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Transformation of Peroxide Products of Olefin Ozonolysis under Treatment with Hydroxylamine and Semicarbazide Hydrochlorides in Acetic Acid

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Abstract—Hydrochlorides of hydroxylamine and semicarbazide efficiently reduce peroxide products of olefin ozonolysis in a system CH_2Cl_2–AcOH leading to the formation of carboxylic acids and their derivatives. The application of water as the solvent component favors the increase in the fraction of nitrogen-containing organic compounds (semicarbazones, keto- and aldoximes, nitriles) and reduction in the yield of carboxylic acids.

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The olefin ozonolysis is widely utilized in synthetic organic chemistry for the preparation of α,ω-bifunctional oxygen-containing compounds used in targeted syntheses of substances possessing desired properties, in particular, of bioregulators of low molecular weight [1]. Numerous studies showed that the ozonolysis conditions, in particular, the solvent, essentially affect the qualitative and quantitative composition of the reaction products. In the course of the ozonolysis in proton-donor solvents (alcohols, carboxylic acids, or water) the arising bipolar ion is stabilized as a rule forming α-substituted hydroperoxides. The part of the acetic acid consists in the binding of the zwitter-ion into α-acetoxyhydroperoxides [2, 3].

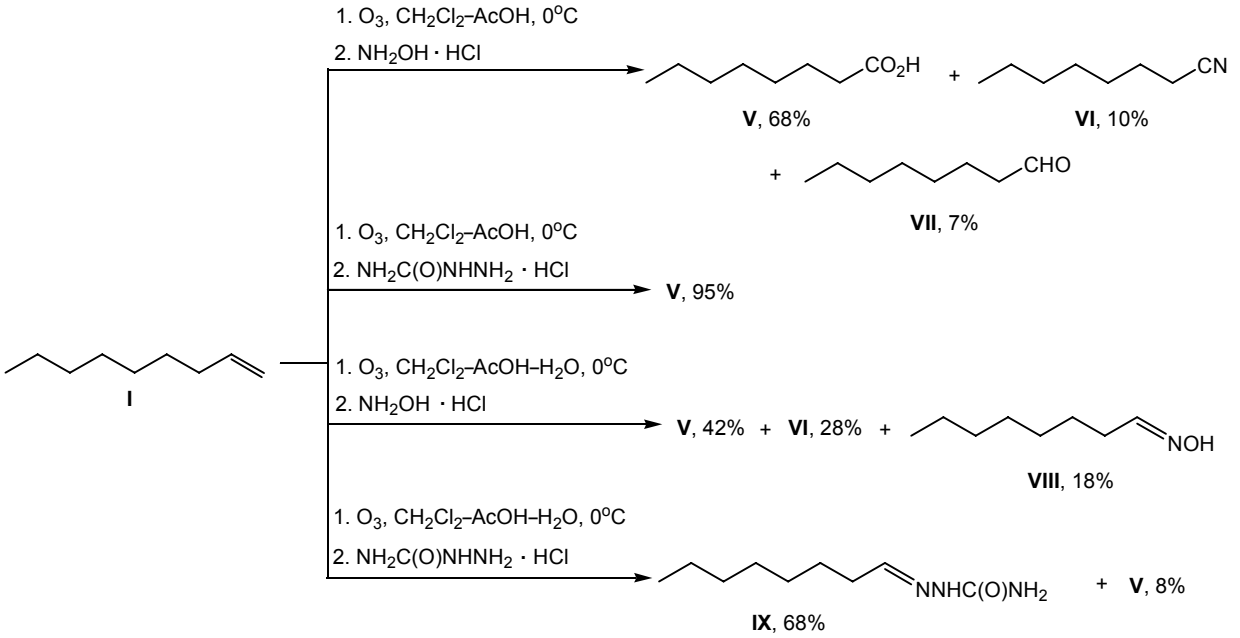
Hydrochlorides of hydroxylamine and semicarbazide efficiently reduce peroxide products of olefin ozonolysis to carbonyl compounds in alcohol solutions: methanol [4], 2-propanol [5], in the methanol–water mixture [6]. The application of water as the solvent component in olefins ozonolysis and the subsequent workup of the peroxides with semicarbazide and hydroxylamine hydrochlorides increases the fraction of nitrogen-containing organic compounds and reduces the part of the carboxy derivatives. In this connection we investigated the transformations of the peroxide products of ozonolysis of versatile olefins distinguished by the nature and the degree of the double bond substitution under the treatment with the same nitrogen organic reagents in the systems CH_2Cl_2–AcOH, 5 : 1, and CH_2Cl_2–AcOH–H_2O, 11 : 3 : 1. We chose as substartes 1-nonene (**I**), castor oil (**II**), Δ^3-carene (*ee* 100%) (**III**), (–)-α-pinene (*ee* 86%) (**IV**).

After the ozonolysis of 1-nonene (**I**) in a mixture CH_2Cl_2–AcOH (0°C) with the subsequent reduction of the peroxides with hydroxylamine hydrochloride we isolated from the reaction mixture octanoic acid (**V**), and also nitrile **VI** and aldehyde **VII**. The ozonolysis of compound **I** under the same conditions followed by the treatment of the peroxides with semicarbazide hydrochloride afforded in a high yield acid **V** as a single reaction product (Scheme 1).

The addition of water as the solvent component under the same reaction conditions resulted in the change in the ozonolysis products. At the reduction with hydroxylamine hydrochloride the fractions of nitrile **VI** and aldoxime **VIII** increased and the fraction of acid **V** decreased. At the treatment of the peroxides with semicarbazide hydrochloride semicarbazone **IX** was isolated as the main product, and octanoic acid **V**

* Deceased

Scheme 1.

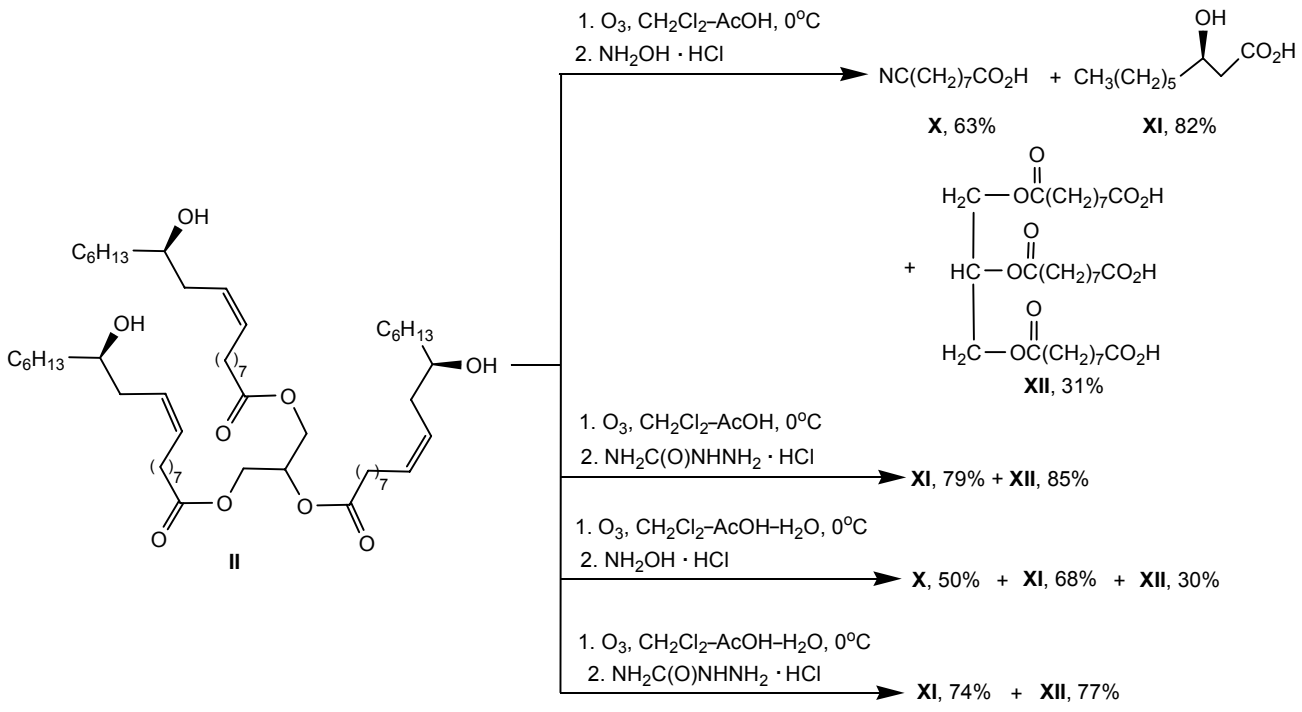


was present in small amount in the reaction mixture (Scheme 1).

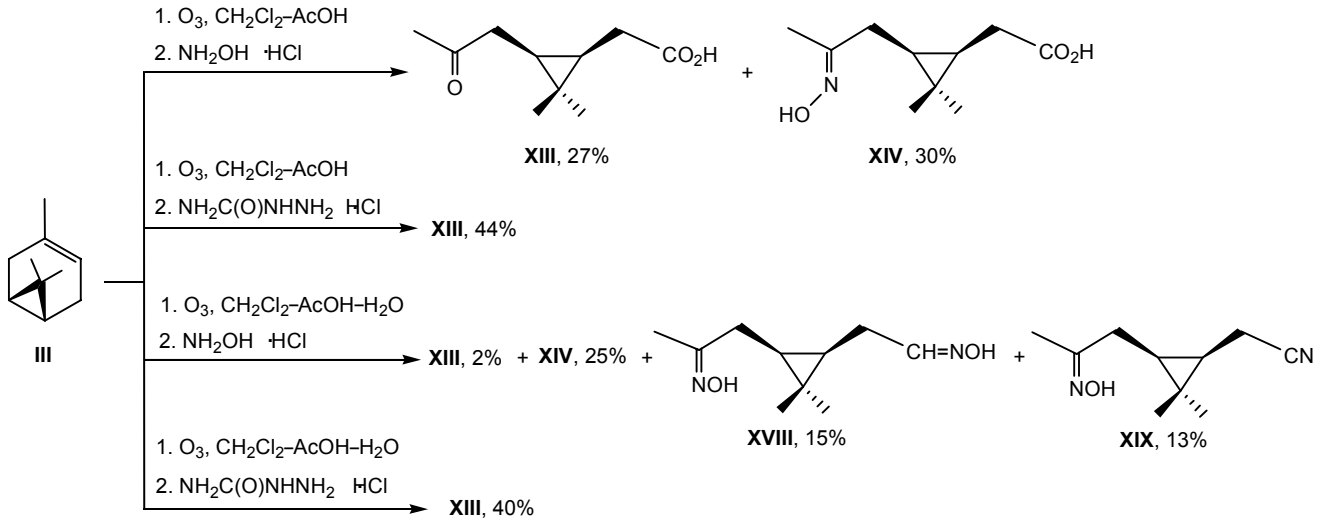
The treatment with hydroxylamine hydrochloride of the peroxide products of castor oil (**II**) ozonolysis in the mixture CH_2Cl_2–AcOH both in the absence and the presence of water resulted in the formation in various ratios of 8-cyanooctanoic (**X**), (*R*)-3-hydroxynonanoic (**XI**) acids, and triacylglycerol **XII**, and at the treatment with semicarbazide hydrochloride two latter compounds formed (Scheme 2).

The ozonolysis of natural bicyclic monoterpenes **III** and **IV** in the system CH_2Cl_2–AcOH followed by workup of the peroxides with hydroxylamine hydrochloride afforded the corresponding ketoacids **XIII** and

Scheme 2.



Scheme 3.



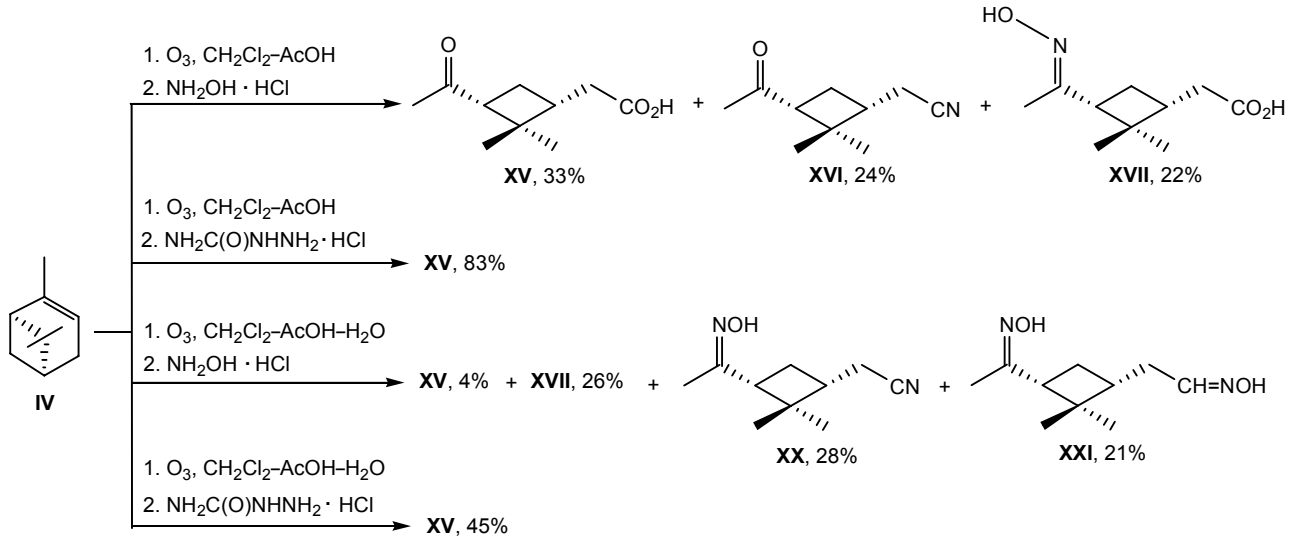
XV and hydroxyimino acids **XIV** and **XVII**. Besides after the treatment of α-pinene (**IV**) peroxides oxonitrile **XVI** was isolated. The treatment of peroxy products of compounds **III** and **IV** ozonolysis with semicarbazide hydrochloride in acetic acid furnished the corresponding ketoacids **XIII** and **XV** (Schemes 3, 4).

The ozonolysis of olefins **III** and **IV** in the presence of water as the solvent component followed by the peroxides treatment with hydroxylamine hydrochloride resulted in a sharp decrease in the fraction of ketoacids **XIII** and **XV** and a simultaneous increase in the yield of nitrogen-containing derivatives **XIV**, **XVIII**, **XIX** and **XVII**, **XX**, **XXI** respectively. At the reduction with semicarbazide hydrochloride the same ketoacids **XIII** and **XV** were obtained but in lower yields (Schemes 3, 4).

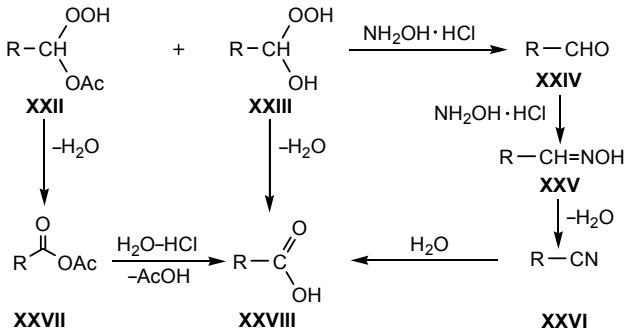
The generalization of all experimental data obtainned leads to the presumable Scheme 5. The main peroxide ozonolysis product is obviously acetoxyhydroperoxide **XXII**. In the course of the ozonolysis in the mixture CH_2Cl_2–AcOH–H_2O both acetoxy- (**XXII**) and/or hydroxy- (**XXIII**) hydroperoxides may form whose ratio depends in turn on the structure of initial olefins.

The treatment of peroxides **XXII** and **XXIII** with hydroxylamine hydrochloride leads to the formation either of acids **XXVIII** or of easily hydrolysable esters **XXVII**. Another reaction path consists in the reduction of peroxides **XXII** and **XXIII** into aldehyde **XXIV** that under the action of hydroxylamine hydrochloride is converted into individual compounds or into mixtures along the route aldoxime **XXV** → nitrile **XXVI** → acid **XXVIII** (Scheme 5).

Scheme 4.



Scheme 5.



We believe that obtaining carboxy derivatives in the presence of semicarbazide hydrochloride may be due to the dehydration under the action of HCl of the intermediately formed acetoxy- (**XXII**) or hydroxy- (**XXIII**) hydroperoxides, or to their reduction into aldehydes **XXIV** which are oxidized to the corresponding carboxylic acids **XXVIII** with nitroso oxide **XXX**, the product of the oxidation of semicarbazide hydrochloride first with peroxide **XXII** and then with oxygen through an intermediate stage of nitrene **XXIX** formation [7]. In the event of the monosubstituted olefin **I** evidently the aldehyde condensation with semicarbazide in the presence of water occurs faster than the oxidation with nitroso oxide resulting in semicarbazone **IX** (Scheme 6).

Thus the results of the research show that hydroxylamine and semicarbazide hydrochlorides are effective reagents for converting peroxy products of olefin ozonolysis into carboxylic acids and their derivatives in mixtures CH_2Cl_2–AcOH and CH_2Cl_2–AcOH–H_2O. At the use of water as the solvent component the growth of the content of nitrogen organic compounds (semicarba-zones, keto- and aldoximes, nitriles) and decreasing yield of carboxylic acids was observed.

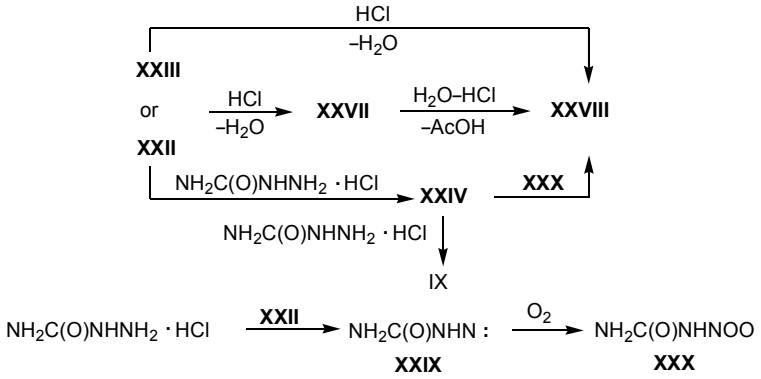
EXPERIMENTAL

IR spectra were recorded on a spectrophotometer IR Prestige-21 (Fourier Transform Spectrophotometer – Shimadzu) from thin films. NMR spectra were registered on high resolution spectrometers Bruker AM-300 and Bruker Avance III 500 [operating frequencies 300 and 500 MHz (^{1}H), 75.47 MHz (^{13}C)] in $CDCl_3$, internal reference TMS. The assignment of signals in ^{1}H NMR spectra and measurement of spin-spin coupling constants were carried out using double resonance methods and 2D homonuclear correlation spectroscopy COSY (H-H). ^{13}C NMR spectra were registered in the modes with the wide-band decoupling from protons and JMOD. GLC was performed on chromatographs Chrom-5 [column 1.2 m long, stationary phase silicone SE-30 (5%) on a carrier Chromaton N-AW-DMCS (0.16–0.20 mm), ramp 50–300°C] and Chrom-41 [column 2.4 m long, stationary phase PEG-6000, ramp 50–200°C], carrier gas helium. TLC monitoring was carried out on SiO_2 of Sorbfil grade (Russia). In column chromatography was used SiO_2 (70–230) Lancaster (England). The optical rotation was measured on a polarimeter Perkin Elmer 241-MC. The elemental analysis data of all compounds were consistent with the calculations. The output of the ozonator was 40 mmol O_3/h.

Ozonolysis of olefins I–IV in the system CH_2Cl_2–AcOH. Through a solution of 10.0 mmol of olefin in a mixture of 20 mL of CH_2Cl_2 and 5.7 mL of AcOH at 0°C was bubbled the ozone-oxygen mixture in a calculated amount: 1 mol of O_3 per 1 mol of the double bond.

Treatment of peroxide ozonolysis products with hydroxylamine hydrochloride. The reaction mixture was flushed with argon, and at stirring and cooling to 0°C 2.43 g (35.0 mmol) of NH_2OH·HCl per one

Scheme 6.



double bond was added, the reaction mixture was stirred at room temperature till the absence of peroxides (iodine-starch test), CH_2Cl_2 and AcOH were distilled off, the residue was dissolved in $CHCl_3$ (150 mL), the solution was washed with water (4 × 15 mL), dried with Na_2SO_4, and evaporated.

The ozonolysis of 1-nonene (**I**) after chromatographing the residue (1.28 g) afforded 0.97 g (68%) of octanoic acid (**V**), 0.12 g (10%) of nitrile **VI**, and 0.09 g (7%) of octanal (**VII**).

Octanoic acid (V). R_f 0.25 (hexane–*tert*-butyl methyl ether, 2 : 1). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, C^8H_3, *J* 6.6 Hz), 1.20–1.37 m (6H, $C^{4-6}H_2$), 1.43–1.58 m (2H, C^7H_2), 1.56–1.69 m (2H, C^3H_2), 2.24 t (2H, C^2H_2, *J* 6.7 Hz), 11.45 br.s (1H, OH). IR and ^{13}C NMR spectra are identical to previously described [8].

Octanonitrile (VI). R_f 0.26 (hexane–*tert*-butyl methyl ether, 2 : 1). IR and NMR spectra are identical to previously described [6].

Octanal (VII). IR spectrum, ν, cm^{-1}: 1718 (C=O). NMR spectra are identical to those described in [9].

The ozonolysis of castor oil (**II**) after chromatographing the residue (10.25 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) gave 3.17 g (63%) of mononitrile **X**, 4.2 g (82%) of hydroxyacid **XI**, 1.86 g (31%) of triacylglycerol **XII**.

8-Cyanooctanoic acid (X). R_f 0.28 (hexane–*tert*-butyl methyl ether, 1 : 1). IR spectrum, ν, cm^{-1}: 2220 (C≡N), 1700 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.10–1.40 m (8H, $C^{3-6}H_2$), 1.57–1.65 m (2H, C^7H_2), 2.31–2.42 m (4H, C^8H_2, C^2H_2), 9.80 br.s (COOH). ^{13}C NMR spectrum, δ, ppm: 17.00 t (C^8H_2), 24.70 t (C^3H_2), 25.24 t (C^7H_2), 28.41 t (C^6H_2) 28.81 t (C^5H_2), 29.09 t (C^4H_2), 33.99 t (C^2H_2), 119.76 s (CN), 177.77 s (COOH).

***(R)*-3-Hydroxynonanoic acid (XI)**. R_f 0.14 (hexane–*tert*-butyl methyl ether, 1 : 1). $[\alpha]_D^{20}$ –5° (CH_2Cl_2, *c* 1.4). IR spectrum, ν, cm^{-1}: 3420 (OH), 1701 (C=O). NMR spectra are identical to previously described [10].

9,9',9"-(Propane-1,2,3-triyltrioxy)tris(9-oxononanoic acid) (XII). R_f 0.07 (hexane–*tert*-butyl methyl ether, 1 : 1). ^{1}H NMR spectrum, δ, ppm: 1.15–1.77 m (12H, $3C^3H_2$, $3C^7H_2$), 1.16–1.40 m (18H, $9CH_2$, $3C^{4-6}H_2$), 2.15 t (6H, $3C^8H_2$, *J* 6.7 Hz), 2.35 t (6H, $3C^2H_2$, *J* 6.6 Hz), 4.15 d.d (2H, $C^{1'}H^A{}_2$, $C^{3'}H^A{}_2$, *J* 11.9, 4.1 Hz), 4.28 d.d (2H, $C^{1'}H^B{}_2$, $C^{3'}H^B{}_2$, *J* 11.9, 5.7 Hz), 5.27–5.32 m (1H, $C^{2'}H$), 9.81 s (3H, COOH). ^{13}C NMR spectrum, δ, ppm: 24.71 t ($3C^7H_2$), 24.88 t ($3C^3H_2$), 28.84 t ($3C^6H_2$), 29.16 t ($3C^5H_2$), 29.63 t ($3C^4H_2$), 33.91 t ($3C^8H_2$), 34.59 t ($3C^2H_2$), 62.06 t ($C^{1'}H_2$, $C^{3'}H_2$), 68.06 d ($C^{2'}H$), 172.63 s ($C^{9'}O_2$), 173.26 s (C^9O_2, $C^{9''}O_2$), 178.77 s (3COOH).

The ozonolysis of (+)-3-carene (**III**) after chromatographing the residue (1.32 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) afforded 0.5 g (27%) of ketoacid **XIII** and 0.60 g (30%) of hydroxyimino acid **XIV**.

[2,2-Dimethyl-3-(2-oxopropyl)cyclopropyl]acetic acid (XIII). R_f 0.19 (hexane–*tert*-butyl methyl ether, 4 : 1), $[\alpha]_D^{20}$ –14° (CH_2Cl_2, *c* 2.23). IR spectrum, ν, cm^{-1}: 3331 (OH), 1712 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H, *cis*-CH_3), 0.98 d.d (1H, C^1H, *J* 10.2, 6.3 Hz), 1.09 d.d (1H, C^3H, *J* 10.2, 5.1 Hz), 1.10 s (3H, *trans*-CH_3), 2.04 s (3H, CH_3CO), 2.11–2.20 m (2H, $C\underline{H}_2COOH$), 2.30–2.38 m (2H). ^{13}C NMR spectrum, δ, ppm: 14.12 q (*cis*-CH_3), 17.09 s (C^2), 20.90 d (C^1H), 22.27 d (C^3), 28.41 q (*trans*-CH_3), 30.78 t ($\underline{C}H_2CO\cdot CH_3$), 30.78 q ($CH_2CO\underline{C}H_3$), 32.96 t ($\underline{C}H_2COOH$), 177.02 s (COOH), 212.38 s (C=O).

{3-[(2*E*)-2-(Hydroxyimino)propyl]-2,2-dimethylcyclopropyl}acetic acid (XIV). R_f 0.17 (hexane–*tert*-butyl methyl ether, 4 : 1). IR spectrum, ν, cm^{-1}: 3334 (OH), 1714 (C=O), 1633 (C=N). ^{1}H NMR spectrum, δ, ppm: 0.76 d.d.d (1H, C^1H, *J* 9.2, 7.2, 1.8 Hz), 0.94 d.d.d (1H, C^3H, *J* 9.2, 7.7, 2.1 Hz), 0.95 s (3H, *cis*-CH_3), 1.09 s (3H, *trans*-CH_3), 1.93 s (3H, CH_3), 2.27–2.33 m (1H, $C\underline{H}^ACO_2H$), 2.28 d.d (1H, $C\underline{H}^ACNOH$, *J* –13.1, 5.2 Hz), 2.31 d.d (1H, $C\underline{H}^BCNOH$, *J* –13.1, 7.1 Hz), 2.48 d.d (1H, $C\underline{H}^BCO_2H$, *J* 15.7, 6.9 Hz), 8.00 br.s (2H, 2OH). ^{13}C NMR spectrum, δ, ppm: 13.49 q ($\underline{C}H_3C$=NOH), 14.90 q (CH_3), 17.42 s (C^2), 21.79 d (C^1H), 22.38 d (C^3H), 28.53 q (CH_3), 29.66 t ($\underline{C}H_2CO\cdot OH$), 30.88 t ($\underline{C}H_2CNOH$), 158.74 s (C=NOH), 175.05 s (COOH).

The ozonolysis of (–)-α-pinene (**IV**) after chromatographing the residue (1.60 g) (SiO_2, hexane–*tert*-butyl methyl ether, 20 : 1→1 : 1) provided 0.61 g (33%) of ketoacid **XV**, 0.4 g (24%) of ketonitrile **XVI**, and 0.43 g (22%) of hydroxyimino acid (**XVII**).

(3-Acetyl-2,2-dimethylcyclobutyl)acetic acid (XV) [11]. R_f 0.21 (hexane–*tert*-butyl methyl ether, 4 : 1), $[\alpha]_D^{20}$ –39.8° (CH_2Cl_2, *c* 0.8164). IR spectrum, ν, cm^{-1}: 3330 (OH), 1715 (C=O). ^{1}H NMR spectrum δ, ppm: 0.83 s (3H, *cis*-CH_3), 1.29 s (3H, *trans*-CH_3), 1.83–1.92 m (1H, *cis*-C^4H_2), 1.94 d.d (1H, *trans*-C^4H_2, *J* 10.1,

10.7 Hz), 2.03 s (3H, CH_3CO), 2.12–2.36 m (1H, C^1H, 2H, CH_2COOH), 2.83 d.d (1H, C^3H, *J* 10.1, 7.5 Hz), 9.70 br.s (1H, COOH). ^{13}C NMR spectrum, δ, ppm: 16.78 q (*cis*-CH_3), 22.12 t (C^4H_2), 29.68 q (CH_3CO), 30.26 q (*trans*-CH_3), 35.95 t ($\underline{C}H_2COOH$), 37.10 d (C^1H), 42.94 s (C^2), 52.88 d (C^3H), 178.28 s (COOH), 208.27 s (C=O).

(3-Acetyl-2,2-dimethylcyclobutyl)acetonitrile (XVI) [11]. R_f 0.33 (hexane–*tert*-butyl methyl ether, 3 : 2), $[\alpha]_D^{20}$ –131.16° ($CHCl_3$, *c* 1.02) [11]. IR spectrum, ν, cm^{-1}: 2220 (CN). ^1H NMR spectrum, δ, ppm: 0.95 s (*cis*-CH_3), 1.40 s (*trans*-CH_3), 1.94 d.t (1H, *cis*-C^4H_2, *J* –11.0, 9.5 Hz), 2.03 d.t (1H, *trans*-C^4H_2, *J* –11.0, 8 Hz), 2.08 s [3H, $CH_3C(O)$], 2.32 d.d (1H, CH_2CN, *J* 15.2, 8.00 Hz), 2.32 d.d (1H, CH_2CN, *J* 15.2, 7.8 Hz), 2.37–2.43 m (1H, C^1H), 2.90 d.d (1H, C^3H, *J* 9.5, 8.0 Hz). ^{13}C NMR spectrum, δ, ppm: 16.54 q (CH_3), 17.25 t (CH_2), 22.89 t (C^4H_2), 29.86 q (CH_3), 30.27 q [$\underline{C}H_3C(O)$], 38.16 d (C^1H), 42.97 s (C^2), 53.81 d (C^3H), 118.56 s (CN), 206.63 s (C=O).

{3-[(*E*)-2-(Hydroxyimino)ethyl]-2,2-dimethylcyclobutyl}acetonitrile (XVII). R_f 0.30 (hexane–*tert*-butyl methyl ether, 3 : 2). IR and NMR spectra are identical to previously described [5].

Treatment of peroxide products of olefins I–IV ozonolysis with semicarbazide hydrochloride. The reaction mixture was flushed with argon, and at stirring and cooling to 0°C 3.90 g (35.0 mmol) of NH_2·C(O)$NHNH_2$·HCl per one double bond was added, the reaction mixture was stirred at room temperature till the absence of peroxides (iodine-starch test), CH_2Cl_2 and AcOH were distilled off, the residue was dissolved in $CHCl_3$ (150 mL), the solution was washed with water (4 × 15 mL), dried with Na_2SO_4, and evaporated.

By the ozonolysis of 1-nonene **(I)** we obtained 1.37 g (95%) of octanoic acid (**V**).

The ozonolysis of castor oil (**II**) after chromatographing the residue (9.84 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) yielded 4.05 g (79%) of hydroxyacid **XI** and 5.12 g (85%) of triacylglycerol **XII**.

The ozonolysis of (+)-3-carene (**III**) after chromatographing the residue (1.63 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) afforded 0.815 g (44%) of ketoacid **XIII**.

The ozonolysis of (–)-α-pinene (**IV**) after chromatographing the residue (2.03 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) provided 1.75 g (83%) of ketoacid **XV**.

Ozonolysis of olefins I–IV in the system CH_2Cl_2–AcOH–H_2O. Through a solution of 10.0 mmol of olefin in a mixture of 20 mL of CH_2Cl_2, 5.7 mL of AcOH, and 1.8 mL of H_2O at 0°C was bubbled the ozone-oxygen mixture in a calculated amount: 1 mol of O_3 per 1 mol of the double bond.

Treatment of peroxide products of olefins I–IV ozonolysis in the system CH_2Cl_2–AcOH–H_2O with hydroxylamine hydrochloride. The reaction mixture was flushed with argon, and at stirring and cooling to 0°C 2.43 g (35.0 mmol) of NH_2OH·HCl per one double bond was added, the reaction mixture was stirred at room temperature till the absence of peroxides (iodine-starch test), CH_2Cl_2 and AcOH were distilled off, the residue was dissolved in $CHCl_3$ (150 mL), the solution was washed with water (4 × 15 mL), dried with Na_2SO_4, and evaporated.

The ozonolysis of 1-nonene (**I**) after chromatographing the residue (1.30 g) afforded 0.61 g (42%) of octanoic acid (**V**), 0.35 g (28%) of nitrile **VI**, and 0.26 g (18%) of octanaloxime (**VIII**).

Octanaloxime (VIII). R_f 0.53 (hexane–*tert*-butyl methyl ether, 2 : 1). IR and NMR spectra are identical to previously described [5].

The ozonolysis of castor oil (**II**) after chromatographing the residue (9.46 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) gave 2.52 g (50%) of mononitrile **X**, 3.48 g (68%) of hydroxyacid **XI**, 1.68 g (30%) of triacylglycerol **XII**.

The ozonolysis of (+)-3-carene (**III**) after chromatographing the residue (1.30 g) (SiO_2, hexane–*tert*-butyl methyl ether, 20 : 1→1 : 1) afforded 0.50 g (25%) of hydroxyimino acid **XIV**, 0.23 g (13%) of hydroxyiminonitrile **XVIII**, 0.3 g (15%) of dioxime **XIX**, and 0.04 g (2%) of ketoacid **XIII**.

{3-[(*E*)-2-(Hydroxyimino)propyl]-2,2-dimethylcyclopropyl}acetonitrile (XVIII). R_f 0.32 (hexane–*tert*-butyl methyl ether, 3 : 2). IR spectrum, ν, cm^{-1}: 2220 (CN), 1642 (C=N). ^1H NMR spectrum, δ, ppm: 0.78 d.d.d (1H, C^1H, *J* 9.1, 7.4, 1.8 Hz), 0.96 d.d.d (1H, C^3H, *J* 9.1, 7.7, 2.1 Hz), 0.93 s (3H, *cis*-CH_3), 1.30 s (3H, *trans*-CH_3), 1.95 s [3H, $CH_3C(NOH)$], 2.00–2.20 m (2H, CH_2CN), 2.29–2.35 m (2H), 6.80 br.s (1H, NOH). ^{13}C NMR spectrum, δ, ppm: 14.63 q (CH_3), 14.70 q [C(NOH)$\underline{C}H_3$], 17.51 s (C^2H), 17.66 t ($\underline{C}H_2CN$), 22.14 d (C^1H), 22.68 d (C^3H), 28.35 q (CH_3), 30.62 t ($\underline{C}H_2CNOH$), 118.57 s (CN), 158.21 s (C=NOH).

{3-[(*E*)-2-(Hydroxyimino)propyl]-2,2-dimethylcyclopropyl}ethanaloxime (XIX). R_f 0.26 (hexane–*tert*-butyl methyl ether, 4 : 1). IR spectrum, ν, cm^{-1}: 3272 (OH). ^{13}C NMR spectrum, δ, ppm: 14.10 q (CH_3), 14.63 q [C(NOH)$\underline{C}H_3$], 16.93 s (C^2H), 17.56 t ($\underline{C}H_2C$=NOH), 21.58 d (C^1H), 22.72 d (C^3H), 28.49 q (CH_3), 30.15 t ($\underline{C}H_2$CNOH), 151.59 s (CN), 157.13 s (C=NOH).

In ozonolysis of (–)-α-pinene (**IV**) after chromatographing the residue (1.70 g) (SiO_2, hexane–*tert*-butyl methyl ether, 20 : 1→1 : 1) we isolated 0.51 g of hydroxyiminonitrile (28%) **XX**, 0.51 g (26%) of hydroxyimino acid **XVII**, 0.43 g (21%) of dioxime **XXI**, 0.07 g (4%) of ketoacid **XV**.

{(1*S*,3*S*)-3-[(*E*)-2-(Hydroxyiminoethyl]-2,2-dimehylcyclobutyl}acetonitrile (XX). R_f 0.30 (hexane–*tert*-butyl methyl ether, 3 : 2). IR and NMR spectra are identical to previously described [5].

(1*E*)-{3-[(*E*)-2-(Hydroxyimino)ethyl]-2,2-dimethylcyclobutyl}acetaldoxime (XXI). R_f 0.25 (hexane–*tert*-butyl methyl ether, 4 : 1). IR spectrum, ν, cm^{-1}: 3330 (OH). ^1H NMR spectrum, δ, ppm: 0.82 s (3H, *cis*-CH_3), 1.18 s (3H, *trans*-CH_3), 1.70–1.78 m [2H, $C\underline{H}_2$CH(NOH)], 1.77 c [3H, $C\underline{H}_3$C(NOH)], 2.15–2.23 m (1H, *cis*-C^4H_2), 2.17–2.20 m (1H, C^1H), 2.32–2.44 m (1H, *trans*-C^4H_2), 2.55–2.64 m (1H, C^3H), 6.20 t (1H, C$\underline{H}$=NOH, *J* 6.1 Hz), 6.50 br.s (*trans*-NOH), 9.60 br.s (*trans*-NOH). ^{13}C NMR spectrum, δ, ppm: 16.48 q ($\underline{C}H_3$C=NOH), 16.86 q (CH_3), 17.32 t ($\underline{C}H_2$CH=N·OH), 24.58 t (C^4H_2), 30.19 q (CH_3), 39.46 d (C^1H), 42.85 s (C^2), 47.87 d (C^3H), 118.58 d (CH=NOH), 156.93 s (C=NOH).

Treatment of peroxide products of olefins I–IV ozonolysis in the system CH_2Cl_2–AcOH–H_2O with semicarbazide hydrochloride. The reaction mixture was flushed with argon, and at stirring and cooling to 0°C 3.90 g (35.0 mmol) of $NH_2C(O)NHNH_2$·HCl per one double bond was added, the reaction mixture was stirred at room temperature till the absence of peroxides (iodine-starch test), CH_2Cl_2 and AcOH were distilled off, the residue was dissolved in $CHCl_3$ (150 mL), the solution was washed with water (4 × 15 mL), dried with Na_2SO_4, and evaporated.

In ozonolysis of 1-nonene (**I**) after chromatogramphing the residue (1.4 g) we obtained 1.26 g (68%) of semicarbazone **VIII**, 0.12 g (8%) of octanoic acid (**V**).

Octanal semicarbazone (VIII). R_f 0.4 (hexane–*tert*-butyl methyl ether, 2 : 1), mp 99–100°C [9]. IR and NMR spectra are identical to previously described [12].

In ozonolysis of castor oil (**II**) after chromatographing the residue (9.32 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) we obtained 3.82 g (74%) of hydroxyacid **XI** and 4.66 g (77%) of triacylglycerol **XII**.

In ozonolysis of (+)-3-carene (**III**) after chromatographing the residue (1.22 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) we obtained 0.74 g (40%) of ketoacid **XIV**.

In ozonolysis of (–)-α-pinene (**IV**) after chromatographing the residue (1.61 g) (SiO_2, hexane–*tert*-butyl methyl ether, 5 : 1→1 : 1) we obtained 0.84 g (45%) of ketoacid **XV**.

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