ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 1, pp. 18–24. © Pleiades Publishing, Ltd., 2012.
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Ozonolytic Transformations of (*S*)-(–)-Limonene

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Received February 24, 2011

Abstract—Partial ozonolysis of (*S*)-(–)-limonene in cyclohexane–methanol yields 1-methyl-4-(prop1-en-2-yl)-7,8,9-trioxabicyclo[4.2.1]nonane as a mixture of diastereoisomers at a ratio of 2:3. Nitrogen-containing organic compounds (semicarbazide and hydroxylamine hydrochlorides) favor cyclization of intermediate ozonolysis–reduction products, whereas the reduction with dimethyl sulfide, $NaBH_4$, and $NaBH(OAc)_3$ follows conventional pattern.

DOI: 10.1134/S1070428012010034

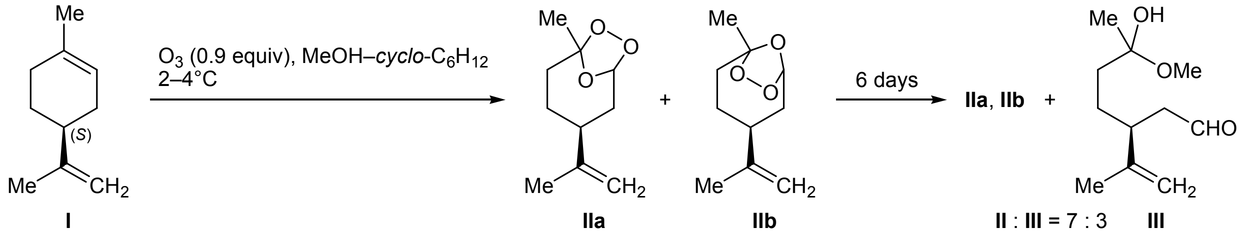
Ozonolytic cleavage of olefins is a widely used method for functionalization of unsaturated compounds. Variation of the conditions of ozonolysis (solvent, temperature, amount of ozone) and reagents and conditions for subsequent transformations (oxidation, reduction, or cleavage) of peroxide compounds could give rise to a broad spectrum of products containing various functional groups. A promising line in organic synthesis is ozonolysis of commercially available natural cyclic olefins, including (*S*)-(–)-limonene, which opens a way to α,ω-difunctional compounds. Griesbaum et al. [1] described the structure of limonene monoozonide and proposed several ways of transformations of its peroxide ozonolysis products, in particular by the action of oxidants (Jones' reagent [2]) and reducing agents (PPh_3 [1], Zn [3], electrolytic reduction [4, 5]).

In the present article we report on the results of our study on the transformations of peroxide ozonolysis products of (*S*)-(–)-limonene (**I**, *ee* 50%) by the action of nitrogen-containing organic and borohydride reducing agents. Partial ozonolysis of (*S*)-limonene (**I**) in cyclohexane–methanol at 2–4°C gives a mixture of diastereoisomeric ozonides **IIa** and **IIb** at a ratio of 2:3 (previously described [1] 1,2,4-trioxolane was obtained at –45°C in pentane as a single stereoisomer), and their structure was determined on the basis of the ^{13}C NMR spectrum of the reaction mixture during the ozonolysis. Peroxides **IIa** and **IIb** are fairly stable; they are slowly converted into hemiketal **III** (by 30% in 6 days at room temperature; Scheme 1). The formation of trioxolanes **IIa** and **IIb** rather than expected methoxy hydroperoxide is likely to be related to the structure of initial cyclic olefin **I**.

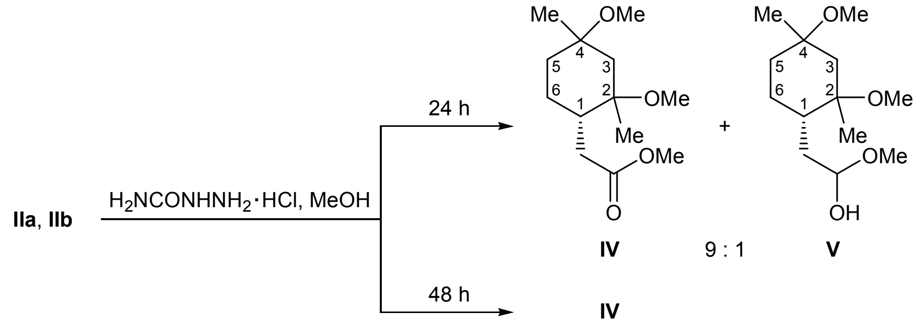
With a view to extend the synthetic potential of (*S*)-limonene (**I**), we examined transformations of its peroxide ozonolysis products by the action of semicarbazide and hydroxylamine hydrochlorides, dimethyl sulfide, sodium triacetoxyhydridoborate, and sodium tetrahydridoborate.

We previously showed that semicarbazide hydrochloride is an efficient reagent for the transformation

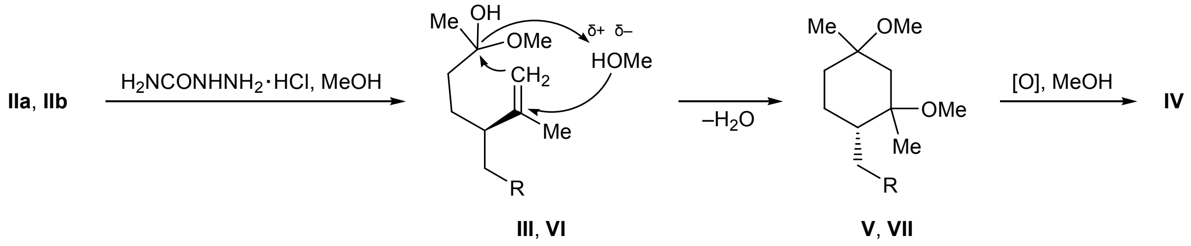
Scheme 1.



Scheme 2.



Scheme 3.



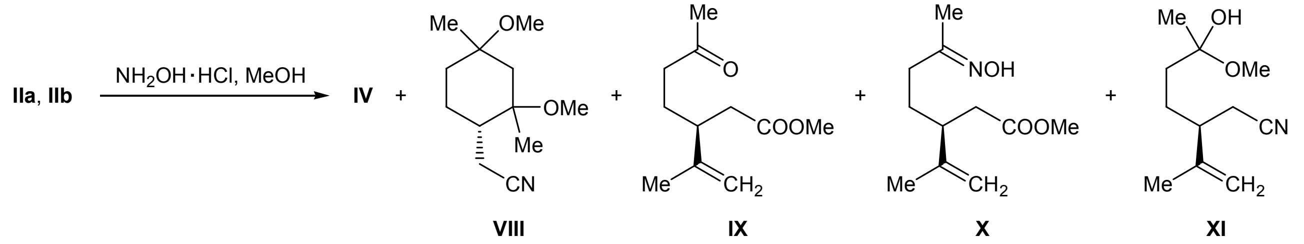
III, **VII**, R = CHO; **V**, **VI**, R = HO(MeO)CH; [O] stands for products of oxidation of semicarbazide hydrochloride with ozonide **II**.

of peroxide products of olefin ozonolysis in methanol into methyl esters which are formed through intermediate hemiacetals [6]. In the present work we found that controlled ozonolysis of limonene (**I**), followed by reaction of peroxides with semicarbazide hydrochloride (reaction time 24 h), apart from the transformation of hemiacetal into ester, resulted in ring closure with formation of cyclohexane derivatives **IV** and **V** at a ratio of 9:1 (Scheme 2).

The formation of substituted diastereoisomeric cyclohexanes **IV** and **V** from diastereoisomeric ozonides **IIa** and **IIb** is confirmed by the presence in the ^{13}C NMR spectra of two couples of downfield singlets from quaternary C^2 and C^4 carbon atoms at δ_C 74–77 ppm. Doublet signals from methylene protons on C^3 (δ 1.73 and 1.91 ppm for **IV** and δ 1.83 and 1.96 ppm for **V**) indicated the position of quaternary carbon atoms in the ring. The NMR spectra of compounds **IV** and **V** contained signals from two methoxy groups (δ_C 49–52 ppm), as well as signals from two methyl groups on C^2 and C^4, in keeping with the structure of 2,4-dimethoxy-2,4-dimethylcyclohexanes. In the ^{13}C NMR spectrum of **IV** (or **V**) we observed sets of signals corresponding to only one couple of diastereoisomers at a ratio of 3:1. When the reaction of peroxide products of ozonolysis of olefin **I** with semicarbazide hydrochloride was prolonged to 48 h, cyclic ester **IV** was formed as the only product (yield 70%, Scheme 2).

We presumed that compounds **IV** and **V** are formed according to Scheme 3. Initially, ozonolysis products **IIa** and **IIb** react with the reducing agent to give unsaturated hemiketal **III** or **VI** in which electron-deficient quaternary carbon atom undergoes attack by electrons of the double bond with simultaneous stabilization by methanol and elimination of water to

Scheme 4.



IV : **VIII** : **IX** : **X** : **XI** = 50 : 30 : 12 : 4 : 4

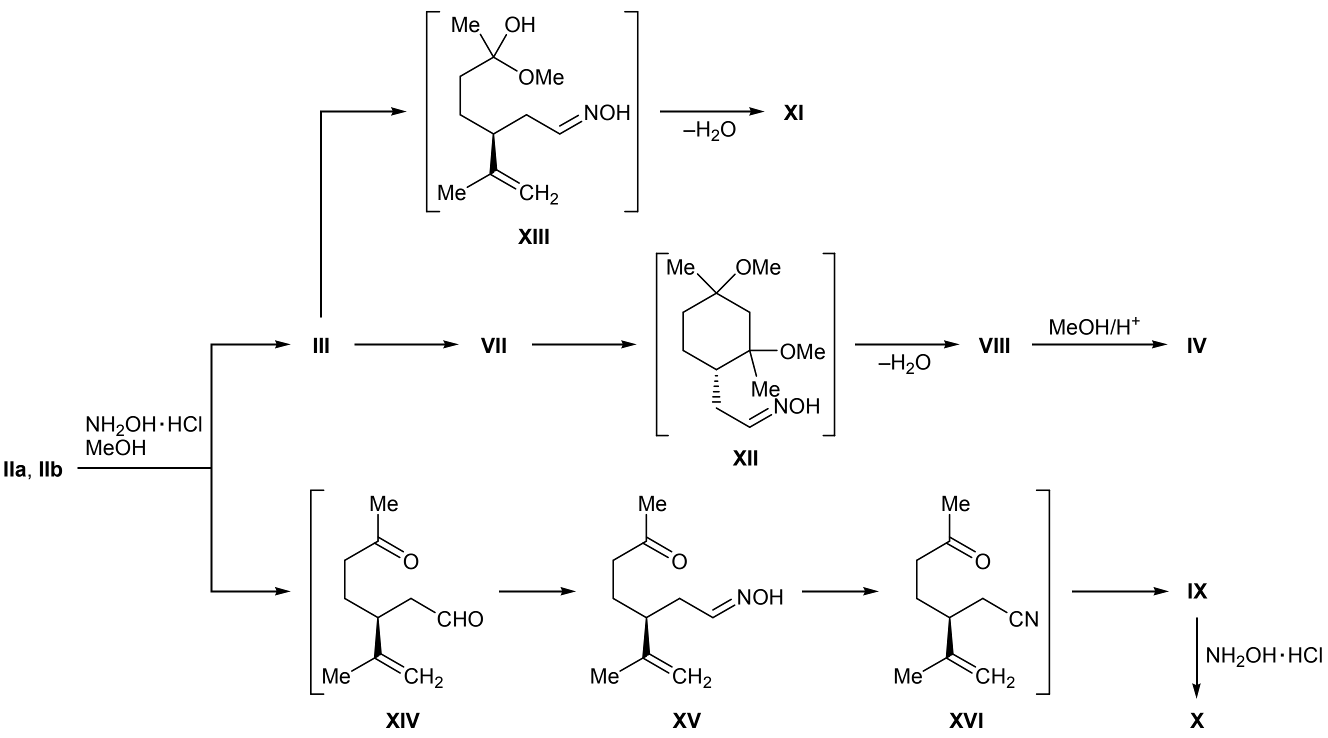
produce cyclohexane derivatives, hemiacetal **V** or aldehyde **VII**. Further oxidative transformations of the hemiacetal or aldehyde moiety into ester in **IV** confirm our previous results [6].

Treatment of peroxide ozonolysis products **IIa** and **IIb** with hydroxylamine hydrochloride gave a mixture of ester **IV** and nitrile **VIII**, as well as unsaturated keto ester **IX**, nitrile **XI**, and ketone oxime **X** (Scheme 4); *syn* configuration of the oxime group in the latter follows from the downfield position of the methyl carbon signal (δ_C 24.86 ppm) [7].

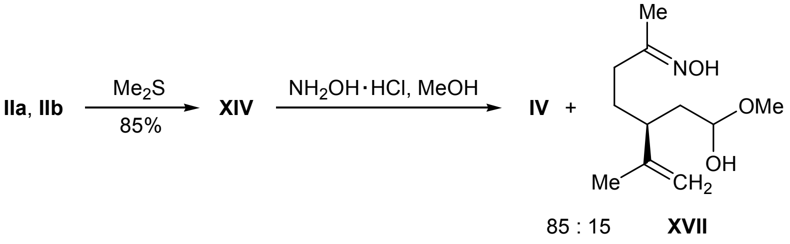
Scheme 5 illustrates possible ways of formation of compounds **IV** and **VIII**–**XI**. Hydroxylamine hydrochloride catalyzes formation of hemiketal functionality from peroxides **IIa** and **IIb**, and cyclization of hemiketal **III** and consecutive transformations following the path aldehyde **VII**→oxime **XII**→nitrile **VIII**→ester **IV** are consistent with the mechanism proposed by us previously [8] for the transformation of aldehyde moiety into ester by the action of hydroxylamine hydrochloride. Some amount of hemiketal **III** does not undergo cyclization but is converted into acyclic unsaturated nitrile **XI** through intermediate aldehyde oxime **XIII**. Compounds **IX** and **X** are likely to be products of concurrent process which involves initial transformation of the aldehyde group in ketoaldehyde **XIV** while the terminal double bond remains intact.

The reduction of peroxide ozonolysis products **II** with dimethyl sulfide gave 85% of expected ketoaldehyde **XIV**. Treatment of compound **XIV** with hydroxylamine hydrochloride in methanol at room temperature led to its cyclization to ester **IV** (Scheme 6). In addition, the reaction mixture contained a small amount of hydroxyimino hemiacetal **XVII**. The presence of the latter suggests that the reaction follows two concurrent pathways and that the cyclization process

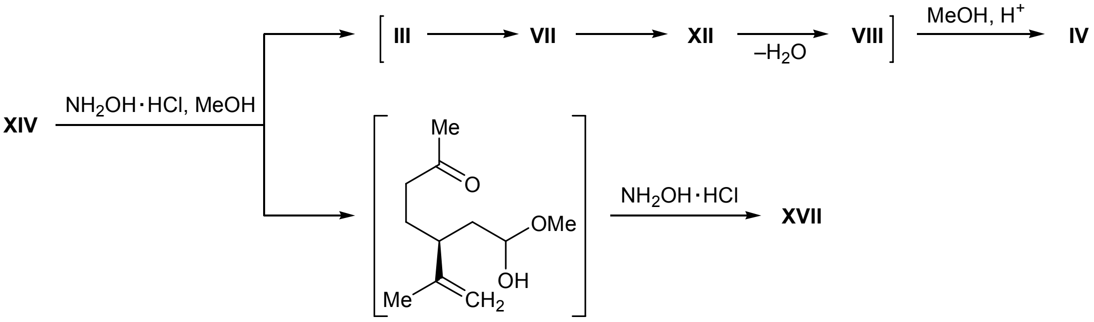
Scheme 5.



Scheme 6.



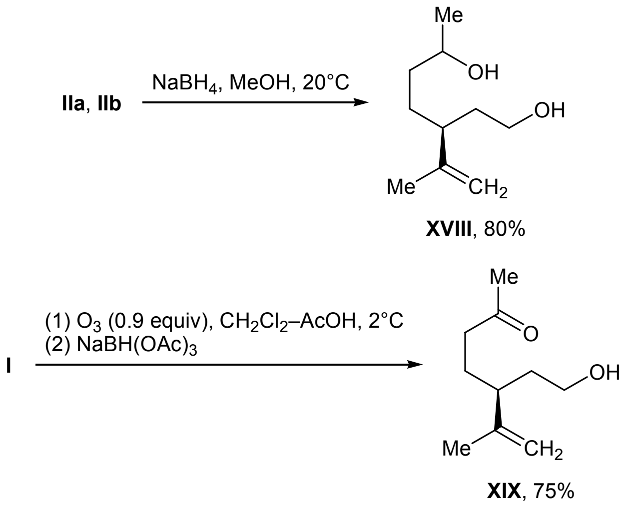
Scheme 7.



predominates over formation of oxime. Presumably, compounds **IV** and **XVII** are formed from ketoaldehyde **XIV** according to Scheme 7. The formation of cyclic ester **IV** follows the path shown in Scheme 5. The concurrent path implies transformation of the aldehyde group in **XIV** into hemiacetal in methanol and simultaneous oximation of the ketone group.

In order to extend the series of difunctional derivatives of limonene (**I**) and examine the effect of the reducing agent on the structure of final products peroxide ozonolysis products obtained from diene **I** were treated with $NaBH(OAc)_3$ and $NaBH_4$. The reduction of ozonolysis products **IIa** and **IIb** with sodium tetrahydridoborate followed a conventional pattern with formation of diol **XVIII** (Scheme 8). It is known that the use of $NaBH(OAc)_3$ as reducing agent for peroxide ozonolysis products ensures selective reduction of aldehyde group while already existing or newly formed keto group remains unchanged [9]. Controlled ozonolysis of olefin **I** and subsequent reduction with sodium triacetoxyhydridoborate afforded 75% of unsaturated keto alcohol **XIX** which can be stored for a long time.

Scheme 8.



Thus the structure of peroxide products of ozonolysis of (*S*)-(–)-limonene and products of their subsequent reduction is largely determined by the nature of the substrate and reducing agent. Nitrogen-containing organic compounds like semicarbazide and hydroxylamine hydrochlorides favor cyclization of intermediate products, whereas the reduction with dimethyl sulfide, $NaBH_4$, and $NaBH(OAc)_3$ follows expected path.

EXPERIMENTAL

The IR spectra were recorded from thin films on a IR-Prestige-21 instrument. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Signals in the ^1H NMR spectra were assigned, and coupling constants were determined, using double resonance and two-dimensional homonuclear correlation (COSY H–H) techniques. GLC analysis was performed on Chrom-5 [1.2-m column packed with 5% of SE-30 on Chromaton N-AW-DMCS (0.16–0.20 mm), oven temperature 50–300°C] and Chrom-41 instruments [2.4-m column packed with PEG-6000, oven temperature 50–200°C]; carrier gas helium. Thin-layer chromatography was performed on Sorbfil silica gel plates (Russia). Silica gel (70–230 μm; Lancaster, England) was used for column chromatography. The optical rotations were measured on a Perkin–Elmer 241-MC polarimeter. Elemental compositions of the isolated compounds were consistent with the calculated data. The efficiency of the ozonizer was 40 mmol of O_3 per hour.

Ozonolysis of (*S*)-(–)-limonene (I). An ozone–oxygen mixture was bubbled through a solution of 2.72 g (20 mmol) of (*S*)-(–)-limonene (**I**) in a mixture of 30 ml of distilled cyclohexane and 1.6 ml (40.0 mmol) of anhydrous methanol at 2–4°C until 18.0 mmol of ozone was absorbed. The mixture was purged with argon, the cyclohexane layer was separated by decanting, 30 ml of anhydrous methanol was added to the residue containing ozonolysis products **II**, and the latter were subjected to subsequent treatment.

A solution of ozonide **II** was kept for 6 days at room temperature, and ^{13}C NMR spectrum of the reaction mixture was recorded every day. The conversion of **II** into hemiketal **III** was 30% in 6 days.

(4*S*)-1-Methyl-4-(prop-1-en-2-yl)-7,8,9-trioxabicyclo[4.2.1]nonane (II). ^{13}C NMR spectrum (MeOH, C_6D_6), δ_C, ppm: 17.91 q (CH_3), 19.30 (20.48)* q (CH_3), 28.05 (28.34) t (CH_2), 41.25 (40.82) t (CH_2), 42.00 (41.63) d (CH), 47.69 (48.30) t (CH_2), 97.99 (99.02) d (CHOO), 106.68 (108.44) s (COO), 112.26 t (**C**H_2=C), 147.24 s (CH_2=**C**).

(3*S*)-[6-Hydroxy-6-methoxy-3-(prop-1-en-2-yl)-heptanal (III). ^{13}C NMR spectrum (MeOH, C_6D_6), δ_C, ppm: 17.83 (17.95) q (CH_3), 19.40 (20.69) q (CH_3), 27.80 (27.17) t (CH_2), 40.97 (40.88) t (CH_2), 41.35 (41.26) t (CH_2), 43.22 (43.08) d (CH), 53.99 (54.43) q (OCH_3), 108.67 (106.53) s [**C**(OH)OCH_3], 113.09 t (**C**H_2=C), 147.23 (146.39) s (CH_2=**C**), 202.63 d (C=O).

Treatment of peroxide products obtained by ozonolysis of limonene (I). *a.* Semicarbazide hydrochloride, 7.75 g (70 mmol), was added under stirring at 0°C to a solution of ozonide **II**, and the mixture was stirred for 24 h at room temperature. The mixture was evaporated, the residue was dissolved in methylene chloride (100 ml), and the solution was washed with water (4 × 25 ml), dried over $MgSO_4$, and evaporated. According to the GLC data, the residue (2.44 g) contained ester **IV** and hemiacetal **V** at a ratio of 9 : 1, which were separated by chromatography on silica gel using petroleum ether and petroleum ether–*tert*-butyl methyl ether (10 : 1 and 5 : 1) as eluents.

Methyl [(1*S*)-2,4-dimethoxy-2,4-dimethylcyclohexyl]acetate (IV). Yield 1.64 g (40%), R_f 0.53 (petroleum ether–*tert*-butyl methyl ether, 2 : 1). IR spectrum (KBr), ν, cm^{-1}: 2827 (OCH_3), 1735 (C=O), 1080 (C–O). ^{1}H NMR spectrum, δ, ppm: 1.12 (1.15) s (3H, CH_3), 1.14 (1.22) s (3H, CH_3), 1.25–1.33 m (2H, 5-H_{ax}, 6-H_{ax}), 1.43–1.60 m (2H, 5-H_{eq}, 6-H_{eq}), 1.73 d (1H, 3-H_{ax}, J = 11.0 Hz), 1.91 d (1H, 3-H_{eq}, J = 11.0 Hz), 1.85–1.96 m (1H, 1-H), 2.50 d.d [1H, C**H**$_2$C(O)OCH_3, J = 9.2, 6.4 Hz], 2.61 d.d [1H, C**H**$_2$C(O)OCH_3, J = 9.2, 6.3 Hz], 3.10 s (3H, OCH_3), 3.17 s (3H, OCH_3), 3.63 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 18.48 (22.02) q (CH_3), 25.06 (23.50) q (CH_3), 25.06 (24.95) t (C^6), 34.53 (33.90) t (**C**$H_2CO_2CH_3$), 35.27 (35.03) t (C^5), 41.75 (42.89) d (C^1), 43.32 (41.07) t (C^3), 49.06 q (OCH_3), 49.47 q (OCH_3), 51.26 q (OCH_3), 74.37 (74.29) s [**C**(CH_3)OCH_3], 75.91 (75.09) s [**C**(CH_3)OCH_3], 174.05 (174.37) s (C=O).

2-[(1*S*)-2,4-Dimethoxy-2,4-dimethylcyclohexyl]-1-methoxyethanol (V). Yield 0.28 g (6%), R_f 0.31 (petroleum ether–*tert*-butyl methyl ether, 2 : 1). ^{1}H NMR spectrum, δ, ppm: 1.09 s (3H, CH_3), 1.20 s (3H, CH_3), 1.41–1.68 m (2H, 5-H_{ax}, 6-H_{ax}), 1.74–1.80 m (2H, 5-H_{eq}, 6-H_{eq}), 1.83 d (1H, 3-H, J = 11.8 Hz), 1.93 d.d [1H, C**H**$_2$CH(OH)OCH_3, J = 14.4, 5.6 Hz], 1.96 d (1H, 3-H, J = 11.8 Hz), 1.96–2.10 m (1H, CH), 2.53 d.d [1H, C**H**$_2$CH(OH)OCH_3, J = 14.4, 5.6 Hz], 3.13 s (3H, OCH_3), 3.19 s (3H, OCH_3), 3.65 s (3H, OCH_3), 4.78 t [1H, C**H**(OH)(OCH_3), J = 6.1 Hz], 5.1 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 18.76 (23.41) q (CH_3), 23.50 (22.06) q (CH_3), 24.95 (22.52) t (C^6), 34.54 (33.82) t (C^5), 35.43 (35.05) t (1-CH_2), 42.88 (40.31) d (C^1), 43.22 (41.06) t (C^3), 50.76 q (OCH_3), 51.32 q (OCH_3), 52.76 q (OCH_3), 75.07 (76.32) s [**C**(CH_3)OCH_3], 76.57 (74.26) s [**C**(CH_3)OCH_3], 103.37 d [**C**H(OH)(OCH_3)].

b. Semicarbazide hydrochloride, 7.75 g (70.0 mmol), was added under stirring at 0°C to a solution of ozonide **II**, and the mixture was stirred for 48 h at room temperature. The mixture was evaporated, the residue was dissolved in 100 ml of methylene chloride, and the solution was washed with water (4 × 25 ml), dried over $MgSO_4$, and evaporated to isolate 2.95 g (70%) of ester **IV** which was identical to a sample of **IV** isolated as described in *a*.

c. Hydroxylamine hydrochloride, 4.87 g (70.0 mmol) was added under stirring at 0°C to a solution of ozonide **II**, and the mixture was stirred for 48 h at room temperature. The mixture was evaporated, the residue was dissolved in 100 ml of methylene chloride, and the solution was washed with water (4 × 25 ml), dried over $MgSO_4$, and evaporated. According to the GLC data, the residue (2.30 g) contained compounds **IV** and **VIII**–**XI** at a ratio of 50:30:12:4:4. The products were separated by chromatography on silica gel using petroleum ether and petroleum ether–*tert*-butyl methyl ether (10 : 1 and 5 : 1) as eluents.

Compound **IV**. Yield 0.98 g (22%), R_f 0.53 (petroleum ether–*tert*-butyl methyl ether, 2 : 1). The product was identical to a sample of **IV** isolated as described in *a*.

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* Hereinafter, signals of the second diastereoisomer are given in parentheses.

[(1*S*)-2,4-Dimethoxy-2,4-dimethylcyclohexyl]-acetonitrile (VIII). Yield 0.61 g (15%), R_f 0.45 (petroleum ether–*tert*-butyl methyl ether, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.11 s (3H, CH_3), 1.15 s (3H, CH_3), 1.34–1.78 m (2H, 5-H_{ax}, 6-H_{ax}), 1.82–2.10 m (2H, 5-H_{eq}, 6-H_{eq}), 1.89–2.03 m (1H, CH), 1.94 d (1H, 3-H, J = 11.2 Hz), 2.01 d (1H, 3-H, J = 11.2 Hz), 2.05 d.d (1H, CH_2CN, J = 8.1, 4.5 Hz), 2.27 d.d (1H, CH_2CN, J = 8.1, 5.4 Hz), 3.18 s (3H, OCH_3), 3.20 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 18.19 (18.50) t ($\mathbf{C}H_2CN$), 18.50 q (CH_3), 25.43 (21.67) q (CH_3), 26.12 (25.05) t (C^6), 35.27 (34.84) t (C^5), 42.75 d (CH), 43.19 (41.66) t (C^3), 49.08 q (OCH_3), 49.52 q (OCH_3), 74.41 (74.19) s [$\mathbf{C}(CH_3)OCH_3$], 75.51 (75.34) s [$\mathbf{C}(CH_3)OCH_3$], 119.75 s (CN).

Methyl (3*S*)-6-oxo-3-(prop-1-en-2-yl)heptanoate (IX). Yield 0.25 g (7%), R_f 0.37 (petroleum ether–*tert*-butyl methyl ether, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.43–1.60 m (2H, CH_2), 1.66 s (3H, CH_3), 1.89–2.43 m (2H, CH_2), 2.08–2.39 m (2H, CH_2), 2.12 s [3H, $CH_3C(O)$], 2.43–2.55 m (1H, CH), 3.64 s [3H, $C(O)OCH_3$], 4.48 d (2H, $C{=}CH_2$, J = 1.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.20 q (CH_3), 29.89 q (CH_3), 26.14 t (CH_2), 34.57 t (CH_2), 41.07 t (CH_2), 43.03 d (CH), 51.34 s ($COO\mathbf{C}H_3$), 112.82 t ($\mathbf{C}H_2{=}C$), 145.23 s ($CH_2{=}\mathbf{C}$), 172.64 s ($\mathbf{C}OOCH_3$), 208.34 s (C=O).

Methyl (3*S*,6*Z*)-6-hydroxyimino-3-(prop-1-en-2-yl)heptanoate (X). Yield 0.07 g (2%), R_f 0.13 (petroleum ether–*tert*-butyl methyl ether, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.40–1.81 m (2H, CH_2), 1.72 s (3H, CH_3), 1.79 s (3H, CH_3), 1.85–2.18 m (2H, CH_2), 1.90–2.50 m (2H, $C\mathbf{H}_2COOCH_3$), 1.90–2.50 m (1H, CH), 3.65 s (3H, $COOCH_3$), 4.41–4.53 m (2H, $C{=}CH_2$, J = 1.7 Hz), 7.40 br.s (1H, NOH). ^{13}C NMR spectrum, δ_C, ppm: 18.08 q (CH_3), 24.65 t (CH_2), 24.86 q (*anti*-CH_3), 33.03 t (CH_2), 34.08 t (CH_2), 42.59 d (CH), 50.83 s ($COO\mathbf{C}H_3$), 112.07 t ($\mathbf{C}H_2{=}C$), 144.95 s ($CH_2{=}\mathbf{C}$), 155.63 s (C=NOH), 173.59 s ($\mathbf{C}OOCH_3$).

(3*S*)-6-Hydroxy-6-methoxy-3-(prop-1-en-2-yl)-heptanenitrile (XI). Yield 0.068 g (2%), R_f 0.10 (petroleum ether–*tert*-butyl methyl ether, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.03 s (3H, CH_3), 1.42–1.82 m (2H, CH_2), 1.85–2.10 m (2H, CH_2), 2.14 s (3H, CH_3), 2.43 d.d (1H, CH_2CN, J = 12.3, 6.1 Hz), 2.61 d.d (1H, CH_2CN, J = 12.3, 5.7 Hz), 2.60–2.71 m (1H, CH), 3.53 s (3H, OCH_3), 3.80 s (1H, OH), 4.30–5.00 m (2H, $C{=}CH_2$). ^{13}C NMR spectrum, δ_C, ppm: 17.68 t ($\mathbf{C}H_2CN$), 18.20 (18.52) q (CH_3), 29.88 (29.54) q (CH_3), 26.14 (25.32) t (CH_2), 41.07 (36.07) t (CH_2), 43.30 d (CH), 51.35 q (OCH_3), 108.53 s [$\mathbf{C}(OH)(OCH_3)$], 112.46 t ($\mathbf{C}H_2{=}C$), 119.75 s ($CH_2\mathbf{C}N$), 145.17 s ($CH_2{=}\mathbf{C}$).

d. Dimethyl sulfide, 6.0 ml (80 mmol), was added under stirring at 0°C to a solution of ozonide **II**, and the mixture was stirred for 16 h at room temperature. The mixture was evaporated, the residue was dissolved in 100 ml of methylene chloride, and the solution was washed with water (4×25 ml), dried over $MgSO_4$, and evaporated to isolate 2.56 g (85%) of ketoaldehyde **XIV**. R_f 0.30 (petroleum ether–*tert*-butyl methyl ether, 2:1). IR spectrum (KBr), ν, cm^{-1}: 2725 [C(O)H], 1710 (C=O), 1645 ($C{=}CH_2$). The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in [1].

Compound **XIV**, 1.6 g (9.5 mmol), was dissolved in 30 ml of methanol, 2.3 g (33.3 mmol) of hydroxylamine hydrochloride was added, and the mixture was stirred for 48 h at room temperature. The mixture was evaporated, the residue was dissolved in 100 ml of methylene chloride, and the solution was washed with water (4×25 ml), dried over $MgSO_4$, and evaporated. According to the GLC data, the residue (1.3 g) contained ester **IV** and oxime **XVII** at a ratio of 85:15. The products were separated by chromatography on silica gel using petroleum ether and petroleum ether–*tert*-butyl methyl ether (10:1 and 5:1) as eluents.

Compound **IV**. Yield 0.95 g (41%), R_f 0.53 (petroleum ether–*tert*-butyl methyl ether, 2:1). The product was identical to a sample isolated as described in *a*.

(3*S*)-6-Hydroxyimino-1-methoxy-3-(prop-1-en-2-yl)heptan-1-ol (XVII). Yield 0.12 g (6%), R_f 0.22 (petroleum ether–*tert*-butyl methyl ether, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.35–1.70 m (2H, CH_2), 1.65 s (3H, CH_3), 1.82 s (3H, CH_3), 2.15–2.25 m [1H, $C\mathbf{H}_2CH(OH)(OCH_3)$], 2.21–2.35 m (1H, CH), 2.23 t (2H, CH_2, J = 7.0 Hz), 2.25–2.40 m [1H, $C\mathbf{H}_2CH(OH)(OCH_3)$], 3.62 s (3H, OCH_3), 4.65 t [1H, $CH_2C\mathbf{H}(OH)(OCH_3)$, J = 6.5 Hz], 4.65–4.93 m (2H, $C{=}CH_2$), 5.17 s (1H, OH), 8.2 br.s (1H, NOH). ^{13}C NMR spectrum, δ_C, ppm: 17.05 q (CH_3), 21.60 q (*anti*-CH_3), 28.49 t (CH_2), 38.66 t (CH_2), 40.86 t (CH_2), 42.81 d (CH), 51.17 q (OCH_3), 101.52 d [$CH(OH)(OCH_3)$], 112.72 t ($\mathbf{C}H_2{=}C$), 145.19 s ($CH_2{=}\mathbf{C}$), 157.83 s (C=N).

e. Sodium tetrahydridoborate, 1.89 g (50.0 mmol), was added under stirring at 10°C to a solution of ozonide **II**, and the mixture was stirred for 3 h at room temperature. A solution of 0.54 ml of acetic acid in 5.4 ml of water was added, the mixture was stirred for 3 h and filtered, and the filtrate was evaporated. The residue was dissolved in 200 ml of methylene chloride, and the solution was washed with a saturated solution of sodium chloride (4 × 25 ml), dried over $MgSO_4$, and evaporated to isolate 2.30 g (80%) of (3*S*)-3-(prop-1-en-2-yl)heptane-1,6-diol (**XVIII**), R_f 0.34 (ethyl acetate). ^1H NMR spectrum, δ, ppm: 1.24 s (3H, CH_3, $J = 7.3$ Hz), 1.29–1.70 m (2H, CH_2), 1.60–1.71 m (1H, $C\mathbf{H}_2CH_2OH$), 1.67 s (3H, CH_3), 1.83–2.10 m (2H, CH_2), 2.11–2.18 m (1H, CH), 2.21–2.28 m (1H, $C\mathbf{H}_2CH_2OH$), 3.61 s (2H, OH), 3.64–3.80 m (2H, $C\mathbf{H}_2OH$), 3.65–3.80 m (1H, $C\mathbf{H}OH$), 4.76 d (CH_2=C, $J = 1.82$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.63 q (CH_3), 23.15 (23.08) q (CH_3), 29.30 (28.67) t (CH_2), 35.94 t (CH_2), 36.86 (36.40) t (CH_2), 43.95 (43.34) d (CH), 60.46 t (CH_2OH), 67.78 (67.11) d (CHOH), 111.82 t ($\mathbf{C}H_2$=C), 146.89 s (CH_2=**C**).

Treatment of peroxide products of ozonolysis of limonene (I) with sodium triacetoxyhydridoborate. An ozone–oxygen mixture was bubbled through a solution of 1.0 g (7.4 mmol) of olefin **I** and 0.86 g (14.8 mmol) of glacial acetic acid in 20 ml of cyclohexane under stirring at 0–2°C until 6.7 mmol of ozone was absorbed. The mixture was purged with argon, the cyclohexane layer was separated, and the residue was diluted with 20 ml of methylene chloride and added under stirring at 10°C to a suspension of $NaBH(OAc)_3$ prepared preliminarily by adding a solution of 5.45 g (90.7 mmol) of glacial acetic acid in 10 ml of methylene chloride to a suspension of 1.12 g (29.5 mmol) of $NaBH_4$ in 46 ml of methylene chloride and subsequent stirring for 2 h. The mixture was allowed to warm up to room temperature, stirred for 3 h, and cooled to 10°C, a solution of 2.25 g of sodium hydroxide in 50 ml of water was added, and the organic phase was separated, washed in succession with a saturated solution of ammonium chloride and water, dried over Na_2SO_4, and evaporated to isolate 0.8 g (75%) of ketoalcohol **XIX**.

(5*S*)-5-(2-Hydroxyethyl)-6-methylhept-6-en-2-one (XIX). R_f 0.20 (hexane–*tert*-butyl methyl ether, 1 : 1), $[\alpha]_D^{20} = -7°$ ($c = 0.12264$, CH_2Cl_2). IR spectrum (KBr), ν, cm^{-1}: 3415 (OH), 1712 (C=O), 1643 ($CH=CH_2$). ^1H NMR spectrum, δ, ppm: 1.52–1.73 m (2H, CH_2), 1.58 s (3H, CH_3), 2.09 s (CH_3), 2.11–2.29 m (1H, $C\mathbf{H}_2CH_2OH$), 2.29 t (2H, CH_2, $J = 7.1$ Hz), 2.45–2.51 m (1H, $C\mathbf{H}_2CH_2OH$), 2.45–2.73 m (1H, CH), 3.55 t (2H, CH_2, $J = 6.9$ Hz), 4.10 s (1H, OH), 4.72 d (CH_2=C, $J = 1.9$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.15 q (CH_3), 26.25 t (CH_2), 29.60 q (CH_3), 35.72 t (CH_2), 40.95 t (CH_2), 43.15 d (CH), 60.16 t ($\mathbf{C}H_2OH$), 112.30 t ($\mathbf{C}H_2$=C), 145.95 s (CH_2=**C**), 209.21 s (C=O).

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 09-03-00831-a) and by the President of the Russian Federation (program for support of young Russian doctors of sciences, project no. MD-3852.2009.3).

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