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Ozonolysis of (1R,*cis*)-4,7,7-Trimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one

O. S. Kukovinets, V. G. Kasradze, F. Z. Galin, L. V. Spirikhin, R. A. Zainullin, M. I. Kislitsyn, M. I. Abdullin, R. V. Kunakova, and G. A. Tolstikov

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, Bashkortostan, 450054 Russia
Bashkirskii State University, Institute of Service Technology of Ufa, Ufa, Bashkortostan, 450054 Russia

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Abstract—The structure of peroxides forming in ozonolysis of enololactone and their further transformations are determined by the structure of the initial substrate and by effect of solvent used for ozonolysis.

The structure of peroxide ozonolysis products is known to depend on the structure of initial substrate and on the solvent for ozonolysis [1–3]. The investigation of ozonolysis of (1*R*,*cis*)-4,7,7-trimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (I) originating from lactonization of ketocaronic acid, potential synthon for preparation of acid components from pyrethroid series [4, 5], furnished an opportunity to establish the structure of key peroxy compounds and to presume the possible transformation routes thereof into the final reaction products. The consideration of probable reaction pathways allows a conclusion that the transformation of zwitter-ions **IIa, b** arising from ozonolysis of compound **I** in various solvents (CH_2Cl_2, ROH, CH_3CN) depends on the structure of the initial substrate (enololactone **I**), and on the character of solvent used in the ozonolysis process.

In the peroxy product obtained by ozonolysis of compound **I** in CD_2Cl_2 at −78°C the ^1H and ^{13}C NMR spectra registered at −78°C revealed the presence of an aldehyde group (δ_H 9.64, δ_C 199.23 ppm). Besides this in the ^{13}C spectrum appeared a singlet at 164.40 ppm that we assigned to the carbonyl of the acetoxy group, and a signal at 105.01 ppm characteristic of a carbon linked to two oxygens.

We believe that during ozonation in CH_2Cl_2 of enololactone **I** which is a cyclic vinyl ester the primarily arising zwitter-ions **IIa, b** undergo an intramolecular rearrangement into secondary bipolar ions **IIIa, b** (Scheme 1). It is also presumable that the peroxide **IIIa, b** is stabilized by formation of a dimer **IIIc** or a dioxirane **IIId**. However the styrene addition to the peroxides just after the ozonation did not afford styrene epoxide in the reaction products. In keeping with the published data [6] it shows fairly reliably that in the reaction mixture dioxirane **IIId** is not present.

At the isolation of peroxides obtained by ozonolysis of enololactone **I** in CH_2Cl_2 by means of solvent evaporation in a vacuum at 0°C further transformations of bipolar ion **IIIa, b** also occur intramolecularly without formation of **IIIc** dimer, for the molecular weight of the products measured by the isopiestic method corresponds to monomer.

The stability of zwitter-ion **IIIa, b** is uncommon for carbonyl oxides, and it may be understood taking into account the capability of halohydrocarbon solvents to stabilize this structure by trimolecular mechanism (see structure A) described by Swain and Eddy [7].

The reduction of peroxides obtained by enololactone **I** ozonolysis in CH_2Cl_2 with zinc in acetic acid or with hydrogen in the presence of Lindlar catalyst affords formerly described [4] mixed anhydride, and its yield is considerably higher when the process is carried out without isolation of peroxides **IIIa, b**. Mixed anhydride **IV** is hydrolyzed via intermediate formation of formylcarboxylic acid (**V**) into 4α-hydroxy-6,6-dimethyl-3-oxabicyclo-[3.1.0]hexan-2-one (**VI**) (Scheme 1).

The stabilization of intermediate zwitter-ion **IIa, b** at enololactone **I** ozonolysis in alcohols occurs by another route. Unexpectedly the peroxy product does not contain alkoxy group that is usually regarded [1] as taking part in ozonides stabilization in the form of alkoxyhydroperoxides. It was demonstrated by ^1H and ^{13}C that two compounds arise with spectral characteristics well consistent with structures **VII** and **VIII**. They apparently result from the attack of zwitter-ions

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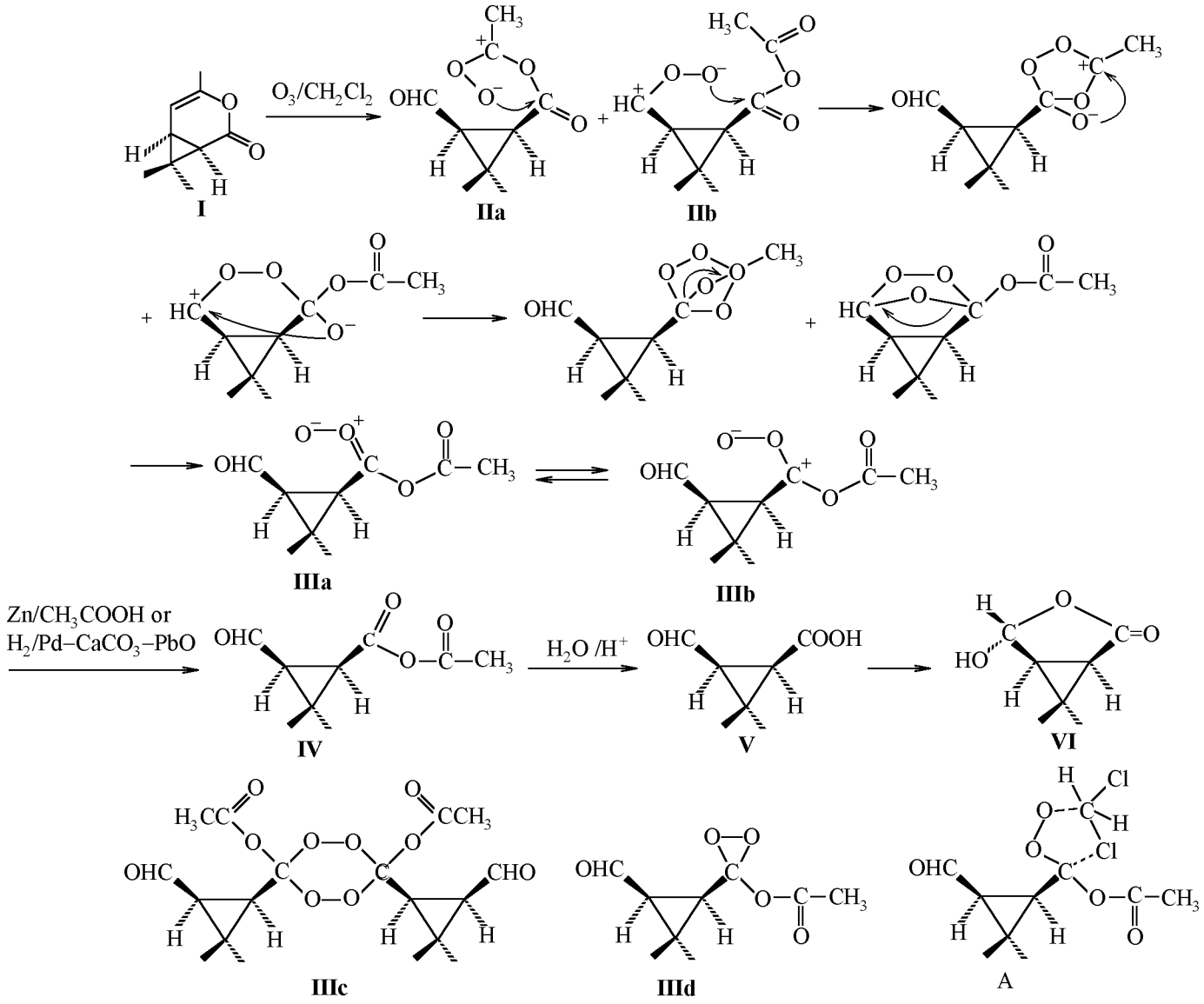
Scheme 1.



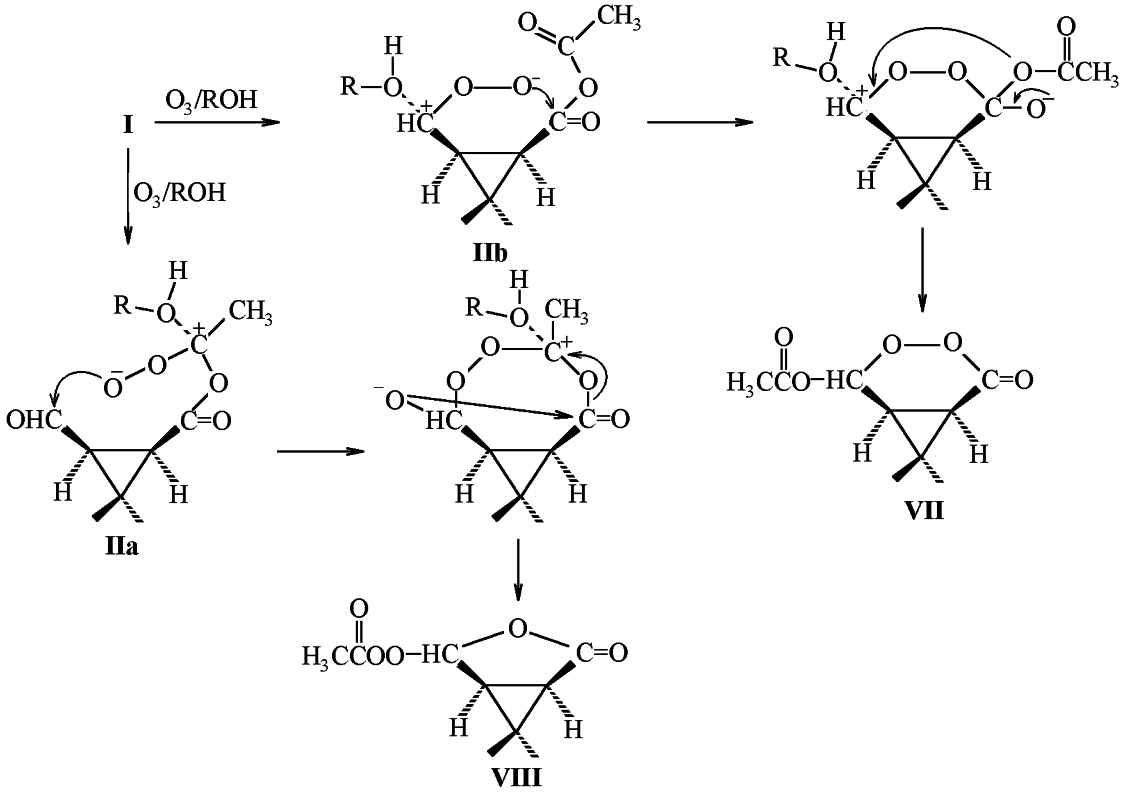
IIa, b stabilized by alcohol on the C=O group of the second fragment of the molecule (Scheme 2).

The formation of monomeric peroxides **VII** and **VIII** was confirmed by measuring their molecular weight by isopiestic method (220) and by the content of active oxygen therein (8.16%). In the ^{1}H NMR spectrum appear signals of two kinds of methyl groups (2.19 and 2.20 ppm) from acetate fragments with intensity ratio 1:2 indicating that one of the peroxides, presumable **VIII**, is present in double amount. The protons linked to two oxygens give rise to peaks at 4.88 and 5.05 respectively. In the ^{13}C NMR spectrum of the ozonides are present four carboxy group signals at 168.17, 168.31, 168.72 and 169.09 ppm, two peaks of carbon atoms attached to two oxygens at 104.80 and 105.22 ppm, and a double set of the signals from the other parts of the molecules.

Since in the ^{13}C NMR spectrum of compounds **VII** and **VIII** after storage in the methanol solution for 24 h alongside the other peaks appear signals at 174.93 and 174.78 ppm corresponding to free carboxy groups it is possible that in the alcoholic solution occur tautomeric transformations shown in Scheme 3.

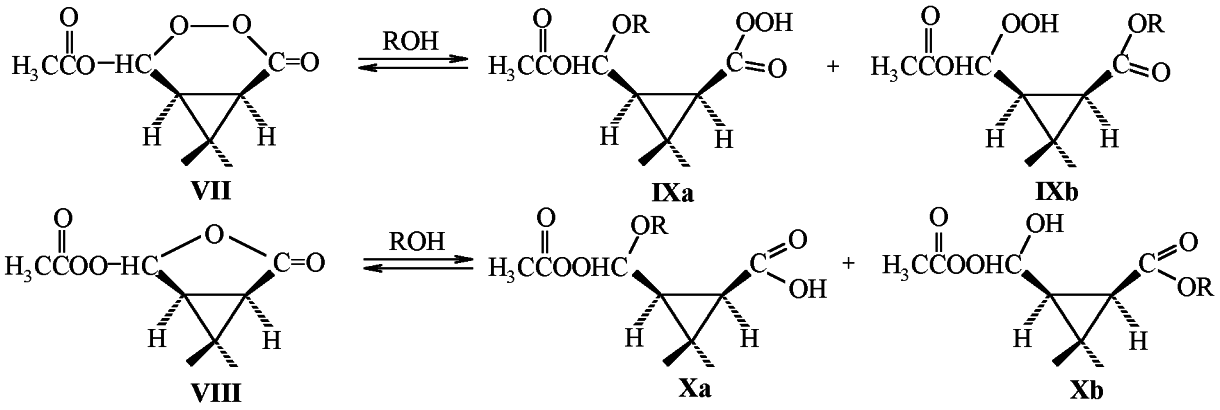
The reduction with dimethyl sulfide of the overall peroxy product obtained by ozonolysis in alcohols in every case afforded virtually a single product, 4α-alk-

Scheme 2.



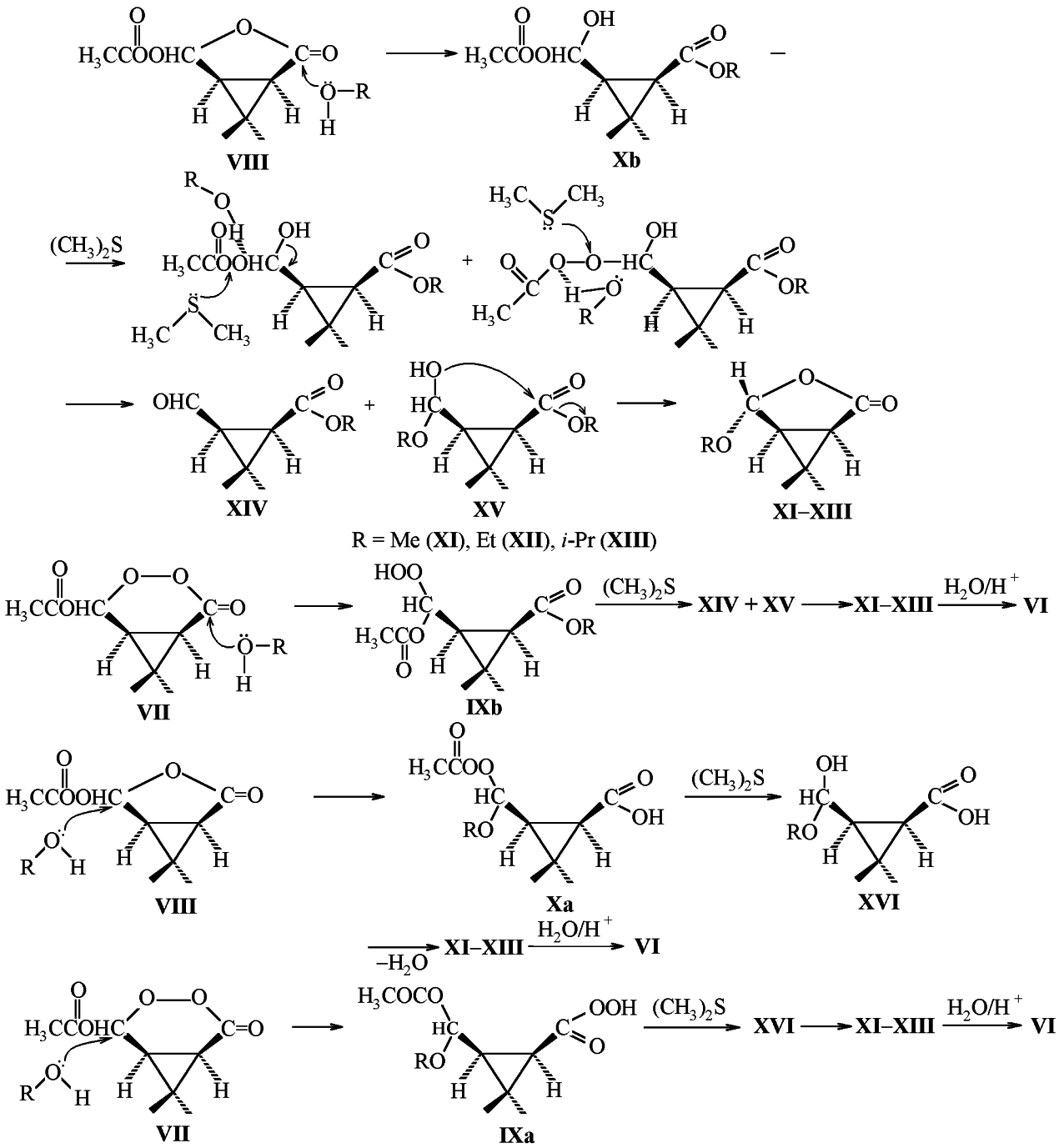
R = Me, Et, *i*-Pr.

Scheme 3.



oxy-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (**XI**–**XIII**). Apparently the reduction starts with alcohol attack on the atoms C^2 or C^5 in bicycle **VII** or atoms C^2, C^4 in oxolane **VIII** (Scheme 4). The reaction proceeds through acyclic forms **IXa, IXb, Xa, Xb, XIV**–**XVI** for in the IR and NMR spectra after separation of crystalline alkoxylactone **XI**–**XIII** are observed signals corresponding to aldehyde, ester, and carboxy groups that might appear only if in the mixture are present nonlactone monocyclic forms **XIV, IXb, XVI**. In the IR spectrum alongside the absorption band of the carbonyl group from the five-membered lactone (1780 cm^{-1}) are seen vibration bands of aldehyde (1725 cm^{-1}), ester (1750 cm^{-1}), and carboxy (1695 cm^{-1}) groups respectively. The carbon atoms of the above carbonyl groups in the ^{13}C NMR spectra appear as peaks at ~173, 201, 180, and 177 ppm.

Scheme 4.



The formation of alkoxy derivatives **XI–XIII** is confirmed by the signals of alkoxy groups in the ^{1}H and ^{13}C NMR spectra (3.60 and 56.30; 4.20 and 52.06; 3.92 and 71.93 ppm for OCH_3, OCH_2, and OCH moieties respectively), and by the signals of carbon atoms linked to two oxygen atoms (102.46, 105.14, and 100.34 ppm respectively). The chemical shift of the carbonyl carbon signal (~173 ppm) virtually is not affected by the change of alkyl in the alkoxy group.

The decrease in the yield of crystalline methoxylactone **XI** at reduction with thiourea of peroxy products obtained by ozonolysis of enololactone **I** in methanol shows that the transformation (**XIV**) → (**XI**)

occurs faster, and the cyclization (**XV**) → (**XI**) is a slower process. This fact is consistent with published data on considerable, sometimes prevailing formation of acetals at reduction of peroxides with thiourea [8], especially as at standing from the mother liquor additionally precipitate crystals of methoxylactone **XI**. The hydrolysis of alkoxylactones obtained in the presence of oxalic or sulfuric acid results in previously described [5] hydroxylactone **VI**.

The primary peroxy product of enololactone **I** ozonolysis in CH_3CN is identical in its spectral characteristics to compound **IIIa, b**. However it is less stable in CH_3CN than in CH_2Cl_2, and it undergoes at storage spontaneous decomposition via labile intermediate compounds to furnish acid **V** that in its turn transforms into lactol **VI**. The latter process is so slow that even in a long time the yield of compound **VI** does not exceed 30%, although its formation is reliably confirmed by appearance in the overall ^{13}C NMR spectrum of signals at 173.02 (C=O) and 105.75 ppm (O–C–O). Lactol **VI** was also isolated from the reaction mixture as individual compound by crystallization.

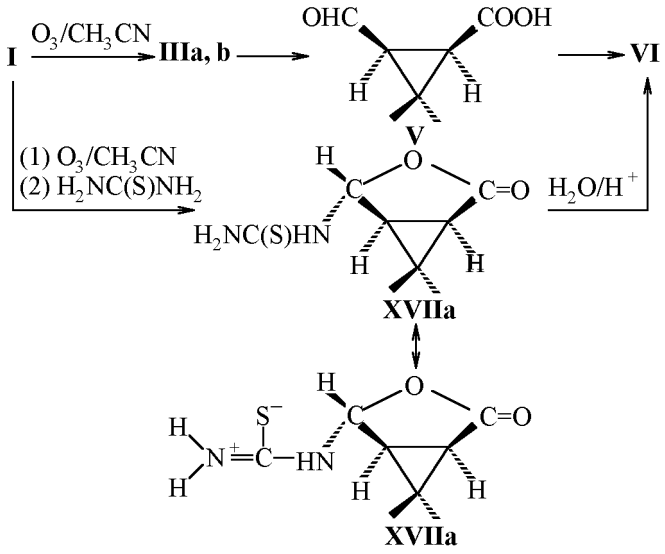
Lower stability of peroxide **IIIa, b** in CH_3CN than in CH_2Cl_2 may be ascribed to less efficient complexing of nitrile dipole with bipolar ion as compared with CH_2Cl_2 [9].

The reduction of the peroxy ozonolysis product obtained with CH_3CN with thiourea just after finish of ozonolysis afford a complex mixture of compounds. From the mixture was isolated by column chromatography on SiO_2 thiourea derivative **XVIIa**. Formation of the latter is proved by the presence in the ^1H NMR spectrum alongside the signals of gem-dimethyl groups at 1.10 and 1.17 ppm and doublets of the protons from the cyclopropane ring (δ, ppm: 1.90 d and 1.97 d, *J* 6.1 Hz) also peaks corresponding to the protons from NH_2 group (5.25 and 7.6 ppm), NH (9.86 ppm) and those attached to C^4 carbon (5.82 ppm) of bicyclic compound **XVIIa**. The unexpected splitting of the signals of terminal protons attached to thioamide nitrogen apparently is caused by the contribution from **XVIIb** structure arising in tautomeric transformations of compounds **XVIIa** and **XVIIb** [10]. This assumption is additionally supported by changing intensity ratio of NH_2 protons at registering the NMR spectrum at 55°C. The downfield shift of the proton linked to the other nitrogen atom (9.86 ppm) is due presumably to the deshielding effect of the neighboring strained bicyclic fragment of the molecule. The ^{13}C NMR spectrum of compound **XIIa** contains signals corresponding to groups H_2NCS (181.27 ppm), C=O (173.65 ppm), NCO (82.81 ppm) and to the other carbon atoms of the molecular skeleton. Analysis of mass spectra revealed the most characteristic for thioamides fragment ions [11], namely those of *m/z* 167 $[M–SH]^+$, 60 $[H_2NCS]^+$. Analytically determined content of sulfur and nitrogen corresponds to the assumed structure **XVIIa**.

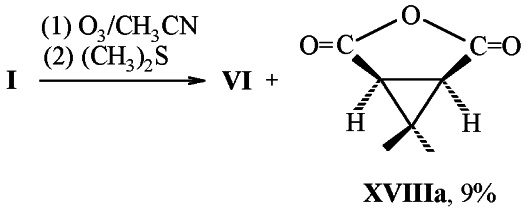
All the reduced bicyclic products **VI, XI–XIII, XVIIa** possess α-structure. This is confirmed by the lack of coupling between protons attached to carbons C^4 and C^5 that are situated at an angle close to 90°. This is possible only at β-position of the proton attached to C^4.

Since in the ^1H NMR spectrum of the overall product obtained by reduction of peroxides with thiourea are present signals corresponding to aldehyde (9.84 ppm) and carboxy (11.20 ppm) groups, the formation of monocyclic compound **V** at reduction is possible, especially as at acid hydrolysis of the overall product the yield of bicyclic lactol is fairly high (82%).

Scheme 5.



Scheme 6.



XVIIIa, 9%

The reduction with dimethyl sulfide of enololactone **I** ozonolysis products obtained in CH_3CN also affords a mixture of compounds. From this mixture by column chromatography alongside the expected hydroxylactone **VI** was isolated in 9% yield 3-oxabicyclo[3.1.0]hexane-2,4-dione (**XVIII**).

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from thin films or mulls in mineral oil. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 at operating frequencies 300.13 and 75.25 MHz respectively, solvent $CDCl_3$, internal reference TMS. GLC analyses were performed on chromatograph Chrom-5 equipped with glass columns 1200×3 mm, stationary phase 5% SE-30 on Chromaton N-AW-DMCS (0.16–0.20 mm), oven temperature 50–300°C programmed at a rate 12 deg min^{-1}, carrier gas helium. Mass spectra were measured on MKh-1303 instrument, ionization temperature 200°C, ionizing electrons energy 80 eV. The optical rotation was registered on polarimeter Perkin–Elmer-141.

Ozonolysis of (1*R*,*cis*)-4,7,7-trimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (I). Through a solution of enololactone **I** (5 g, 0.033 mol) in anhydrous CH_2Cl_2, MeOH, or CH_3CN (50, 36, or 40 ml respectively) was passed at –78°C a flow of O_3–O_2 mixture till complete disappearance of compound **I** from the solvent (TLC monitoring). The ozone consumption was 46.5 mmol h^{-1}, ozonation time 43.5 min. After the end of reaction the solution was flushed with argon, and the peroxides were isolated by cautious evaporation of the solvent under reduced pressure. As a result were separated respectively peroxides **III** (5.6 g, 92%), a mixture of **VII** and **VIII** (5.7 g, 87%), and **IIIa, b** (5.9 g, 90%).

1-(Acetoxyperoxydehydromethyl)-2,2-dimethyl-3-formylcyclopropane (IIIa, b). IR spectrum (cm^{-1}): 2760 m, 1745 s, 1725 s, 1120 s, 960 m ^1H NMR spectrum (δ, ppm): 1.01 s and 1.40 s (6H, CH_3), 1.98 d (1H, H^1, *J* 6.2 Hz) 2.03 m (1H, H^3), 2.15 s (3H, CH_3CO), 9.64 br.s (CHO). ^{13}C NMR spectrum (δ, ppm): 14.84 q and 27.95 q (CH_3), 17.46 (CH_3CO), 22.40 s (C^2), 29.94 d (C^1), 36.58 d (C^3), 105.01 s (O–C–O), 166.40 s (C=O), 199.23 d (CHO). Found, %: O_{act} 7.30. $C_9H_{12}O_5$. Calculated, %: O_{act} 8.00.

Mixture of 5-acetoxy-7,7-dimethyl-3,4-dioxabicyclo[4.1.0]heptan-2-one (VII) and 7,7-dimethyl-4-peracetoxy-3-oxabicyclo[3.1.0]hexan-2-one (VIII). IR spectrum (cm^{-1}): 1775 s, 1740 s, 1115 s, 940 m. ^1H NMR spectrum (δ, ppm): 1.22 s, 1.23 s, 1.30 s, 1.31 s (6H, CH_3), 1.72–1.78 m (2H, H^1, H^3), 2.19 s and 2.20 s (3H, CH_3CO), 4.88 and 5.05 m (1H, OCHO). ^{13}C NMR spectrum (δ, ppm): 15.13 q and 20.83 q (CH_3), 26.32 s and 26.96 s (C^2), 32.90 d, 32.99 d, 33.49 d and 34.17 d (C^1 and C^3), 104.80 d and 105.22 d (O–C–O), 168.17 s, 168.31 s, 168.72 s, 169.09 s (O=C). Found, %: O_{act} 8.16. $C_9H_{12}O_5$. Calculated, %: O_{act} 8.00.

2-Acetoxycarbonylcyclopropanecarboxaldehyde IV (mixed anhydride of acetic and caronic acids). (a) To peroxide **IIIa, b** prepared as above without separation thereof from solution in CH_2Cl_2 was added 20 ml of glacial acetic acid, and then by portions activated zinc powder (11.9 g, 0.18 mol). The mixture was stirred for 2 h at room temperature, the precipitate was filtered off, the solvent was removed in a vacuum of a water-jet pump, and the residue was subjected to chromatography on SiO_2, eluent pentane–ether, 2:1. We obtained 5.3 g (88%) of anhydride **IV**, mp 112–113°C, identical to compound described in [4]. (b) From peroxide **IIIa, b** prepared as above was distilled off CH_2Cl_2 under reduced pressure. The residue was dissolved in a mixture of glacial acetic acid (24 ml) and anhydrous ethyl ether (106 ml). To the solution was added by portions the activated zinc powder (11.9 g, 0.18 mol) maintaining the temperature at 20°C. Then the reaction mixture was stirred for 2 h at the same temperature. The mixture was filtered, the filtrate was evaporated in a vacuum. We obtained 3.28 g of compound **IV**. The precipitate that was filtered off was washed with ethyl ether to isolate additionally 0.09 g of anhydride **IV**, overall yield attained 56%.

4α-Alkoxy-6,6-dimethyl-3-oxabicyclo[4.1.0]-hept-4-en-2-ones (XI–XIII). (a) Through a solution of enololactone **I** (5 g, 0.033 mol) in anhydrous methanol, ethanol, or 2-propanol (36 ml) was passed a flow of O_3–O_2 mixture till compound **I** completely disappeared from the solution (TLC monitoring). Then the reaction mixture was flushed with nitrogen, and 2.9 ml of dimethyl sulfide was added thereto at stirring. The stirring was continued till complete disappearance of peroxides (~12 h) (test with acid solution of KI). Methanol was evaporated in a vacuum, to the residue was added 20 ml of $CHCl_3$, and the solution obtained was washed with saturated NaCl solution (2×10 ml), dried with $MgSO_4$, filtered, the solvent was evaporated in a vacuum of water-jet pump. As a residue was obtained 3.9 g

(76%) of compound **XI**, or 4.1 g (73%) of compound **XII**, or 4.1 g (68%) of compound **XIII**.

(b) Enololactone I (5 g, 0.033 mol) was ozonized as above in 36 ml of anhydrous methanol, and to the solution obtained was added thiourea (1.35 g, 0.0177 mol). The reaction mixture thus obtained was stirred for 10 min, the separated precipitate was filtered off, the solvent was removed, and from the residue was isolated by chromatography on SiO_2 (eluent pentane–ether, 3 : 1)1.6 g (31%) of methoxylactone **XI** identical to that obtained by procedure a.

Compound (XI). IR spectrum (cm^{-1}): 1760 s, 1220 s, 1190 s, 1140 s, 1010 m, 940 s, 860 w ^{1}H NMR spectrum (δ, ppm): 1.16 s, 1.18 s (6H, CH_3), 2.01 d (1H, H^5, ^1J 6.7 Hz), 2.04 d (1H, H^1, ^5J 6.7 Hz), 3.60 s (3H, OCH_3), 5.05 s (1H, OCHO). ^{13}C NMR spectrum (δ, ppm): 15.06 q, 25.40 q (CH_3), 24.47 s (C^6), 29.93 d (C^5), 35.22 d (C^1), 56.30 q (OCH_3), 102.46 d (OCHO), 173.39 s (C=O). Mass spectrum [*m/z* (*I*, %)]: 156 $[M]^+$ (0.1), 155 $[M-1]^+$ (18.1), 124 $[M-CH_3OH]^+$ (37.6), 31 $[OCH_3]^+$ (100). Found, %: C 61.62; H 7.81. $C_8H_{12}O_3$. Calculated, %: C 61.52; H 7.74.

Compound (XII). IR spectrum (cm^{-1}): 1755 s, 1225 s, 1205 s, 1140 s, 1015 m, 935 s 860 m. ^{1}H NMR spectrum (δ, ppm): 1.16 s, 1.19 s (6H, CH_3), 1.25 t (3H, $C\underline{H}_3CH_2$, *J* 7.0 Hz), 2.00 d (1H, H^5, ^1J 6.3 Hz), 2.05 d (1H, H^1, ^3J 6.3 Hz), 4.20 q (2H, CH_2O, *J* 7.0 Hz), 5.12 s (1H, OCHO). ^{13}C NMR spectrum (δ, ppm): 15.06 q, 25.40 q (CH_3), 20.94 q ($\underline{C}H_3CH_2$), 24.51 s (C^6), 29.81 d (C^5), 35.28 d (C^1), 52.06 t (OCH_2), 105.14 d (OCHO), 174.42 s (C=O). Found, %: C 63.24; H 8.40. $C_9H_{14}O_3$. Calculated, %: C 63.50; H 8.31.

Compound (XIII). IR spectrum (cm^{-1}): 1760 s, 1225 s, 1200 s, 1135 s, 1010 m, 940 s, 860 m ^{1}H NMR spectrum (δ, ppm): 1.11 s, 1.34 s (6H, CH_3C^6), 1.15 d and 1.22 d (6H, CH_3, *J* 6.0 Hz), 1.98 br.s (2H, H^1 and H^5), 3.93 d (1H, CHO, *J* 6.0 Hz), 5.20 s (1H, OCHO). ^{13}C NMR spectrum (δ, ppm): 15.06 q and 25.42 q ($C\underline{H}_3C^6$), 21.83 q and 23.38 q ($C\underline{H}_3CH$), 24.25 s (C^6), 30.37 d (C^5), 35.74 d (C^1), 71.93 d (CHO), 100.34 d (C^4), 173.31 s (C=O).

4α-Hydroxy-6,6-dimethyl-3-oxabicyclo[4.1.0]-hept-4-en-2-one (VI). (a) Through a solution of enololactone **I** (5 g, 0.033 mol) in anhydrous dichloromethane (50 ml) was passed a flow of O_3–O_2 mixture till compound **I** completely disappeared from the solution (TLC monitoring) (ozone consumption 44.2 mmol h^{-1}, ozonolysis time 45 min). Then the reaction mixture was flushed with argon, to the solvent obtained was added 0.5 g of Lindlar catalyst, and the mixture was stirred under argon till negative test for peroxides (with acid solution of KI). The catalyst was filtered off, the solvent was evaporated in a vacuum of water-jet pump, and as residue was obtained 5.4 g (89%) of anhydride **IV** with characteristics identical to those reported in [5].

Anhydride **IV** (5.2 g, 0.03 mol) was stirred in 1% water solution of oxalic acid (50 ml) for 3 h, then the product was extracted into ethyl acetate, and the extract was dried on $MgSO_4$. The solvent was distilled off, and the residue was subjected to column chromatography on SiO_2 (eluent pentane–ether, 3 : 1). We obtained 3.4 g (87%) of lactol **VI**, mp 116.5–117°C, $[\alpha]_D^{28}$ –101.5° (*c* 1.0, EtOH), spectral characteristics were the same as published in [5].

(b) Enololactone **I** (5 g, 0.033 mol) was ozonized as above in 36 ml of anhydrous methanol, and to the solution obtained was added at stirring 2.9 ml of $(CH_3)_2S$. In 12 min MeOH was distilled off, to the residue was added 1% water solution of oxalic acid (50 ml), and the suspension obtained was stirred for 3 h; and the suspension got homogenous. Then the hydrolysis product was extracted into ethyl acetate, the extract was dried on $MgSO_4$, filtered, two thirds of the solvent was evaporated at 20 mm Hg, and the separated crystals were filtered off. We obtained 3.83 g (82%) of compound **VI** identical to the above described. From the mother liquor after evaporation was additionally isolated 0.47 g (10%) of compound **VI**. (c) Compound **XVIIa** (2 g, 0.01 mol) was stirred with 18 ml of 1% water solution of oxalic acid. Lactol **VI** resulting from hydrolysis was isolated as described above in amount 1.23 g (87%).

(–)-*N*-(6,6-Dimethyl-4-oxo-3-oxabicyclo[3.1.0]-hexan-2α-yl)thiourea (XVIIa). To peroxide obtained by ozonolysis of enololactone (5 g, 0.033 mol) in 40 ml of CH_3CN was added at cooling to 0°C in several portions 1.35 g (0.0177 mol) of thiourea. On completion of addition the mixture was stirred for 10 min, the separated precipitate was filtered off, the solvent was evaporated, and the residue was subjected to column chromatography on SiO_2, eluent hexane–ethyl acetate, 4 : 1. We obtained 3.16 g (48%) of compound **XVII**, $[\alpha]_D^{20}$ –33.44° (*c* 0.01, $CHCl_3$). IR spectrum (cm^{-1}): 3380 s, 3300 s, 1765 s, 1610 m, 1520 m, 1290 s, 920 s, 870 m. ^{1}H NMR spectrum (δ, ppm): 1.10 s, 1.17 s (6H, CH_3), 1.90 d (1H, H^1, ^5J 6.1 Hz), 1.97 d (1H, H^5, ^1J 6.1 Hz), 5.82 s (1H, H^2, *J* 2.7 Hz), 9.86 s (NH), 5.25 br.s and 7.6 br.s (2H, NH_2). ^{13}C NMR spectrum (δ, ppm): 14.55 q

and 26.11 q (CH_3), 26.51 s (C^6), 30.47 d and 33.95 d (C^1 and C^5), 82.81 d (N–C–O), 173.65 s (C=O), 181.27 s (C=S). Mass spectrum [*m/z* (*I*, %)]: 200 $[M]^+$ (0.6), 185 $[M–CH_3]^+$ (26.1), 183 $[M–OH]^+$ (18.6), 172 $[M–CO]^+$ (37.2), 167 $[M–CH_3–H_2O]^+$ (6.9), 41 (100). Found, %: C 48.15; H 6.2; N 13.2; S 15.24. $C_8H_{12}N_2O_2S$. Calculated, %: C 48.00; H 5.99; N 14.00; S 16.01.

3-Oxabicyclo[3.1.0]hexane-2,4-dione (XVIII). To peroxide obtained by ozonolysis of enololactone (5 g, 0.033 mol) in 40 ml of CH_3CN was added at cooling to 0°C 2.9 ml of dimethyl sulfide, and stirring was continued till complete disappearance of peroxides (test with acid solution of KI). The solvent was distilled off, the residue was subjected to chromatography on SiO_2 (eluent pentane–ether, 3 : 1). We obtained 1.49 g (32%) of lactol VI identical to that described above, and 0.37 g (9%) of dione **XVIII**.

Compound (XVIII). $[\alpha]_D^{20}$ –12.90° (*c* 0.01, $CHCl_3$). IR spectrum (cm^{-1}): 1840 s, 1788 s, 1210 s, 840 m. ^1H NMR spectrum (δ, ppm): 1.31 s and 1.40 s (6H, CH_3), 2.6 s (2H, H^1 and H^5). ^{13}C NMR spectrum (δ, ppm): 16.84 q (CH_3), 34.73 s (C^6), 34.92 d (C^1 and C^5), 167.21 s (C=O). Mass spectrum [*m/z* (*I*, %)]: 140 $[M]^+$ (0.06), 125 $[M–CH_3]^+$ (1.8), 122 $[M–H_2O]^+$ (6.91), 112 $[M–CO]^+$ (28.3), 96 (100). Found, %: C 59.89; H 5.83. $C_7H_8O_3$. Calculated, %: C 60.00; H 5.75.

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