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Transformations of Peroxide Olefin Ozonolysis Products under the Action of Hydroxylamine and Semicarbazide Hydrochlorides in Isopropyl Alcohol

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Abstract—Hydroxylamine and semicarbazide hydrochlorides were shown to be efficient as reducing agents toward peroxide products of ozonolysis of various olefins with different degrees of substitution. The rate of the transformations aldehyde→aldehyde oxime→nitrile→ester upon treatment of peroxides with hydroxylamine hydrochloride in isopropyl alcohol was lower than in methanol.

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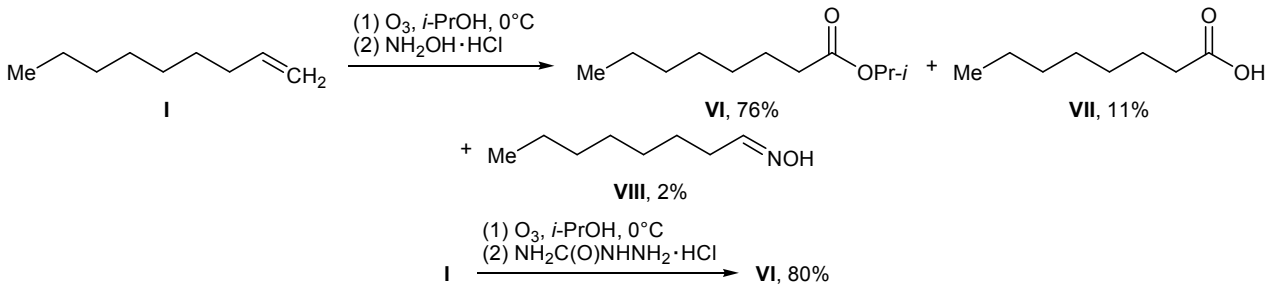
Hydroxylamine and semicarbazide hydrochlorides are known to effectively reduce peroxide olefin ozonolysis products in methanol to carbonyl compounds [1–3]. Depending on the substrate nature and conditions of treatment with hydroxylamine hydrochloride, the resulting aldehydes are converted into individual compounds or their mixtures along the aldehyde→aldehyde oxime→nitrile→methyl ester pathway [1, 2]. Treatment of peroxide olefin ozonolysis products with semicarbazide hydrochloride leads to methyl esters through the corresponding hemiacetals [2, 3].

In continuation of studies in this line we examined transformations of peroxide ozonolysis products derived from olefins with different degrees of substitution at the double bond under the action of hydroxylamine and semicarbazide hydrochlorides in isopropyl alcohol. As substrates we selected mono-, di-, and trisubstituted olefins, namely non-1-ene (**I**), cyclooctene (**II**), castor oil (**III**) (containing 90% of ricinoleic acid), Δ^3-carene (**IV**, *ee* 100%), and (–)-α-pinene (**V**, *ee* 86%).

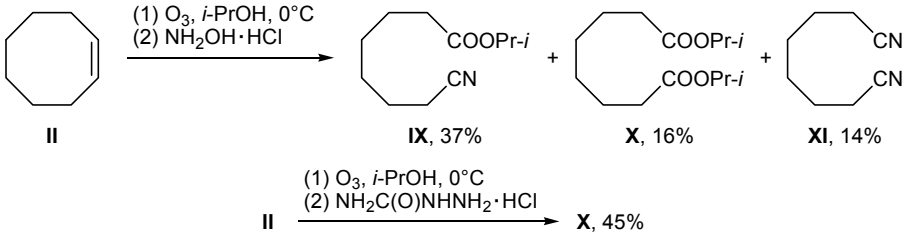
Ozonolysis of non-1-ene (**I**) in isopropyl alcohol at 0°C, followed by treatment of the peroxide ozonolysis products with hydroxylamine hydrochloride gave a mixture of compounds, among which the major product was isopropyl octanoate (**VI**). We also isolated from the reaction mixture octanal oxime (**VIII**) and octanoic acid (**VII**). Presumably, the latter was formed

Scheme 1.

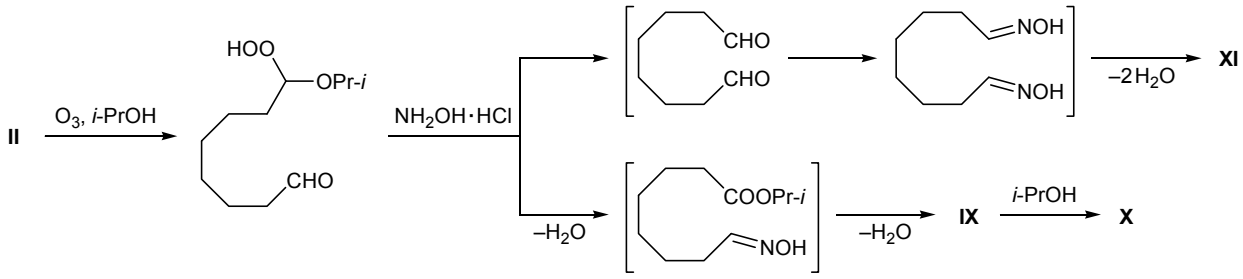


† Deceased.

Scheme 2.



Scheme 3.

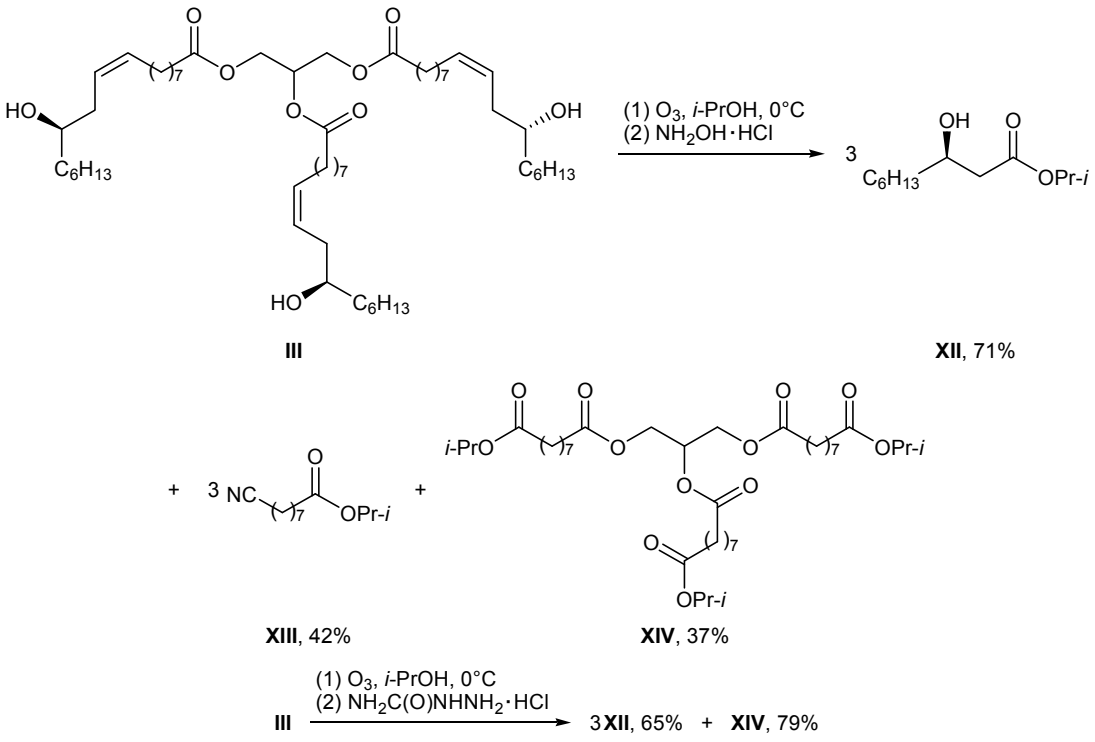


via hydrolysis of ester **VI** or the corresponding nitrile. Treatment of the ozonolysis products with semicarbazide hydrochloride afforded only ester **VI** (Scheme 1).

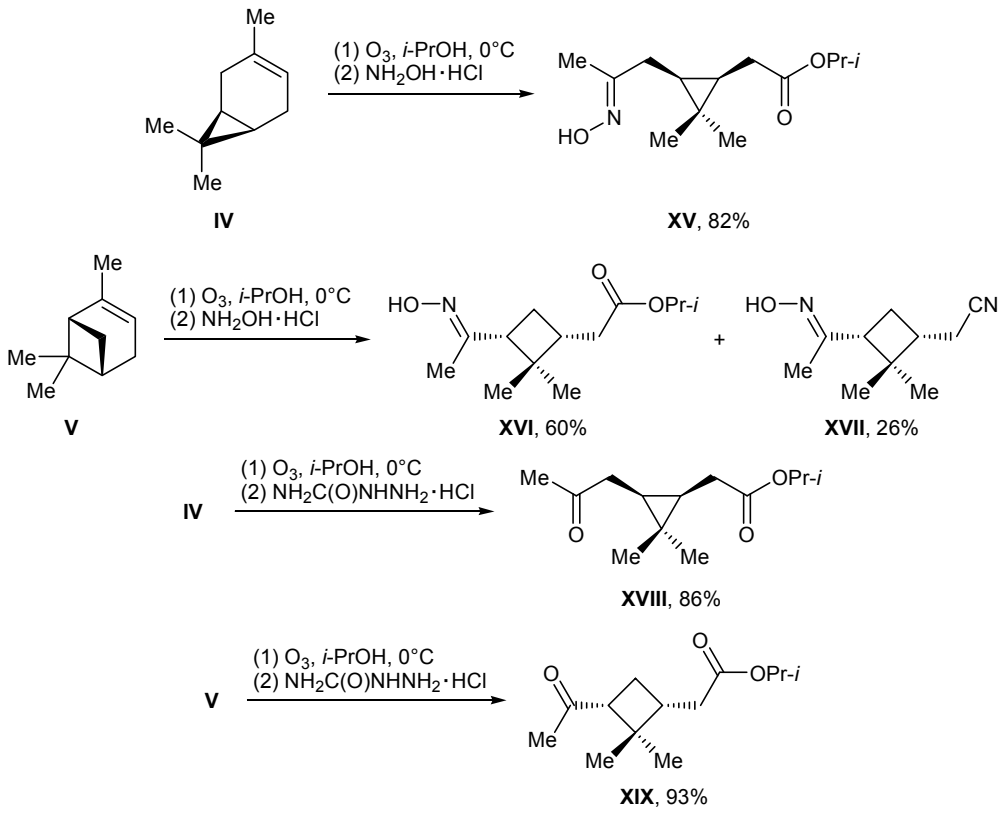
Under analogous conditions, from cyclooctene (**II**) in the presence of hydroxylamine hydrochloride we obtained cyano ester **IX**, diester **X**, and dinitrile **XI** (Scheme 2). The formation of nitriles **IX** and **XI** confirmed the mechanism proposed by us previously for the formation of ester group from nitrile upon treatment of peroxide olefin ozonolysis products with hydroxylamine in alcohol. The ozonolysis of cyclooctene (**II**) in isopropyl alcohol, followed by treatment with semicarbazide hydrochloride, gave 45% of diisopropyl octanedioate (**X**) (Scheme 2).

Scheme 3 illustrates possible reaction paths leading to compounds **IX**–**XI** upon treatment of peroxide

Scheme 4.



Scheme 5.



ozonolysis products of cyclooctene (**II**) with hydroxylamine hydrochloride.

By ozonolysis of ricinoleic acid triglyceride (**III**) and subsequent treatment of the ozonolysis products with hydroxylamine hydrochloride we obtained isopropyl (*R*)-3-hydroxynonanoate (**XII**), isopropyl 8-cyanooctanoate (**XIII**), and triglyceride **XIV**, which were isolated by column chromatography. When semicarbazide hydrochloride was used, the products were hydroxy ester **XII** and triester **XIV** (Scheme 4).

As we showed previously [4], treatment with hydroxylamine hydrochloride of the peroxide ozonolysis products obtained from Δ^3-carene (**IV**) and α-pinene (**V**) in methanol gives in high yield the corresponding keto ester oximes having *E*-configuration. The ozonolysis of olefins **IV** and **V** in isopropyl alcohol led to the formation of isopropyl esters **XV** and **XVI**, respectively. In addition, in the reaction with α-pinene (**V**) we isolated keto nitrile oxime **XVII** which is precursor of ester **XVI** (Scheme 5).

The reduction of peroxide ozonolysis products of Δ^3-carene (**IV**) and (+)-α-pinene (**V**) in methanol with semicarbazide hydrochloride produced the corresponding keto acid methyl esters [4]. Treatment of the peroxide ozonolysis products obtained from the same trisubstituted monoterpenes with semicarbazide hydrochloride in isopropyl alcohol afforded isopropyl esters **XVIII** and **XIX** in high yields (Scheme 5).

Thus, the results of the reactions of peroxide ozonolysis products derived from various olefins with hydroxylamine and semicarbazide hydrochlorides in isopropyl alcohol confirmed their efficiency as reducing agents ensuring transformation of peroxides to carbonyl compounds. In the presence of excess hydroxylamine hydrochloride, the resulting carbonyl compounds are converted into the corresponding oximes. The latter undergo dehydration to nitriles which are converted into isopropyl esters. The rate of the transformation aldehyde→aldehyde oxime→nitrile→isopropyl ester is lower than in methanol, as follows from the qualitative and quantitative compositions of the products. The use of isopropyl alcohol as solvent slows down transesterification of the peroxide ozonolysis products of castor oil upon treatment with hydroxylamine or semicarbazide hydrochloride.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer with Fourier transform. The NMR spectra were recorded on a Bruker AM-300

spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C; $CDCl_3$ was used as solvent, and tetramethylsilane, as internal reference. Signals in the ^{1}H NMR spectra were assigned, and coupling constants were determined, with the aid of double resonance and two-dimensional homonuclear correlation techniques (COSY H–H). The ^{13}C NMR spectra were recorded with broad-band decoupling from protons and *J* modulation (JMOD). GLC analyses were carried out on Chrom-5 [1.2-m column, stationary phase 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, stationary phase PEG-6000, oven temperature 50–200°C); carrier gas helium. TLC monitoring was performed using Sorbfil silica gel (Russia). The products were isolated by column chromatography on silica gel (70–230 μm; Lancaster, United Kingdom). The optical rotations were measured on a Perkin Elmer 241-MC polarimeter. The elemental compositions of all compounds were consistent with the assumed structures. The ozonizer efficiency was 40 mmol of O_3 per hour.

Treatment of peroxide ozonolysis products of olefins I–V with hydroxylamine hydrochloride. An ozone–oxygen mixture was bubbled through a solution of 10.0 mmol of compound **I**–**V** in 30 ml of anhydrous isopropyl ether cooled to 0°C until 1 mol of O_3 per mole of double bond was absorbed. The mixture was then purged with argon, 2.4 g (35.0 mmol) of $NH_2OH \cdot HCl$ per double bond was added under stirring at 0°C, and the mixture was stirred for 48 h (72 h in the reaction with **III**) at room temperature until peroxide compounds disappeared according to iodine–starch test. The solvent was distilled off, the residue was dissolved in 150 ml of chloroform, and the solution was washed with brine (4×15 ml), dried over Na_2SO_4, and evaporated.

Ozonolysis of non-1-ene (I). The product mixture, 1.65 g, was subjected to column chromatography on silica gel using first hexane–*tert*-butyl methyl ether (20:1 to 1:1) and then chloroform as eluents to isolate 1.41 g (76%) of isopropyl octanoate (**VI**), 0.16 g (11%) of octanoic acid (**VII**), and 0.03 g (2%) of octanal oxime (**VIII**).

Isopropyl octanoate (VI). R_f 0.75 (hexane–*t*-BuOMe, 2:1). IR spectrum (KBr): ν 1730 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, C^{8}H$_3$, *J* = 6.6 Hz), 1.19 d [6H, CH(C**H**$_3$)$_2$], 1.20–1.38 m (6H, 4-H, 5-H, 6-H), 1.41–1.52 m (2H, 7-H), 1.54–1.70 m (2H, 3-H), 2.32 t (2H, 2-H, *J* = 7.1 Hz), 4.90 sept [1H, C**H**(CH$_3$)$_2$, *J* = 6.0 Hz]. ^{13}C NMR spectrum, δ_C, ppm: 13.92 q (C^8), 21.68 d [CH(**C**H$_3$)$_2$], 22.48 t (C^7), 26.47 t (C^3), 28.48 t (C^5), 29.38 t (C^4), 30.90 t (C^6), 34.59 t (C^2), 67.27 d [**C**H(CH$_3$)$_2$], 173.49 s (C=O).

Octanoic acid (VII). R_f 0.25 (hexane–*t*-BuOMe, 2:1). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, C^{8}H$_3$, *J* = 6.6 Hz), 1.20–1.37 m (6H, 4-H, 5-H, 6-H), 1.43–1.58 m (2H, 7-H), 1.56–1.69 m (2H, 3-H), 2.24 t (2H, 2-H, *J* = 6.7 Hz), 11.45 br.s (1H, OH). The IR and ^{13}C NMR spectra of compound **VII** were identical to those reported in [5].

Octanal oxime (VIII). R_f 0.53 (hexane–*t*-BuOMe, 2:1). IR spectrum (KBr): ν 1633 cm^{-1} (C=N). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, C^{8}H$_3$, *J* = 6.7 Hz), 1.18–1.38 m (6H, 4-H, 5-H, 6-H), 1.40–1.52 m (2H, 7-H), 1.52–1.72 m (2H, 3-H), 2.18 d.t (2H, 2-H, *J* = 6.3, 7.1 Hz), 2.41 t (1H, 1-H, *J* = 6.1 Hz), 11.42 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 13.89 q (C^8), 22.46 t (C^7), 24.76 t (C^2), 28.86 t (C^3), 29.22 t (C^5), 29.35 t (C^4), 31.55 t (C^6), 151.85 d (C^1).

Ozonolysis of cyclooctene (II). The product mixture, 1.36 g, was subjected to column chromatography on silica gel using first hexane–*tert*-butyl methyl ether (20:1 to 1:1) and then chloroform as eluents to isolate 0.73 g (37%) of ester **IX**, 0.41 g (16%) of diester **X**, and 0.19 g (14%) of dinitrile **XI**.

Isopropyl 7-cyanoheptanoate (IX). R_f 0.49 (hexane–*t*-BuOMe, 2:1). IR spectrum (KBr), ν, cm^{-1}: 2245 (C≡N), 1724 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.18 d (6H, CH$_3$, *J* = 6.2 Hz), 1.28–1.52 m (4H, 4-H, 5-H), 1.56–1.72 m (4H, 3-H, 6-H), 2.23 t (2H, 2-H, *J* = 7.4 Hz), 2.34 t (2H, 7-H, *J* = 7.0 Hz), 4.92 sept [1H, C**H**(CH$_3$)$_2$, *J* = 6.2 Hz]. ^{13}C NMR spectrum, δ_C, ppm: 16.98 t (C^7), 21.77 q (CH$_3$), 24.55 t (C^3), 25.11 t (C^6), 28.12 t (C^4), 28.23 (C^5), 34.37 t (C^2), 67.44 d [**C**H(CH$_3$)$_2$], 119.44 s (CN), 173.18 s (C=O).

Diisopropyl octanedioate (X). R_f 0.75 (hexane–*t*-BuOMe, 2:1). IR spectrum (KBr): ν 1734 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 1.19 d (12H, CH$_3$, *J* = 6.3 Hz), 1.27–1.46 m (4H, 4-H, 5-H), 1.50–1.68 m (4H, 3-H, 6-H), 2.26 t (4H, 2-H, 7-H, *J* = 7.4 Hz), 4.98 sept [2H, C**H**(CH$_3$)$_2$, *J* = 6.3 Hz]. ^{13}C NMR spectrum, δ_C, ppm: 21.76 q (CH$_3$), 24.75 t (C^3, C^6), 28.65 t (C^4, C^5), 34.52 t (C^2, C^7), 67.29 d [**C**H(CH$_3$)$_2$], 173.18 s (C=O).

Octanedinitrile (XI). R_f 0.25 (hexane–*t*-BuOMe, 2:1). IR spectrum (KBr): ν 2245 cm^{-1} (C≡N). The ^{1}H NMR spectrum was identical to that reported previously [6]. ^{13}C NMR spectrum, δ_C, ppm: 16.98 t (C^2, C^7), 25.02 t (C^3, C^6), 27.78 t (C^4, C^5), 119.65 s (CN).

Ozonolysis of castor oil (III). The product mixture, 12.5 g, was subjected to chromatography on silica gel using hexane–*tert*-butyl methyl ether (4:1) as eluent to isolate 4.61 g (71%) of ester **XII**, 2.66 g (42%) of **XIII**, and 2.66 g (37%) of **XIV**.

Isopropyl (*R*)-3-hydroxynonanoate (XII). R_f 0.52 (hexane–*t*-BuOMe, 2:1). IR spectrum (KBr), ν, cm^{-1}: 3420 (OH), 1740 (C=O), 1140 (C–O). ^1H NMR spectrum, δ, ppm: 0.89 t (3H, C^9H_3, J = 6.7 Hz), 1.18 d [6H, $CH(CH_3)_2$, J = 6.3 Hz], 1.10–1.42 m (6H, 5-H, 6-H, 7-H), 1.25–1.40 m (1H, 4-H), 1.42–1.65 m (3H, 4-H, 8-H), 2.20 br.s (1H, OH), 2.41 d.d (1H, 2-H, J = 16.4, 3.3 Hz), 2.28 d.d (1H, 2-H, J = 16.4, 4.4 Hz), 3.86–4.0 m (1H, 3-H), 4.93 sept [1H, $CH(CH_3)_2$, J = 6.3 Hz]. ^{13}C NMR spectrum, δ_C, ppm: 13.95 q (C^9), 21.70 q [$CH(CH_3)_2$], 22.94 t (C^8), 25.36 t (C^5), 28.80 t (C^6), 31.70 t (C^7), 36.52 t (C^4), 41.66 t (C^2), 67.20 d [$CH(CH_3)_2$], 67.92 d (C^3), 172.43 s (C=O).

Isopropyl 8-cyanooctanoate (XIII). R_f 0.20 (hexane–*t*-BuOMe, 2:1). IR spectrum (KBr), ν, cm^{-1}: 2220 (C≡N), 1745 (C=O). ^1H NMR spectrum, δ, ppm: 1.15–1.40 m (8H, 3-H, 4-H, 5-H, 6-H), 1.19 d [6H, $CH(CH_3)_2$, J = 6.4 Hz], 1.55–1.68 m (2H, 7-H), 2.28–2.40 m (4H, 2-H, 8-H), 4.99 sept [1H, $CH(CH_3)_2$]. ^{13}C NMR spectrum, δ_C, ppm: 17.00 t (C^8), 21.78 q [$CH(CH_3)_2$], 24.68 t (C^3), 25.20 t (C^7), 28.36 t (C^6), 28.65 t (C^5), 28.80 t (C^4), 33.89 t (C^2), 67.38 d [$CH(CH_3)_2$], 119.69 s (CN), 173.18 s (C=O).

Propane-1,2,3-triyl tris(9-isopropoxy-9-oxononanoate) (XIV). R_f 0.14 (hexane–*t*-BuOMe, 2:1). ^1H NMR spectrum, δ, ppm: 1.15–1.77 m (12H, 3-H, 7-H), 1.16–1.40 m (18H, 4-H, 5-H, 6-H), 1.22 d (18H, CH_3, J = 6.3 Hz), 2.15 t (6H, 8-H, J = 6.7 Hz), 2.35 t (6H, 2-H, J = 6.6 Hz), 4.15 d.d (2H, 1′-H, 3′-H, J = 11.9, 4.1 Hz), 4.28 d.d (2H, 1′-H, 3′-H, J = 11.9, 5.7 Hz), 5.01 sept [3H, $CH(CH_3)_2$, J = 6.3 Hz], 5.27–5.32 m (1H, 2′-H). ^{13}C NMR spectrum, δ_C, ppm: 21.78 q (CH_3), 24.71 t (C^7), 24.88 t (C^3), 28.84 t (C^6), 29.16 t (C^5), 29.63 t (C^4), 33.91 t (C^8), 34.59 t (C^2), 62.06 t ($C^{1'}$, $C^{3'}$), 67.34 d [$CH(CH_3)_2$], 68.06 d ($C^{2'}$), 172.63 s (2′-OC=O), 173.18 s (C^9), 173.26 s (1′-OC=O, 3′-OC=O).

Ozonolysis of Δ^3-carene (IV). By chromatography on silica gel using hexane–*tert*-butyl methyl ether (4:1) as eluent we isolated 1.99 g (82%) of isopropyl {3-[(2*E*)-2-(hydroxyimino)propyl]-2,2-dimethylcyclopropyl}acetate (**XV**). R_f 0.53 (hexane–*t*-BuOMe, 3:2), $[\alpha]_D^{20}$ = +0.8° (CH_2Cl_2, c = 0.30). IR spectrum (KBr), ν, cm^{-1}: 3334 (OH), 2870 (C–H), 1730 (C=O), 1640 (C=N). ^1H NMR spectrum, δ, ppm: 0.84 d.d.d (1H, 1-H, J = 9.5, 7.4, 4.0 Hz), 1.03 s (3H, *cis*-CH_3), 1.05 d.d.d (1H, 3-H, J = 9.5, 7.1, 5.0 Hz), 1.18 s (3H, *trans*-CH_3), 1.31 s [6H, $CH(CH_3)_2$, J = 6.3 Hz], 1.97 s [3H, $CH_3C(NOH)$], 2.24 d.d (1H, 3-CH_2, J = 13.2, 5.0 Hz), 2.32 d.d (1H, 1-CH_2, J = 10.4, 5.6 Hz), 2.38 d.d (1H, 3-CH_2, J = 13.2, 7.1 Hz), 2.54 d.d (1H, 1-CH_2, J = 10.4, 4.0 Hz), 5.02 sept [1H, $CH(CH_3)_2$], 8.30 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 12.29 q (CH_3C=NOH), 13.79 q (*cis*-CH_3), 16.31 s (C^2), 20.71 d (C^1), 21.73 d (C^3), 21.97 q [$CH(CH_3)_2$], 27.45 q (*trans*-CH_3), 29.31 t (3-CH_2), 29.88 t (1-CH_2), 66.52 d [$CH(CH_3)_2$], 157.02 s (C=NOH), 172.0 s (C=O).

Ozonolysis of (–)-α-pinene (V). The product mixture, 1.90 g, was subjected to chromatography on silica gel using first hexane and then hexane–*tert*-butyl methyl ether (20:1 to 1:1) as eluents to isolate 1.45 g (60%) of oxime **XVI** and 0.46 g (26%) of nitrile **XVII**.

Isopropyl {(1*S*,3*S*)-3-[(1*E*)-*N*-hydroxyethanimidoyl]-2,2-dimethylcyclobutyl}acetate (XVI). R_f 0.57 (hexane–*t*-BuOMe, 3:2). IR spectrum (KBr), ν, cm^{-1}: 3300 (OH), 2887 (C–H), 1637 (C=N). ^1H NMR spectrum, δ, ppm: 0.84 s (3H, *cis*-CH_3), 1.21 d (3H, *trans*-CH_3), 1.22 d [6H, $CH(CH_3)_2$, J = 6.3 Hz], 1.80 s [3H, $CH_3C(NOH)$], 1.88 d.t (1H, 4-H_{cis}, J = –10.8, 7.4 Hz), 2.02 d.t (1H, 4-H_{trans}, J = 10.8, 10.6 Hz), 2.20 d.d (1H, 1-CH_2, J = 14.6, 7.3 Hz), 2.21–2.45 m (1H, 1-H), 2.28 d.d (1H, 1-CH_2, J = –14.6, 6.3 Hz), 2.59 d.d (1H, 3-H, J = 10.6, 7.4 Hz), 4.98 sept [1H, $CH(CH_3)_2$, J = 6.3 Hz], 8.30 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 14.52 q [$CH_3C(NOH)$], 16.74 q (*cis*-CH_3), 21.79 q [$CH(CH_3)_2$], 24.52 t (C^4), 30.15 q (*trans*-CH_3), 35.54 t (CH_2), 38.24 d (C^1), 42.83 s (C^2), 47.61 d (C^3), 67.51 d [$CH(CH_3)_2$], 157.35 s [$C(NOH)CH_3$], 172.40 s (C=O).

{(1*S*,3*S*)-3-[(1*E*)-*N*-Hydroxyethanimidoyl]-2,2-dimethylcyclobutyl}acetonitrile (XVII). R_f 0.30 (hexane–*t*-BuOMe, 3:2). IR spectrum (KBr), ν, cm^{-1}: 2220 (C≡N), 1640 (C=N). ^{13}C NMR spectrum, δ_C, ppm: 14.52 q [$CH_3C(NOH)$], 16.77 q (CH_3), 17.25 t (C), 24.86 t (C^4), 29.86 q (CH_3), 38.14 d (C^1), 42.59 s (C^2), 47.85 d (C^3), 118.69 s (CN), 156.93 s (C=NOH).

Treatment of peroxide products of ozonolysis of olefins I–V with semicarbazide hydrochloride. An ozone–oxygen mixture was bubbled through a solution of 10.0 mmol of olefin **I**–**V** in 30 ml of anhydrous isopropyl alcohol on cooling to 0°C until 1 mol of O_3 per mole of double bond was absorbed. The mixture was purged with argon, 3.90 g (35.0 mmol) of semicarbazide hydrochloride per double bond was added under stirring at 0°C, and the mixture was

stirred for 48 h (72 h in the reaction with **III**) at room temperature until peroxide compounds disappeared according to iodine–starch test. The solvent was distilled off, the residue was dissolved in 150 ml of chloroform, and the solution was washed with brine (4×15 ml), dried over Na_2SO_4, and evaporated.

By ozonolysis of non-1-ene (**I**) we obtained 1.48 g (80%) of isopropyl octanoate (**VI**), R_f 0.75 (hexane–*t*-BuOMe, 2:1); the IR and NMR spectra of the product were identical to those given above.

By ozonolysis of cyclooctene (**II**) we obtained 1.16 g (45%) of diester **X**, R_f 0.60 (hexane–*t*-BuOMe, 2:1); the IR and NMR spectra of the product were identical to those given above.

By ozonolysis of castor oil (**III**) we obtained 13.52 g of a mixture of products which was subjected to chromatography on silica gel using hexane–*tert*-butyl methyl ether (4:1) as eluent to isolate 4.24 g (65%) of ester **XII** and 5.73 g (79%) of triglyceride **XIV**, whose IR and NMR spectra were identical to those given above.

Ozonolysis of Δ^3-carene (IV). By chromatography on silica gel using hexane–*tert*-butyl methyl ether (4:1) as eluent we isolated 1.91 g (86%) of isopropyl [(1*R*,3*S*)-2,2-dimethyl-3-(2-oxopropyl)cyclopropyl]-acetate (**XVIII**), R_f 0.58 (hexane–*t*-BuOMe, 3:2). IR spectrum (KBr), ν, cm^{-1}: 1735 (C=O, ester), 1718 (C=O, ketone). ^{1}H NMR spectrum, δ, ppm: 0.91 d.d (1H, 1-H, J = 10.2, 7.4 Hz), 0.96 s (3H, *cis*-CH_3), 1.03 d.d.d (1H, 3-H, J = 10.2, 5.2, 6.2 Hz), 1.18 s (3H, *trans*-CH_3), 1.28 s [6H, CH(C**H**$_3$)$_2$, J = 6.3 Hz], 2.21 s (3H, CH_3), 2.23 d.d (1H, 1-CH_2, J = –11.2, 3.2 Hz), 2.4 d.d (1H, 3-CH_2, J = 15.8, 6.2 Hz), 2.31 d.d (1H, 3-CH_2, J = 15.8, 5.2 Hz), 2.31 d.d (1H, 1-CH_2, J = 11.2, 7.4 Hz), 4.95 sept [1H, C**H**$(CH_3)_2$, J = 6.4 Hz]. ^{13}C NMR spectrum, δ_C, ppm: 14.90 q (*cis*-CH_3), 17.17 s (C^2), 21.04 d (C^1), 21.58 d (C^3), 21.97 q [CH(**C**H_3)$_2$)], 28.3 q (*trans*-CH_3), 29.60 t (3-CH_2), 30.01 t (1-CH_2), 30.99 q [$CH_2C(O)$**C**H_3], 68.79 d [**C**H$(CH_3)_2$], 177.78 s (1-CH_2**C**=O), 209.10 s (3-CH_2**C**=O).

Ozonolysis of (–)-α-pinene (V). By chromatography on silica gel using hexane–*tert*-butyl methyl ether (4:1) as eluent we isolated 2.25 g (93%) of isopropyl [(1*S*,3*S*)-3-acetyl-2,2-dimethylcyclobutyl]-acetate (**XIX**), R_f 0.60 (hexane–*t*-BuOMe, 3:2), $[\alpha]_D^{20}$ = –31.6° (CH_2Cl_2, c = 0.61). IR spectrum (KBr), ν, cm^{-1}: 1735 (C=O, ester), 1718 (C=O, ketone). ^{1}H NMR spectrum, δ, ppm: 0.88 s (3H, *cis*-CH_3), 1.23 d [6H, CH(C**H**$_3$)$_2$, J = 6.3 Hz], 1.34 s (3H, *trans*-CH_3), 1.83 d.t (1H, 4-H_{cis}, J = –11.0, 9.7 Hz), 1.92 d.t (1H, 4-H_{trans}, J = –11.0, 7.9 Hz), 2.08 s (3H, CH_3CO), 2.15 d.d (1H, 1-CH_2, J = 15.40, 8.00 Hz), 2.21 d.d (1H, 1-CH_2, J = 15.40, 8.40 Hz), 2.25–2.31 m (1H, 1-H), 2.79 d.d (1H, 3-H, J = 9.80, 7.90 Hz), 5.02 m [1H, C**H**$(CH_3)_2$]. ^{13}C NMR spectrum, δ_C, ppm: 17.18 q (CH_3), 21.70 q [CH(**C**H_3)$_2$], 22.87 t (C^4), 29.54 q [**C**$H_3C(O)$], 30.08 q (CH_3), 34.56 t (C), 43.07 s (C^2), 54.03 d (C^3), 57.62 d (C^1), 67.46 d [**C**H$(CH_3)_2$], 172.41 s (1-CH_2**C**=O), 208.02 s (3-C=O).

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