. $C_6H_9NO_2S$. Calculated, %: C 45.3, H 5.7, N 8.8.

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*The anisotropic temperature factors can be obtained from the authors.

3-Hydroxymethyl-4-methyltetrahydro-1,4-thiazine (XI). A solution of 1.59 g (10 mmole) of VIII in 10 ml of dry tetrahydrofuran (THF) was added dropwise with stirring in a nitrogen atomosphere to a suspension of 0.57 g (15 mmole) of lithium aluminum hydride in 25 ml of dry THF, after which the temperature of the reaction mixture was raised to 40-45°C, and stirring was continued at this temperature for 2 h. After the starting VIII had vanished (determined by monitoring by TLC with ethyl acetate as the eluent), the mixture was cooled, and 1 ml of water was added slowly with stirring to the mixture. The resulting mixture was poured into a chromatographic column and leached out with 100 ml of THF, after which the solvent was removed in vacuo. According to analytical GLC, the mixture consisted of two components, which were isolated by preparative GLC.

The first substance was identical to X [2] with respect to its physicochemical characteristics, and the second was identified as XI.

Only thiazine XI in the form of a viscous oil was formed in 94% yield when a threefold excess of $LiAlH_4$ was used in this reaction. IR spectrum: ν_{OH} 3200-3324 cm^{-1}. Mass spectrum, m/z (relative intensity), %: 147 (M) (8.3), 130 (M − OH) (18.6), 129 (M − H_2O) (12.1), 115 (M − CH_3OH) (20.7), 103 (5.8), 102 (100), 101 (16.8), 100 (4.0). Found, %: C 48.9, H 8.9, N 9.7. $C_6H_{13}NOS$. Calculated, %: C 49.0, H 8.8, N 9.5.

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