ISSN 1070-4280, Russian Journal of Organic Chemistry, 2016, Vol. 52, No. 11, pp. 1708–1710. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © Yu.V. Legostaeva, L.R. Garifullina, I.S. Nazarov, A.A. Kravchenko, L.V. Kravchenko, G.Yu. Ishmuratov, 2016, published in Zhurnal Organicheskoi Khimii, 2016, Vol. 52, No. 11, pp. 1712–1714.

SHORT COMMUNICATIONS

Transformations of Peroxide Ozonolysis Products of Terminal Olefins Treated with Tosylhydrazide

Yu. V. Legostaeva, L. R. Garifullina, I. S. Nazarov, A. A. Kravchenko, L. V. Kravchenko, and G. Yu. Ishmuratov*

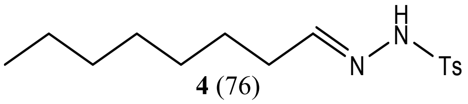
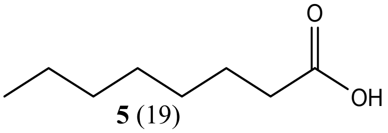
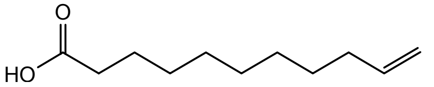
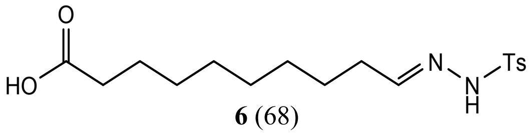
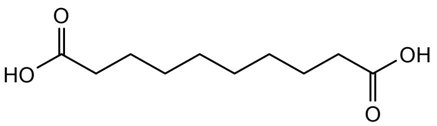
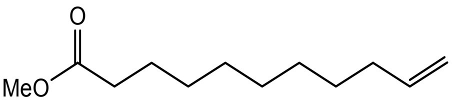
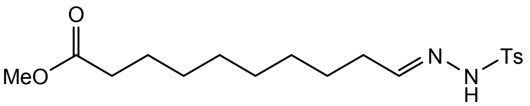
Ufa Institute of Chemistry, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Russia
**e-mail: insect@anrb.ru*

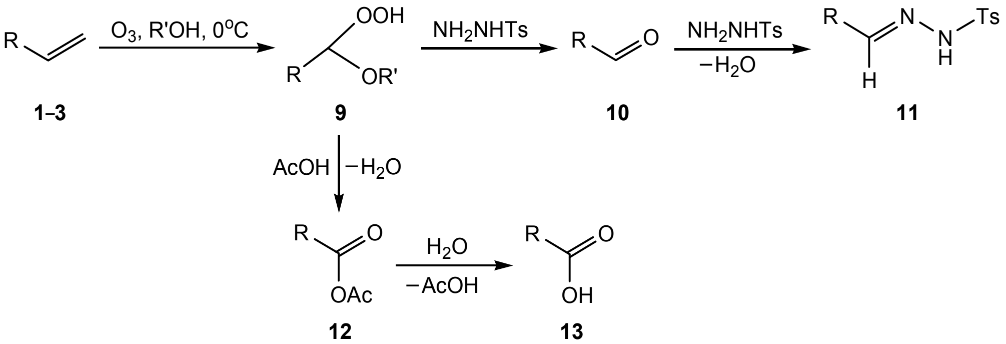
Received June 7, 2016

DOI: 10.1134/S1070428016110294

Hydrazine derivatives (semicarbazide, 2,4-dinitrophenylhydrazine, and also hydrochlorides of phenylhydrazine, semicarbazide, thiosemicarbazide) [1, 2] and hydroxylamine hydrochloride [1, 3] in solvents of diverse nature efficiently reduce the peroxide ozonolysis products of versatile substituted alkenes into carbonyl compounds and their *O*- or *N*-derivatives.

Transformation of peroxide ozonolysis products of alkenes **1–3** treated with tosylhydrazide in protic solvents at 0°C

Run no.	Unsaturated compound	Solvent	Reaction product (yield, %)
1	 **1**	MeOH	 **4** (76)
2	**1**	*i*-PrOH	**4** (70)
3	**1**	AcOH–CH_2Cl_2	**4** (42) +  **5** (19)
4	 **2**	MeOH	 **6** (68)
5	**2**	*i*-PrOH	**6** (82)
6	**2**	AcOH–CH_2Cl_2	 **7** (80)
7	 **3**	MeOH	 **8** (70)
8	**3**	*i*-PrOH	**8** (74)
9	**3**	AcOH–CH_2Cl_2	**8** (86)



R = C_7H_{15} (**1**), $C_8H_{16}COOH$ (**2**), $C_8H_{16}COOMe$ (**3**); R' = Me, *i*-Pr, Ac.

The ability of *p*-toluenesulfonic acid hydrazide to reduce efficiently peroxide ozonolysis products of terminal olefins in protic solvents underlies the one-pot ozonolysis synthesis of *nor*-analogs of tosylhydrazones. The results of the conversion of synthesized at 0°C peroxide ozonolysis products of terminal alkenes (1-nonene **1**, 10-undecenoic acid **2**, its methyl ester **3**) in protic solvents (MeOH, *i*-PrOH, AcOH–CH_2Cl_2) under the treatment with tosylhydrazide are compiled in the table.

The analysis of obtained experimental data makes it possible to conclude that we have developed a one-pot ozonolysis method of conversion of terminal alkenes in methanol and 2-propanol into the corresponding nor-analogous tosylhydrazones by using tosylhydrazi-de in the reduction stage of the intermediate peroxides. In the system AcOH–CH_2Cl_2 along with tosylhydrazo-nes the corresponding carboxylic acids formed as an admixture (run no. *5*) or as a single reaction product (run no. *6*) due apparently to the nature of the unsaturated compound.

The formation of tosylhydrazones **11** originates from the condensation of tosylhydrazide with aldehydes **10**, products of hydride reduction of primary formed hydroperoxides **9**. In the solvent system AcOH–CH_2Cl_2 apparently alongside the reduction of peroxides **9** their dehydration occurs affording mixed anhydrides **12**, which are hydrolyzed giving the corresponding carboxylic acids **13**.

Ozonolysis of alkenes (1–3). General procedure. Through a solution of 10.0 mmol of alkene **1–3** in 25 mL of anhydrous alcohol (MeOH or *i*-PrOH) or in a mixture of 25 mL of CH_2Cl_2 and 5.7 mL of AcOH at 0°C was bubbled the ozone-oxygen mixture till 10 mmol of ozone was consumed. The reaction mixture was flushed with argon. At 0°C 6.51 g (35.0 mmol) of $TsNHNH_2$ was added, the reaction mixture was stirred at room temperature till disappearance of preoxides (monitoring by the starch iodide test), the solvent was distilled off, the residue was dissolved in 150 mL of $CHCl_3$, washed with brine (4 × 35 mL), dried with Na_2SO_4, and evaporated.

4-Methyl-*N*′-octilidenebenzene-1-sulfonohydrazide (4). *a*. After chromatographing on SiO_2 (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) of 2.60 g of the reaction mixture obtained by ozonolysis of 1-nonene **1** in methanol, yield 2.25 g (76%). R_f 0.60 (eluent petroleum ether–*tert*-butyl methyl ether, 1 : 2). IR spectrum, ν, cm^{-1}: 3215 (NH). ^1H NMR spectrum, δ, ppm: 1.00–1.80 m (13H, $5CH_2$, CH_3, C^3H_2–C^8H_3), 2.40 s (3H, CH_3), 2.75–2.95 m (2H, C^2H_2), 7.10 m (CH=N), 7.45 d ($2H_{arom}$), 7.70 d ($2H_{arom}$), 7.95 br.s (NH). ^{13}C NMR spectrum, δ, ppm: 13.75 q (C^8H_3), 21.06 q (CH_3), 22.26 t (C^7H_2), 25.35 t (C^3H_2), 28.57 t (C^4H_2), 28.74 t (C^5H_2), 29.31 t (C^6H_2), 33.75 t (C^2H_2), 128.51 d ($2C_{arom}H$), 129.41 d ($2C_{arom}H$), 136.11 s (C–S), 144.62 s ($\underline{C}_{arom}$–CH_3), 165.28 d (C^1H=N). Found, %: C 60.67; H 8.30; N 9.51; S 10.71. $C_{15}H_{24}N_2O_2S$. Calculated, %: C 60.78; H 8.16; N 9.45; S 10.82.

b. After chromatographing on SiO_2 (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) of 2.40 g of the reaction mixture obtained by ozonolysis of 1-nonene **1** in 2-propanol, yield 2.01 g (70%).

c. After chromatographing on SiO_2 (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) of 1.7 g of the reaction mixture obtained by ozonolysis of 1-nonene **1** in a mixture AcOH–CH_2Cl_2, yield 1.26 g (42%) of hydrazone **4** and 0.27 g (19%) acid **5**.

Octanoic acid (5). R_f 0.25 (hexane–*tert*-butyl methyl ether, 2 : 1). IR, ^{13}C and ^1H NMR spectra are identical to previously described [4, 5].

10-[(2-Methylbenzene-1-sulfonyl)hydrazinylidene]decanoic acid (6). *a*. After chromatographing on SiO_2 (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) of 2.75 g of the reaction mixture obtained by ozonolysis of 10-undecenoic acid **2** in methanol, yield 2.40 g (68%). R_f 0.25 (eluent petroleum ether–*tert*-butyl methyl ether, 1 : 2). IR spectrum, ν, cm^{-1}: 3250 (NH, COOH), 1709 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.10–1.40 m (12H, 6CH$_2$), 1.45–1.60 m (2H, $\underline{\mathrm{CH_2}}$CH=N), 2.15–2.40 m (2H, CH$_2$CO$_2$), 2.40 s (3H, CH$_3$), 7.10 m (CH=N), 7.20 d (2H$_{\mathrm{arom}}$), 7.70 d (2H$_{\mathrm{arom}}$), 9.70–10.25 br.s (NH, OH). ^{13}C NMR spectrum, δ, ppm: 21.28 q (CH$_3$), 23.63, 24.64, 24.90, 28.92, 28.97, 29.14 t (6CH$_2$), 33.98 t ($\underline{\mathrm{C}}$H$_2$CH=N), 34.62 t ($\underline{\mathrm{C}}$H$_2$CO$_2$), 128.62 d (2C$_{\mathrm{arom}}$H), 129.54 d (2C$_{\mathrm{arom}}$H), 136.39 d (CH=N), 142.07 s (C–S), 143.91 s ($\underline{\mathrm{C}}_{\mathrm{arom}}$–CH$_3$), 179.11 s (CO$_2$H). Found, %: C 57.45; H 7.44; N 8.02; S 9.01. $C_{17}H_{26}N_2O_4S$. Calculated, %: C 57.60; H 7.39; N 7.90; S 9.05.

b. After chromatographing on SiO$_2$ (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) 3.22 g of the reaction mixture obtained by ozonolysis of 10-undecenoic acid **2** in 2-propanol, yield 2.87 g (82%).

1,10-Decandioic acid (7). After chromatographing on SiO$_2$ (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) of 1.88 g of the reaction mixture obtained by ozonolysis of 10-undecenoic acid **2** in a mixture AcOH–CH$_2$Cl$_2$, yield 1.62 g (80%). R_f 0.35 (hexane–*tert*-butyl methyl ether, 1 : 1), mp 130–132°C. IR spectrum, ν, cm^{-1}: 3180, 1703 (CO$_2$H). ^{1}H and ^{13}C NMR spectra are identical to previously described [6].

Methyl 10-[(2-methylbenzene-1-sulfonyl)hydrazinylidene]decanoate (8). *a*. After chromatographing on a SiO$_2$ (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) of 6.30 g of the reaction mixture obtained by ozonolysis of methyl 10-undecenoate **3** in methanol, yield 2.57 g (70%). R_f 0.41 (eluent petroleum ether–*tert*-butyl methyl ether, 1 : 2). IR spectrum, ν, cm^{-1}: 3226 (NH), 1738 (C=O), 1174–1234 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.10–1.40 m (12H, 6CH$_2$), 1.45–1.60 m (2H, $\underline{\mathrm{CH_2}}$CH=N), 2.18–2.30 m (2H, CH$_2$CO$_2$), 2.35 s (3H, CH$_3$), 3.50 s (3H, COOCH$_3$), 7.05 m (CH=N), 7.25 d (2H$_{\mathrm{arom}}$), 7.65 d (2H$_{\mathrm{arom}}$), 9.05 br.s (NH). ^{13}C NMR spectrum, δ, ppm: 21.17 q (CH$_3$), 25.33, 28.69, 28.74, 28.92, 29.07, 29.23 t (6CH$_2$), 33.66 t ($\underline{\mathrm{C}}$H$_2$CH=N), 33.77 t ($\underline{\mathrm{C}}$H$_2$CO$_2$), 51.21 q (CH$_3$O), 128.62 d (2C$_{\mathrm{arom}}$H), 129.28 d (2C$_{\mathrm{arom}}$H), 136.17 d (CH=N), 141.86 s (C–S), 144.47 s ($\underline{\mathrm{C}}_{\mathrm{arom}}$–CH$_3$), 174.15 s ($\underline{\mathrm{C}}O_2$Me). Found, %: C 58.55; H 7.71; N 7.76; S 8.62. $C_{18}H_{28}N_2O_4S$. Calculated, %: C 58.67; H 7.66; N 7.60; S 8.70.

b. After chromatographing on SiO$_2$ (eluent petroleum ether, petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1) of 3.10 g of the reaction mixture obtained by ozonolysis of compound **3** in 2-propanol yield 2.71 g (74%).

c. After chromatographing on SiO$_2$ (eluent petroleum ether–*tert*-butyl methyl ether, 10 : 1→1 : 1, MeOH) of 3.60 g of the reaction mixture obtained by ozonolysis of compound **3** in the mixture AcOH–CH$_2$Cl$_2$ yield 3.20 g (86%).

The study was performed using the equipment of the Center of joint busage "Chemistry" of the Ufa Institue of Chemistry of the Russian Academy of Sciences. IR spectra were recorded on a spectrophotometer IR Prestige-21 (Fourier Transform Spectrophotometer – Shimadzu) from thin films. NMR spectra were registered on a spectrometer Bruker AM-300 [operating frequencies 300 (^{1}H), 75.47 (^{13}C) MHz] in CDCl$_3$, internal reference TMS. GLC was performed on a chromatograph Chrom-5 [column 1.2 m long, stationary phase SE-30 (5%) on the carrier Chromaton N-AW-DMCS (0.16–0.20 mm), ramp 50–300°C], carrier gas helium. TLC monitoring was carried out on SiO$_2$ Sorbfil (Russia). For column chromatography SiO$_2$ (70–230) Lancaster (England) was used. The elemental analysis data of all studied compounds were in agreement with the calculated values. Ozonator output was 40 mmol O$_3$/h.

The study was carried out under the financial support of Bashkortostan Republic Government for young scientists and young scientific teams (grant no. 48 of 18.02.2016).

REFERENCES

1. Ishmuratov, G.Yu., Legostaeva, Yu.V., Botsman, L.P., and Tolstikov, G.A., *Russ. J. Org. Chem.*, 2010, vol. 46, p. 1593.
2. Ishmuratov, G.Yu., Legostaeva, Yu.V., Botsman, L.P., Muslukhov, R.R., Yakovleva, M.P., and Talipov, R.F., *Vestn. Bashkir. Univer.*, 2009, vol. 1, p. 27.
3. Ishmuratov, G.Yu., Shayakhmetova, A.Kh., Yakovleva, M.P., Legostaeva, Yu.V., Shitikova, O.V., Galkin, E.G., and Tolstikov, G.A., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 1114.
4. Ishmuratov, G.Yu., Legostaeva, Yu.V., Garifullina, L.R., Botsman, L.P., Muslukhov, R.R., and Tolstikov, G.A., *Russ. J. Org. Chem.*, 2014, vol. 50, p. 1075.
5. Arivazhagan, G., Parthipan, G., and Thenappan, T., *Spectrochim. Acta. A*, 2009, vol. 74, p. 860.
6. Yang, X. and Müller, K., *J. Mol. Struct.*, 2011, vol. 1006, p. 113.