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Ozonolysis of Alkenes and Study of Reactions of Polyfunctional Compounds: LXVIII.* Investigation of Transformations of Peroxide Products of Olefins Ozonolysis Treated with Hydroxylamine Hydrochloride

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Abstract—Hydroxylamine hydrochloride efficiently reduces peroxide products of olefins ozonolysis into carbonyl compounds. Depending on the substrate character, solvent, and the treatment conditions the arising aldehydes transformed along the route aldehyde→aldoxime→nitrile→ester into individual compounds or their mixtures, or give the corresponding acetals.

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The conversion of peroxide products of olefins ozonolysis into carbonyl compounds (aldehydes, ketones) is extensively used in preparative organic synthesis. The most often applied traditional reducers are dimethyl sulfide, triphenylphosphine, thiourea, sodium bisulfite, zinc powder, sodium thiosulfate, lower metal salts, and alkali metals iodides. The chemoselective hydrogenation catalyzed by platinum group metals is an efficient method for ozonoysis products reduction [2, 3]. Oxidative decomposition of ozonolysis products into carboxylic acids and their derivatives is carried out under the action of oxygen at elevated temperature or under the treatment of oxidation catalysts (ozone, compounds of variable valence metals, amino acids etc.). Other oxidants employed are silver oxide suspension in an alkaline solution, potassium permanganate, chromic and nitric acids, and especially often hydrogen peroxide in the presence of selenium dioxide [2–5].

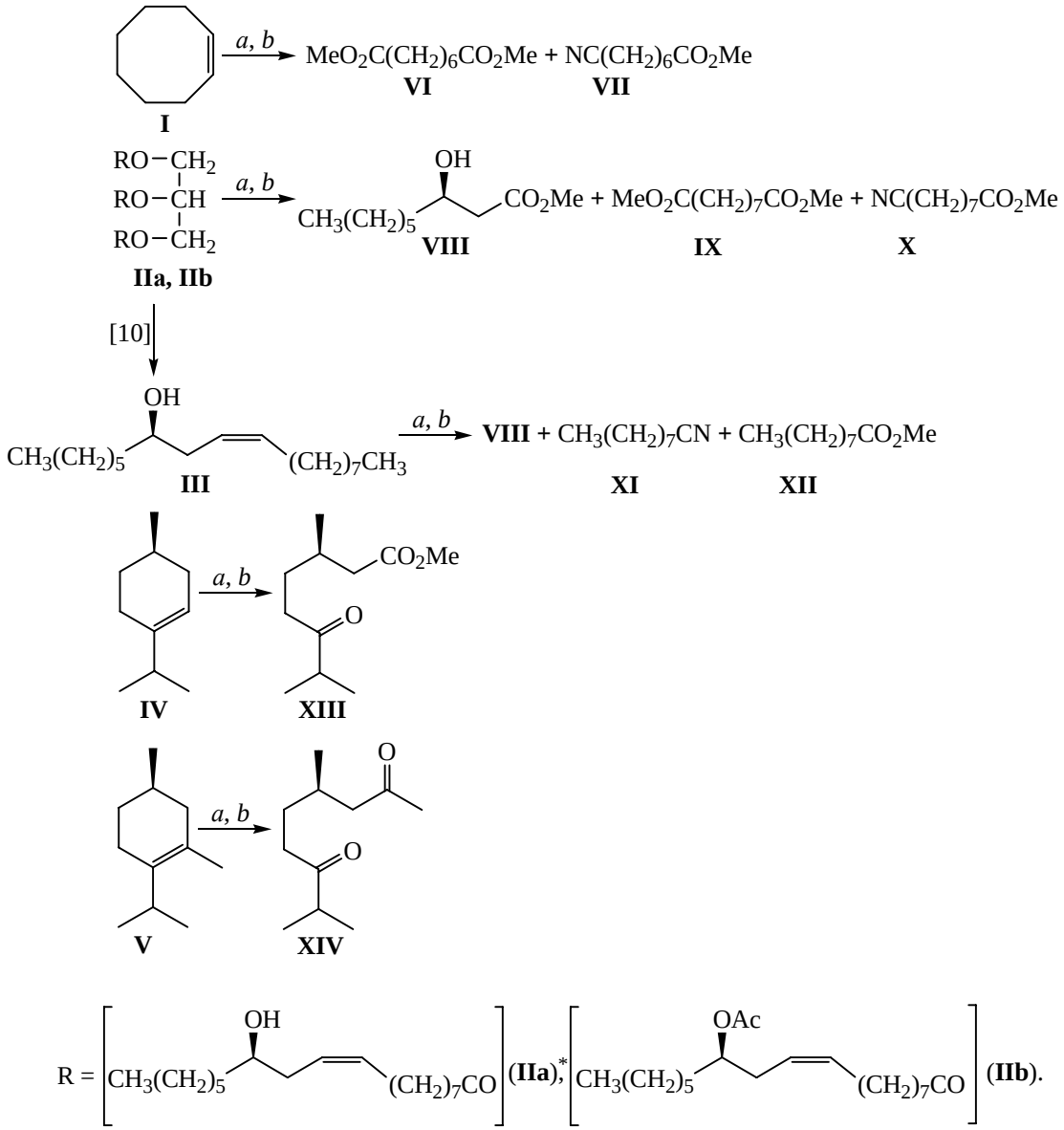
We applied hydroxylamine hydrochloride to the conversion of peroxide ozonolysis products obtained from a series of olefin compounds. The reactions were performed in methanol and depending on the substrate character we obtained aldehydes [6], aldoxime [7, 8], and ester [9]. It was presumable that at the treatment with hydroxylamine hydrochloride in methanol the ozonolysis products first formed aldehydes converted further into aldoximes which suffered cleavage by Beckmann reaction into the corresponding nitriles whose cyano group transformed into methoxycarbonyl group.

To prove this assumption we carried out the reaction with hydroxylamine hydrochloride of peroxide ozonolysis products obtained from a series of disubstituted (**I, IIa, IIb,** and **III**), trisubstituted (**IV**), and tetrasubstituted (**V**) olefins (Scheme 1).

The oxidation of cyclooctene (**I**) with equimolar amount of ozone in methanol at 0°C followed by the treatment with hydroxylamine hydrochloride (0°C, 0.5 h; boiling, 10 h) provided a mixture of dimethyl octanedioate (**VI**) and nitriloester **VII**, 1:1. A similar treatment of the castor oil (**IIa**) (~85% of ricinoleic acid) and its acetate **IIb** led to the formation of mixtures of hydroxyester **VIII**, dimethyl nonanedioate (**IX**), and its monocyano derivative **X**, 1.6:4.9:1 and 1:4.6:2.4 respectively. The ozonolysis of homoallyl alcohol **III** obtained from castor oil (**IIa**) [10] after the treatment with the hydroxylamine hydrochloride yielded a mixture of the same hydroxyester **VIII**, nitrile **XI**, and methyl nonanoate **XII** in a ratio 1:1:1.6. The treatment of peroxide products of olefins **IV** and **V** ozonolysis confirmed the low reactivity of keto group as compared with aldehyde

* For Communication LXVII, see [1].

Scheme 1.



Reagents: (*a*) O_3/MeOH; (*b*) NH_2OH·HCl/MeOH.

function with respect to hydroxylamine. These cycloolefins were in high yield converted into formerly described [11, 12] ketoester **XIII** and diketone **XIV**.

The identification of compounds obtained was performed by NMR spectroscopy and GC-MS method.

Compound **XI** was identified as nonanenitrile. The interpretation of its mass spectrum was performed applying a hunt system HPChem Station that used the spectral library NISTO2. The identity index of the registered spectrum and that from the library (002243-27-8 CAS) was 95%.

The main feature of the mass spectrum of compound **XI** with a linear carbon chain [13] is the presence of two homologous ion series [here and hereinafter on Schemes *m/z* (I_{rel}, %)]: (1) $[N{\equiv}CC_nH_{2n}]^+$ 40 (8), 64 (48), 68 (11), 82 (94), 96 (98), 110 (47), 124 (10); (2) $[N{\equiv}CC_nH_{2n+1}]^+$ 41 (100), 55 (42), 69 (38), 83 (58), 111 (11).

In the mass spectra of compounds **VII** and **X** both homologous ion series typical of nitriles were registered: (1) $[N{\equiv}CC_nH_{2n}]^+$, (2) $[N{\equiv}CC_nH_{2n+1}]^+$ (Scheme 2). Besides ion peaks $[(CH_2)_nCOOMe]^+$, *m/z* 59, 73, 87, 101, 115 were present characteristic of carboxylic acids esters

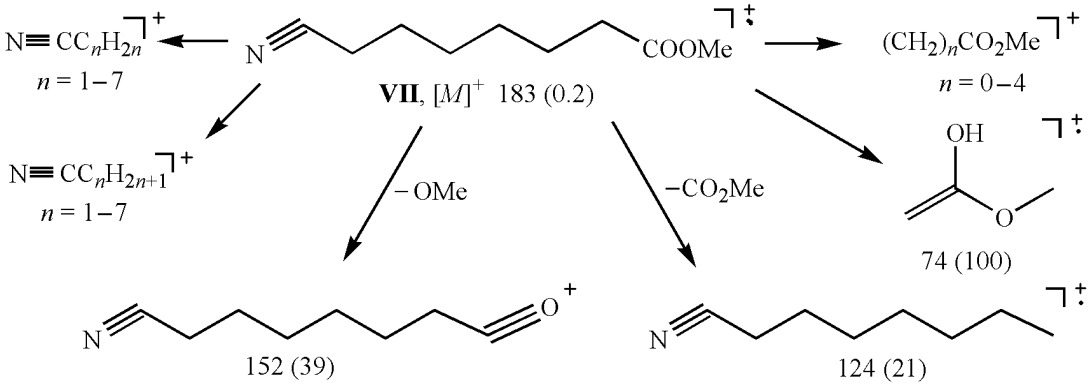
[13]. The main decomposition directions of esters molecular ions are well known to occur by bond cleavage on both sides of the carbonyl group [13, 14]. Therewith the acyl ions peaks $[M - OMe]^+$, *m/z* (I_{rel}, %): 138 (57) (**VII**); 152 (39) (**X**) are as a rule more intensive than those of ions $[M - COOMe]^+$ 110 (31) (**VII**); 124 (21) (**X**). The maximum abundance was found for the rearranged fragments with odd electrons number $[CH_2C(OH)OMe]^{+\cdot}$, *m/z* 74 (100%) (Scheme 2). Thus the presence of nitrile and ester functions separated by methylene groups in compounds **VII** and **X** results in the formation of diagnostic ion series.

In the spectrum of methyl (3*R*)-3-hydroxynonanoate (**VIII**) peaks of ions belonging to alcohol series were observed $[(CH_2)_nOH]^+$, [*m/z* (I_{rel}, %): 31 (10), 45 (7), 59 (8), 87 (8), 101 (4), 115 (2)], and a peak $[CH_2C(OH)OMe]^{+\cdot}$ *m/z* (I_{rel}, %): 74 (33) typical of aliphatic acids methyl esters. The position of the hydroxy group is established from the known fact [13] that the point of the carbon chain branching is preferable for bond cleavage. The most abundant peak in the mass spectrum of compound **VIII** was that of ion *m/z* 103 (100%), and its formation was possible only for the 3-hydroxy-substituted derivative (Scheme 3).

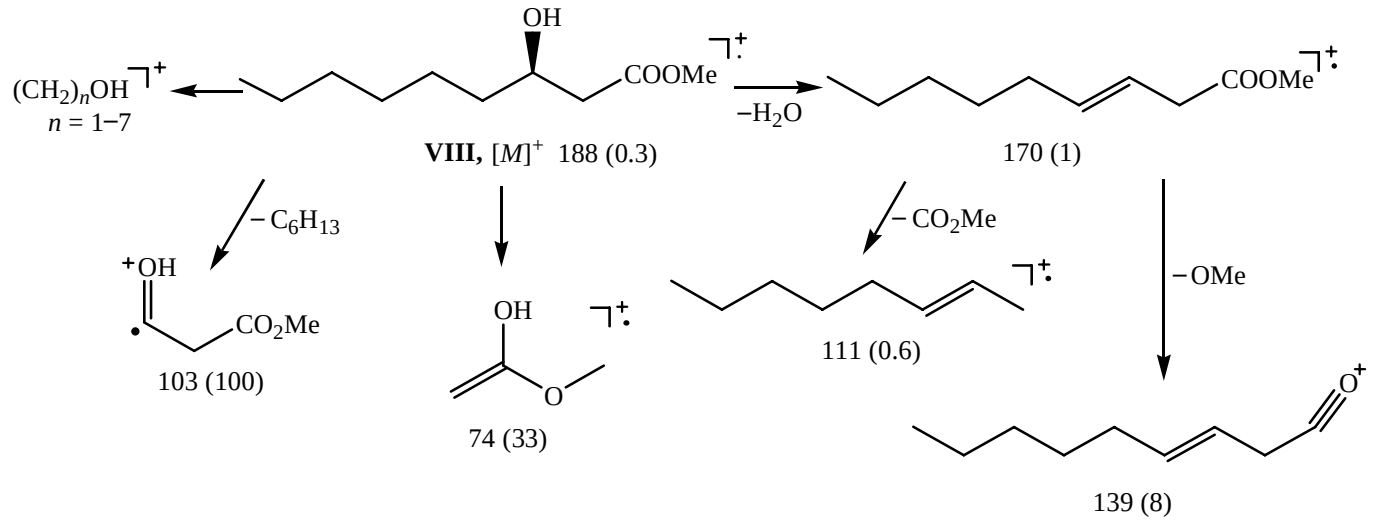
The presence in the molecule of compound **VIII** of hydroxy and ester groups governed the directions of the molecular ion decomposition. The alcohols [13] characteristically eliminate water [*m/z* 170 (1) ($M - H_2O$)], methyl esters, methoxy and methoxycarbonyl groups, occurring after water elimination (Scheme 3). As was presumed [13], the intensity of acyl ion peak [*m/z* 139 (8)] was higher than that of hydrocarbon ion peak [*m/z* 111 (0.6)].

The successive treatment of the ozonolysis product of castor oil (**IIa**) in dichloromethane with hydroxylamine hydrochloride (boiling, 10 h) and methanol in the presence of *p*-toluenesulfonic acid (boiling, 6 h) resulted in a single product of low molecular weight, hydroxy-

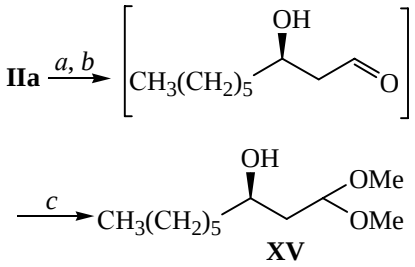
Scheme 2.



Scheme 3.



Scheme 4.



Reagents: (*a*) O_3/CH_2Cl_2; (*b*) $NH_2OH·HCl/CH_2Cl_2$; (*c*) MeOH/TsOH.

acetal **XV**. These findings show, that the hydroxylamine hydrochloride acts just as a reducer of the ozonides most probably formed under the conditions producing the precursor of compound **XV**, (3*R*)-3-hydroxynonanal.

Thus it follows from the previous data [6–9] and the findings reported here that the hydroxylamine hydrochloride is an efficient reducer of peroxide products of olefins ozonolysis to carbonyl compounds. Depending on the substrate, solvent [15], and the treatment conditions the arising aldehydes undergo further transformations along the route aldehyde → aldoxime → nitrile → ester, or form the corresponding acetal.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker AMX-300 [at operating frequencies 300.13 (^{1}H) and 75.47 MHz (^{13}C)], TMS reference. IR spectra were recorded on a spectrophotometer Specord M-82 from thin films. Chromatographic analysis was carried out on a chromatograph GC-9A Shimadzu (quartz capillary column 25 m long, stationary phase OV-101, oven temperature 80–260°C). Mass spectra were measured on a system with coupled chromatograph, mass spectrometer, and computer (chromatograph HP 5890 with a mass-selective detector HP 5972A, chromatographic column HP 5MS 25 m × 0.25 mm, column temperature conition: 40°C, isotherm 5 min, heating rate 8 deg/min tillO 250^{O}C, injector temperature 260^{O}C, mass spectrum scanning: 1 s per spectrum from 28 to 300 a.m.u.). The optical rotation was measured on a polarimeter Perkin-Elmer 241-MC. TLC control was carried out on SiO_2 Sorbfil grade (Russia). For column chromatography was used SiO_2 (70–230) Lancaster (GB). Ozonizer capacity 40 mmol of O_3 per hour.

Ozonolysis of olefins I, IIa, IIb, III–V. Through a solution of 10 mmol of olefin in 50 ml of anhydrous MeOH at 0°C was bubbled a mixture of ozone with oxygen till amount of consumed O_3 was 1 mol per 1 mol of double bonds. The reaction mixture was flushed with argon, then at stirring at 0°C was added within 0.5 h 2.4 g (35 mmol) of $NH_2OH·HCl$ per 1 mol of double bonds. The reaction mixture was boiled till disappearance of peroxides (10 h), MeOH was distilled off, the residue was diluted with CH_2Cl_2, washed with H_2O, the organic layer was dried over Na_2SO_4, and evaporated.

Ozonolysis of cyclooctene (I). We obtained 1.0 g of reaction product containing according to GLC dimethyl octandioate (**VI**) and methyl 7-cyanoheptanoate (**VII**) in a ratio 1:1.

Methyl 7-cyanoheptanoate (VII). Mass spectrum, *m/z* (I_{rel}, %): 169 (0.4) $[M]^+$, 138 (57), 110 (31), 109 (24), 97 (18), 96 (57), 83 (58), 82 (24), 74 (100), 69 951), 68 (13), 55 (48), 54 (19), 41 (48), 40 (7). NMR and IR spectra of compounds **VI** and **VII** are identical to published data [16].

Ozonolysis of castor oil (IIa). We obtained 10.1 g of reaction product containing according to GLC methyl (3*R*)-3-hydroxynonanoate (**VIII**), dimethyl nonanedioate (**IX**), and methyl 8-cyanooctanoate (**X**) in a ratio 1.6 : 4.9:1.

Methyl (3*R*)-3-hydroxynonanoate (VIII). $[\alpha]_D^{20}$ –198.7° (*c* 0.08, CH_2Cl_2). IR spectrum, ν, cm^{-1}: 1140 (C–O), 1740 (C=O), 3420 (OH). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 0.93 t (3H, CH_3, ^3J 7.0), 1.35 m (8H, $4CH_2$), 1.52 m (2H, H^4), 2.41 d.d (1H, H^{2A}, ^2J 15.1, ^3J 8.1), 2.50 d.d (1H, H^{2B}, ^2J 15.1, ^3J 4.8), 3.67 s (3H, CH_3), 3.98–4.03 m (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 13.32 q (C^9), 22.24 t (C^8), 25.21 t (C^5), 28.97 t (C^6), 31.56 t (C^7), 36.90 t (C^4), 41.96 t (C^2), 50.50 q (CH_3), 67.54 d (C^3), 171.89 s (C^1). Mass spectrum, *m/z* (I_{rel}, %): 188 (0.3) $[M]^+$, 170 (1), 139 (8), 138 (8), 111 (0.6), 115 (1), 113 (8), 103 (100), 97 (8), 96 (10), 87 (8), 74 (100), 59 (8), 45 (7), 31 (10).

Methyl 8-cyanooctanoate (X). IR spectrum, ν, cm^{-1}: 1745 (C=O), 2220 (C≡N). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 1.35 m (6H, $3CH_2$), 1.40–1.50 m (2H, H^7), 1.55–1.65 m (2H, H^3), 2.30 t (2H, H^2, ^3J 7.2), 2.46 t (2H, H^8, ^3J 7.0), 3.61 s (3H, CH_3). ^{13}C NMR spectrum, δ, ppm: 16.04 t (C^8), 24.47 t (C^3), 25.08 t (C^7), 28.57 t (C^4–C^6), 34.85 t (C^2), 50.42 q (CH_3), 120.00 (C^9), 173.03 s (C^1). Mass spectrum, *m/z* (I_{rel}, %): 183 (0.2) $[M]^+$, 152 (39), 124 (21), 123 (20), 110 (19), 111 (7), 98 (9), 97 (32), 96 (9), 83 (32), 82 (25), 74 (100), 69 (11), 68 (7), 59 (39), 54 (8), 41 (25), 40 (8).

Ozonolysis of castor oil acetate (IIb). We obtained 9.2 g of reaction product containing according to GLC methyl (3*R*)-3-hydroxynonanoate (**VIII**), dimethyl nonanedioate (**IX**), and methyl 8-cyanooctanoate (**X**) in a ratio 1:4.6:2.4.

Ozonolysis of (*Z*, 7*R*)-octadec-9-en-7-ol (III). We obtained 2.6 g of product containing according to GLC nonanenitrile (**XI**), methyl nonanoate (**XII**), and methyl (3*R*)-3-hydroxynonanoate (**VIII**) in a ratio 1:1.6:1.

Nonanenitrile (XI). IR spectrum, ν, cm^{-1}: 2230 (C≡N). ^1H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 0.94 t (3H, H^9, ^3J 7.0), 1.3–1.5 m (10H, $5CH_2$), 1.68 q (2H, H^3, ^3J 7.0), 2.50 t (2H, H^2, ^3J 7.0). ^{13}C NMR spectrum, δ, ppm: 13.39 q (C^9), 16.09 t (C^2), 22.32 t (C^8), 25.17 t (C^3), 29.06 q (C^4–C^6), 31.46 q (C^7), 92.41 s (C^1).

Ozonolysis of (1*R*)-menth-3-ene (IV). From compound **IV** prepared as described in [11] we obtained after chromatographic isolation (SiO_2, petroleum ether–methyl *tert*-butyl ether, 50:1, R_f 0.34) 1.30 g (65%) of methyl (3*R*)-3,7-dimethyl-6-oxooctanoate (**XIII**), $[\alpha]_D^{23}$ +9.50 (*c* 5.27, $CHCl_3$). IR and NMR spectra of compound **XIII** were identical to those published before [17].

Ozonolysis of (1*R*)-3-methylmenth-3-ene (V). From compound **V** prepared as described in [12] we obtained 1.59 g (86%) of (4*R*)-4,8-dimethyl-2,7-nonanedione (**XIV**), $[\alpha]_D^{20}$ +8.88° (*c* 2.5, $CHCl_3$). IR and NMR spectra of compound **XIV** were virtually identical to those published before [12].

(3*R*)-1,1-Dimethoxy-3-nonanol (XV). Through a solution of 1.0 g (1.1 mmol) of castor oil in 10 ml of CH_2Cl_2 at 0°C was bubbled a mixture of ozone with oxygen till amount of consumed O_3 was 3 mol per 1 mol of castor oil. The reaction mixture was flushed with argon, then diluted with 6 ml of CH_2Cl_2, and at stirring was added thereto at 0°C within 0.5 h 0.8 g (11.55 mmol) of $NH_2OH{\cdot}HCl$. The reaction mixture was boiled till disappearance of peroxides (10 h), then it was diluted with 100 ml of CH_2Cl_2, washed with H_2O, the organic layer was dried with Na_2SO_4 and evaporated. The residue (0.94 g was boiled for 6 h in 5 ml (112 mmol) of MeOH in the presence of a catalytic quantity of *p*-TsOH and evaporated. Then 100 ml of methyl *tert*-butyl ether was added, the solution was washed with H_2O, the organic layer was dried with Na_2SO_4 and evaporated. We obtained 0.86 g of reaction product that yielded after column chromatography (SiO_2, CH_2Cl_2, R_f 0.45) 0.42 g (98%) of (3*R*)-1,1-dimethoxy-3-nonanol (**XV**). IR and NMR spectra of compound **XV** were virtually identical to those published before [18].

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