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OZONOLYSIS OF RICINOLIC ACID DERIVATIVES AND TRANSFORMATIONS OF THE OZONOLYSIS PRODUCTS UNDER BARTON REACTION CONDITIONS

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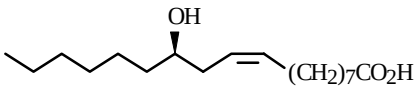
The possibility of functionalizing the alkyl part of ricinolic acid using the Barton reaction was investigated.

Key words: castor oil, ozonolysis, Barton reaction, ricinolic acid.

Ricinolic acid (**1**) is a promising substrate for preparing chiral polyfunctional compounds that can in turn act as convenient building blocks for the synthesis of organic compounds with more complicated structures because of its availability from castor oil and the presence of asymmetric C-12 with the *R*-configuration.



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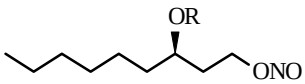
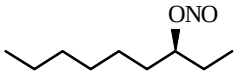


2, 3

2: R = Ac; **3:** R = CH_2Ph



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Herein we report results of investigations on expanding the synthetic potential of **1** by further functionalization of the chemically stable alkyl part of the molecule (C-12—C-18) using the Barton photochemical rearrangement of nitrites **2**-**4** in the key step.

In order to simplify the structure of starting **1**, it was fragmented by ozonolysis to produce the desired secondary monoacetate of diol **6**.

Compound **6** was prepared previously by ozonolysis of methyl *R*-12-acetoxyoctadec-9-enoic acid (**5**) in MeOH [1]. Under the conditions described for reduction of the intermediate peroxides ($NaBH_4$—MeOH) in the reaction mixture, the product of thermodynamic control, primary acetate **7** (ratio **6**:**7**, 1:2.5), dominated and was formed as a result of intramolecular *trans*-esterification. Furthermore, an equimolar amount of methyl 9-hydroxynonanoic acid (**8**), which is difficult to separate from monoesters **6** and **7**, was necessarily formed as a side product.

We investigated ways of optimizing the ozonolysis of ricinolic acid to synthesize secondary acetate **6**. The first approach was based on transformation of the carboxylic acid in **1** to a methyl, for which we used successive hydride reduction of castor oil **9** (ricinolic acid content ~85%) to diol **10** and subsequent deoxygenation of the primary hydroxyl in it through monotosylate **11**. The resulting chiral homoallyl alcohol **12** was converted to acetate **13** or benzyl ether **14**.

Ozonolytic cleavage of the double bond in **13**, carried out in CH_2Cl_2 in the presence of MeOH (2 equiv.) and subsequent treatment of the peroxide products with $NaBH_4$, gave a mixture (9:5:1) of acetates **6** and **7** and diol **15** with the desired **6** predominating. These were readily freed from the necessary ozonolysis—reduction product 1-nonanol (**16**) by vacuum distillation. Replacing $NaBH_4$ by KBH_4 increased the content of **6** (ratio **6**:**7**:**15**, 6:1.1:1). The best results (ratio **6**:**7**:**15**, 8.6:1.6:1) were obtained for ozonolysis in CH_2Cl_2 in the presence of two equivalents of AcOH per double bond and with the mild reducing agent $NaBH(OAc)_3$.

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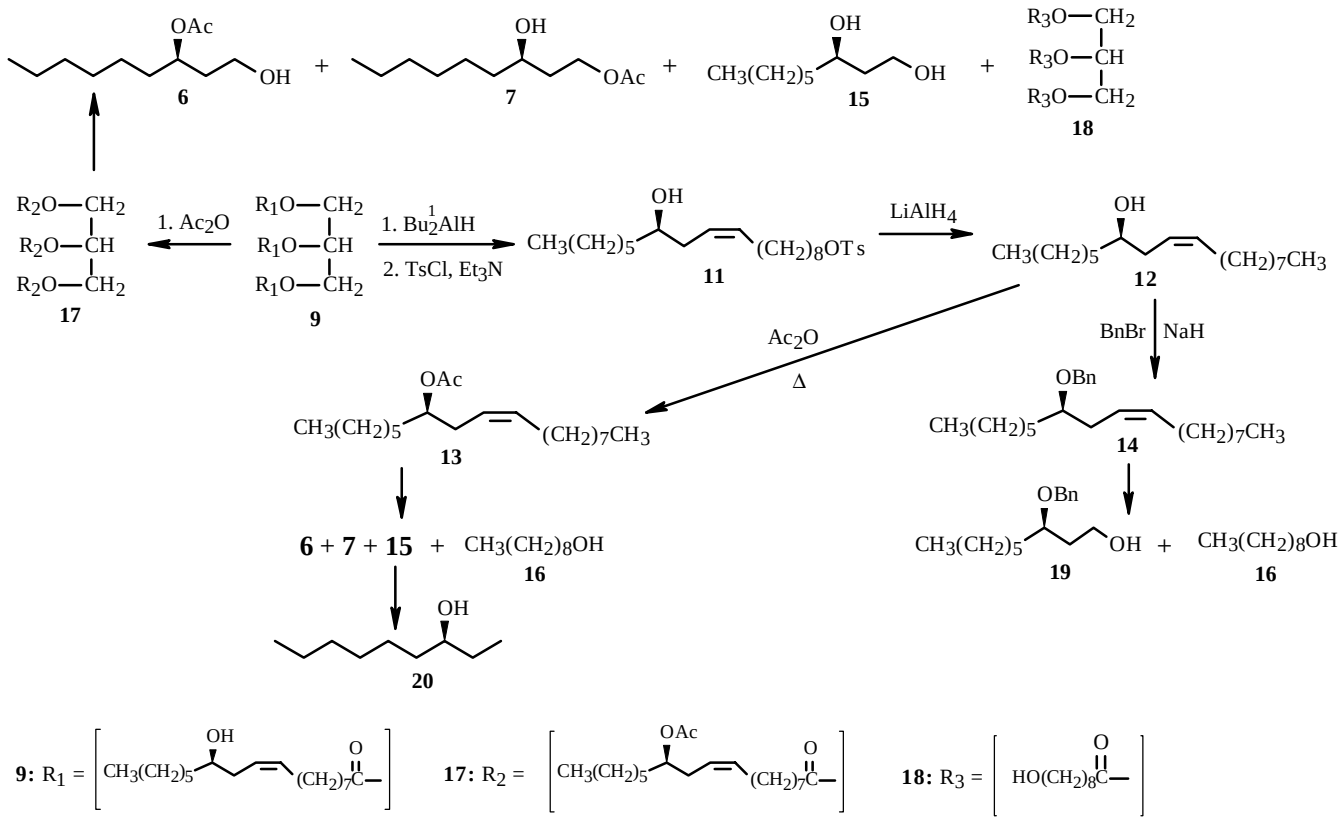


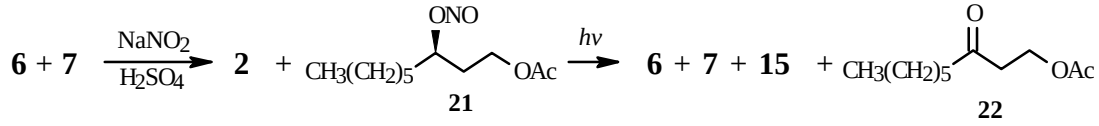
In order to extend the results to castor oil, we ozonolyzed **17**, which furthermore enabled the side product of highly polar triglyceride **18** to be easily removed. The highest yield of **6** (ratio **6**:**7**:**15**, 17.7:1.5:1) was obtained, like for **13**, for ozonolysis in CH_2Cl_2 in the presence of two equivalents of AcOH per one double bond and the use of $NaBH(OAc)_3$ as reductant.

Benzyl ether **14** was ozonolyzed without any complications to give the other key hydroxyether **19** in high yield.

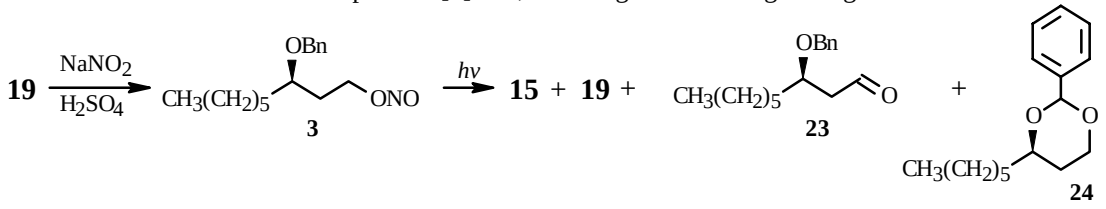
The precursor of alkylnitrate **4**, secondary alcohol **20**, was prepared from diol **15** by deoxygenation of the corresponding primary tosylate.

The Barton reaction of nitrites **2**-**4**, which were prepared from alcohols **6**, **19**, and **20** by the standard method [2], was carried out in an inert atmosphere and an aprotonic medium (benzene).

Photolysis of nitrites **2** and **21**, synthesized from a mixture (14:1) of hydroxyacetates **6** and **7**, produced the starting **6** and **7** in addition to diol **15**, which were isolated from the reaction mixture and identified. 1-Acetoxy-3-nonanone (**22**), the product of disproportionation or a "cage radical" reaction between the alkoxyradical and NO [3] that were formed from nitrite **21**, was also observed.



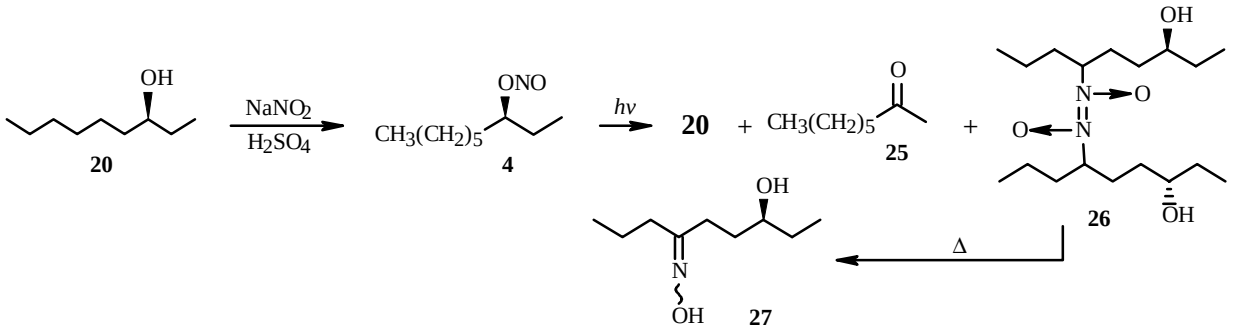
Because the secondary acetate in **6** was labile, we used the corresponding benzyl derivative **19**. Photolysis of its primary nitrite **3** led to an unusual result. The usual product [4] of 1,5-cleavage was missing among the isolated and identified reaction products.



The principal product was 2-phenyl-4*R*-hexyl-1,3-dioxane (**24**) resulting from 1,6-cleavage in addition to impurities of **19**, **15**, and aldehyde **23**. This was confirmed by spectral data. The PMR spectrum had signals at chemical shifts for a phenyl

ring (δ 7.25-7.55 ppm) and a singlet for an acetal proton (δ 5.52 ppm). The ^{13}C NMR spectrum had a doublet (δ 101.09 ppm) for C-2 and other characteristic signals.

Conversely, photolysis of nitrite **4**, prepared from optically pure secondary alcohol **20**, followed by chromatography of the reaction mixture isolated a compound with a modified alkyl chain of the starting material, 6-nitroso-3*S*-nonanol, existing primarily [5] as the more stable dimer **26**, and **20** and **25** [3].



Thermolysis of **26** gave quantitatively the γ-hydroxyoxime **27** as an equal mixture of the *syn*- and *anti*-isomers. Two-dimensional CH CORR and double resonance were used in order to assign unambiguously signals in the PMR and ^{13}C NMR spectra of the stereoisomers of **27**. The signals for C-5 [23.46 (*syn*-), 29.76 (*anti*-)] and C-7 [35.88 (*syn*-), 30.45 (*anti*-)] and their protons H-7 [2.35 (*anti*-), 2.15 (*syn*-)] and H_a-5 [2.40 (*syn*-), 2.70 (*anti*-)] were nonequivalent because of different shielding of the corresponding atoms in this pair of compounds and agreed well with the literature [6] (see Experimental).

EXPERIMENTAL

IR spectra were recorded on a Specord M-82 instrument as thin layers. NMR spectra were obtained on a Bruker AMX-300 spectrometer (working frequency 300.13 MHz for ^1H and 75.47 MHz for ^{13}C) in $CDCl_3$ with an internal standard of the $CDCl_3$ signals (^1H δ 7.27 ppm, ^{13}C δ 77.00 ppm). Chromatography was carried out in a Chrom-5 instrument [column length 1.2 m, stationary phase silicone SE-30 (5%) on Chromaton N-AW-DMCS (1.16-0.20 mm), working temperature 50-300°C, He carrier gas] and in a Shimadzu GC-9A chromatograph (quartz capillary column, 25 m, stationary phase OV-101, working temperature 80-260°C). Optical rotation was measured in a Perkin—Elmer 241 MC polarimeter. Photolysis was performed using a mercury lamp OKN-14, TU 64-1-1618-77 (220 V, 950 VA, 1000 W, 50 Hz). The Barton reaction was performed in a thermostatted Pyrex glass cell (λ > 320 nm, 80 mL). TLC monitoring used Sorbfil SiO_2 (Russia). Column chromatography was carried out over SiO_2 (70-230, Lancaster, England) with elution by petroleum ether (40-70°C). The ozonator production was 38 mmol O_3/h. Elemental analyses agreed with those calculated.

Castor Oil Acetate (17). Castor oil (**9**, 20.00 g) and Ac_2O (40.29 g, 394.9 mmol) were refluxed for 5 h, washed with hot water (3 × 100 mL), diluted with CH_2Cl_2 (300 mL), dried over Na_2SO_4, and evaporated to afford **17** (22.24 g, 98%). IR spectrum (ν, cm^{-1}): 3016 (C=C), 1740 (C=O), 1240, 1164 (C–O–C), 736 (C=C).

***R*-Octadec-9*Z*-en-1,12-diol (10).** A solution of **9** (10.9 g) in absolute THF (270 mL) and Et_2O (150 mL) (Ar, -10°C) was treated dropwise with a solution of *i*-Bu_2AlH (23.0 mL, 102.4 mmol, 73%). After the entire amount of *i*-Bu_2AlH was added, the reaction mixture was stirred for 1.5 h at 0°C, treated dropwise with H_2O (22 mL, 0-5°C), warmed to room temperature, and stirred for another 2 h. The resulting solid was filtered off and washed with Et_2O. The filtrate was dried over Na_2SO_4 and evaporated to afford the product (8.74 g), column chromatography of which (SiO_2, PE:CH_2Cl_2, 2:1) isolated **10** (7.70 g, 94%), $[\alpha]_D^{18}$ +2.24° (*c* 0.03, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 3304 (OH), 3010, 1660, (C=C), 1110, 1054, (C–O), 724 (C=C).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.89 (3H, t, J = 6.8, CH_3), 1.20-1.45 (18H, m, 9CH_2), 1.49 (2H, m, H-13), 1.53 (2H, m, H-2), 1.64 (2H, br.s, 2OH), 2.04 (2H, q, J = 6.7, H-8), 2.22 (2H, t, J = 7.2, H-11), 3.54 (1H, quintet, J = 5.8, H-12), 3.63 (2H, t, J = 6.6, H-1), 5.40 (1H, dt, J = 10.8, 7.4, H-10), 5.55 (1H, dt, J = 10.8, 7.1, H-9).

***R*-Octadec-9*Z*-en-7-ol (12).** A solution of **10** (8.80 g, 30.9 mmol) in dry Et_3N (7 mL, 128.5 mmol) was stirred (Ar, 0°C), treated in portions over 1 h with TsCl (7.05 g, 36.7 mmol), left overnight in a refrigerator, diluted with *t*-BuOMe (200 mL), washed successively with H_2O, aqueous HCl (10%), and saturated $NaHCO_3$ and NaCl solutions, and dried over Na_2SO_4 to give **11** (13.56 g), which was used without further purification.

IR spectrum (ν, cm^{-1}): 3346 (OH), 3010, 1650 (C=C), 1605 (Ar), 1378, 1185, (S=O), 1110, 1048, (C–O), 724 (C=C).

A solution of **11** (13.56 g, 30.9 mmol) in absolute THF (80 mL) and absolute Et_2O (80 mL) (Ar, 0°C) was treated with $LiAlH_4$ (2.65 g, 71.0 mmol), stirred for 3 h at room temperature, cooled to 0°C, diluted with H_2O (3.3 mL), warmed to room temperature, and stirred for another 3 h. The resulting solid was filtered off and washed with *t*-BuOMe. The filtrate was dried over Na_2SO_4 and evaporated to give a product (7.02 g), column chromatography of which (SiO_2, PE:CH_2Cl_2, 2:1, R_f 0.3) isolated **12** (4.12 g, 50%), $[\alpha]_D^{20}$ +2.6° (*c* 0.03, CH_2Cl_2).

IR spectrum (ν, cm^{-1}): 3346 (OH), 3010, 1650 (C=C), 1110, 1048 (C–O), 724 (C=C).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.88 (6H, t, J = 6.5, $2CH_3$), 1.20-1.45 (20H, m, $10CH_2$), 1.47-1.50 (2H, m, H-6), 1.58 (1H, br.s, OH), 2.05 (2H, q, J = 6.8, H-11), 2.22 (2H, t, J = 6.6, H-8), 3.62 (1H, quintet, J = 5.9, H-7), 5.35-5.65 (2H, m, H-9, H-10).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 14.01 (both q, C-1, C-18), 22.60 (both t, C-2, C-17), 25.68 (t, C-5), 27.40 (t, C-11), 29.27, 29.30, 29.34 (C-12, C-13, C-14), 29.47 (t, C-4), 29.66 (t, C-15), 31.82 (both t, C-3, C-16), 35.32 (t, C-8), 36.82 (t, C-6), 71.47 (d, C-7), 125.10 (d, C-9), 133.37 (d, C-10).

***R*-7-Acetoxyoctadec-9*Z*-ene (13).** A mixture of **12** (2.50 g, 9.3 mmol) and Ac_2O (20.13 mL, 57.0 mmol) was refluxed for 2 h, washed with hot H_2O (3 × 20 mL), diluted with CH_2Cl_2, dried over Na_2SO_4, and evaporated to afford **13** (2.87 g, 99%), $[\alpha]_D^{18}$ +25.2° (*c* 0.02, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 1738 (C=O), 3010, 1654 (C=C), 1110, 1048 (C–O), 724 (C=C).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.86 (6H, t, J = 6.7, $2CH_3$), 1.20-1.45 (20H, m, $10CH_2$), 1.50-1.62 (2H, m, H-6), 2.00-2.10 (4H, m, H-11, AcO), 2.32 (2H, dd, J = 6.7, J = 6.2, H-8), 4.88 (1H, quintet, J = 6.2, H-7), 5.35 (1H, dt, J = 10.8, J = 7.2, H-9), 5.48 (1H, dt, J = 10.8, J = 7.2, H-10).

***R*-7-Benzyloxyoctadec-9*Z*-ene (14).** A suspension of NaH (0.56 g, 14.6 mmol, 60% in mineral oil) in DMF (5 mL) was treated dropwise (Ar, 0°C) with **12** (3.5 g, 13.0 mmol) in DMF (5.5 mL), stirred at 0°C for 1 h, treated with BnBr (2.3 mL, 18.3 mmol), stirred for 6 h at room temperature, left overnight, diluted with *t*-BuOMe (200 mL), washed with water and saturated NaCl solution, dried over Na_2SO_4, and evaporated. The solid (5.23 g) was chromatographed (SiO_2, PE) to afford **14** (4.06 g, 87%), $[\alpha]_D^{20}$ +18.1° (*c* 0.02, CH_2Cl_2).

IR spectrum (ν, cm^{-1}): 3010, 1662 (C=C), 1625 (Ar), 1110, 1048 (C–O), 755 (C=C).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.90 (6H, t, J = 6.7, $2CH_3$), 1.20-1.55 (20H, m, $10CH_2$), 1.50-1.62 (2H, m, H-6), 2.06 (2H, q, J = 6.3, H-11), 2.25-2.45 (2H, m, H-8), 3.43 (1H, quintet, J = 5.8, H-7), 4.51 (1H, d, J = 11.7, $PhCH_a$), 4.60 (1H, d, J = 11.7, $PhCH_b$), 5.35-5.60 (2H, m, H-9, H-10), 7.25-7.40 (5H, m, Ph).

Ozonolysis and reduction of peroxide ozonolysis products: a) An ozone—oxygen mixture was bubbled through a solution of **13** (1.80 g, 8.8 mmol) in CH_2Cl_2 (18 mL) and absolute MeOH (0.7 mL, 17.6 mmol) at 0°C at an O_3:**13** mole ratio of 1:1. The reaction mixture was purged with Ar, diluted with CH_2Cl_2 (20 mL), stirred (10°C), treated with $NaBH_4$ (0.44 g, 11.6 mmol), stirred at room temperature for 3 h, treated with AcOH (0.14 mL) and H_2O (1.4 mL) (10°C), stirred at room temperature for 0.5 h, and washed with saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated to give a product (0.95 g) that contained **6**, **7**, and **15** in a ratio of 9:5:1, respectively, according to GC.

b) The peroxide ozonolysis product obtained by method **a)** was reduced with KBH_4 (0.63 g, 11.6 mmol), stirred at room temperature for 3 h, treated with AcOH (0.14 mL) and H_2O (1.4 mL) (10°C), stirred at room temperature for 0.5 h, and washed with saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated to give a product (0.90 g) that contained **6**, **7**, and **15** in a ratio of 6:1.1:1 according to GC.

c) An ozone—oxygen mixture was bubbled through a solution of **13** (0.90 g, 4.4 mmol) in CH_2Cl_2 (9 mL) and glacial AcOH (0.35 mL, 8.8 mmol) at 0°C at an O_3:**13** mole ratio of 1:1. The reaction mixture was purged with Ar, diluted with CH_2Cl_2 (20 mL), stirred (10°C), treated wth a previously prepared suspension of $NaBH(OAc)_3$ [addition of glacial AcOH (3.4 mL, 60.5 mmol) in CH_2Cl_2 (6 mL) to a suspension of $NaBH_4$ (0.76 g, 20.17 mmol) in CH_2Cl_2 (30 mL) with stirring for 2 h], warmed to room temperature, stirred for 3 h, cooled to 10°C, treated with AcOH (0.24 mL) and H_2O (2.4 mL), stirred at room temperature for 0.5 h, and washed with saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated to give a product (1.03 g) that contained **6**, **7**, and **15** in a 8.6:1.6:1 ratio according to GC.

d) An ozone—oxygen mixture was bubled through a solution of **17** (5.0 g, 4.7 mmol) in CH_2Cl_2 (50 mL) and MeOH (1.1 mL, 28.3 mmol) at 0°C at an O_3:**17** mole ratio of 3:1. The reaction mixture was purged with Ar, diluted with CH_2Cl_2 (30 mL), stirred (10°C), treated with $NaBH_4$ (1.4 g, 37.2 mmol), stirred at room temperature for 3 h, treated with AcOH (0.44 mL) and H_2O (4.4 mL) (10°C), stirred at room temperature for 0.5 h, and washed with saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated to give a product (5.46 g) that contained **6** and **7** in a 1.6:1 ratio according to GC.

e) The peroxide ozonolysis product obtained by method **d)** was reduced with KBH_4 (2.0 g, 37.2 mmol), stirred at room temperature for 3 h, treated with AcOH (0.44 mL) and H_2O (4.4 mL) (10°C), stirred at room temperature for 0.5 h, and washed with saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated to give a product (4.9 g) that contained **6**, **7**, and **15** in a 8.7:1.6:1 ratio according to GC.

f) An ozone—oxygen mixture was bubbled through a solution of **17** (5.00 g, 4.7 mmol) in CH_2Cl_2 (50 mL) and glacial AcOH (1.6 mL, 28.3 mmol) at 0°C at an O_3:**17** mole ratio of 3:1. The reaction mixture was purged with Ar, diluted with CH_2Cl_2 (20 mL), stirred (10°C), treated with a previously prepared suspension of $NaBH(OAc)_3$ [glacial AcOH (11.2 mL, 194.7 mmol) and $NaBH_4$ (2.46 g, 64.9 mmol) in CH_2Cl_2 (120 mL)], warmed to room temperature, stired for 3 h, cooled to 10°C, treated with glacial AcOH (0.86 mL) and H_2O (8.6 mL), stirred at room temperature for 0.5 h, and washed with saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated to give a product (4.97 g) that contained **6**, **7**, and **15** in a 17.7:1.5:1 ratio according to GC. Column chromatography isolated a mixture of **6** and **7** (1.14 g) in a ratio of 14:1, respectively.

The IR and NMR spectra of **6**, **7**, and **15** were practically identical to those in the literature [1].

3*R*-Benzyloxynonan-1-ol (19). Ozonolysis of **14** (4.00 g, 11.2 mmol) by method **a)** followed by vacuum distillation at 1 mm Hg and 100°C produced **19** (2.66 g, 95%), $[\alpha]_D^{20}$ -44.07° (*c* 0.003, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 3420 (OH), 1660 (Ar), 1110, 1048 (C–O).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.91 (3H, t, J = 7.0, CH_3), 1.20-1.40 (6H, m, $3CH_2$), 1.48-1.60 (2H, m, H-5), 1.60-1.73 (2H, m, H-4), 1.70-1.80 (2H, m, H-2), 2.50 (1H, br.s, OH), 3.60-3.65 (1H, m, H-3), 3.65-3.85 (2H, m, H-1), 4.48 (1H, d, J = 11.5, $PhCH_a$), 4.51 (1H, d, J = 11.5, $PhCH_b$), 7.20-7.50 (5H, m, Ph).

3*S*-Nonanol (20). A solution of **15** (5.38 g, 33.6 mmol) in Py (11 mL) at 0°C was stirred, treated in portions with TsCl (6.90 g, 36.7 mmol), left overnight in a refrigerator, diluted with *t*-BuOMe (200 mL), washed successively with HCl (10%) and saturated $NaHCO_3$ and NaCl solutions, dried over Na_2SO_4, and evaporated to afford the tosylate (8.83 g, 80%) [IR spectrum (ν, cm^{-1}): 1605 (Ar), 1375, 1180 (S=O), 1112 (C–O)], which was dissolved in absolute *t*-BuOMe (150 mL). The resulting solution was cooled to 0°C, treated with $LiAlH_4$ (2.38 g, 62.7 mmol), warmed to room temperature, stirred for 3 h, cooled to 0°C, diluted with H_2O (5 mL), warmed to room temperature, and stirred for 3 h. The solid was filtered off and washed with *t*-BuOMe. The filtrate was dried over Na_2SO_4 and evaporated to give a product (4 g), column chromatography of which (SiO_2, PE:EtOAc, 3:1) gave **20** (3.0 g, 75%), $[\alpha]_D^{20}$ +8.3° (*c* 0.05, CH_3Cl).

IR spectrum (ν, cm^{-1}): 3400 (OH), 1150, 1078 (C–O).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, t, J = 7.0, CH_3), 0.94 (3H, t, J = 7.3, CH_3), 1.25-1.37 (7H, m, $3CH_2$, OH), 1.30-1.60 (6H, m, H-2, H-4, H-5), 3.45-3.55 (1H, m, H-3).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 9.79 (q, C-1), 13.98 (q, C-9), 22.56 (t, C-8), 25.56 (t, C-5), 29.32 (t, C-6), 30.00 (t, C-2), 31.78 (t, C-7), 36.85 (t, C-2), 73.20 (d, C-3).

Nitrite Syntheses. 1. A 3-necked flask equipped with a thermometer, stirrer, and dropping funnel reaching to the bottom of the flask was charged with $NaNO_2$ (0.42 g, 6.1 mmol) and H_2O (1.66 mL) and cooled to 0°C. A cold (0°C) solution of a mixture of **6** and **7** (14:1, 1.12 g, 5.5 mmol) prepared as above in H_2SO_4 (0.28 g, 2.8 mmol) and H_2O (0.11 mL) was added through the dropping funnel with stirring at a rate so that gas was practically not evolved and the temperature did not rise. After the addition the reaction mixture was diluted with *t*-BuOMe (50 mL), washed with saturated NaCl solution, dried over Na_2SO_4, and evaporated to give a mixture of **2** and **21** (1.11 g) that was used without further purification.

IR spectrum (ν, cm^{-1}): 1750, 1650, 1620 (N=O), 790, 780, 620 (O–N).

2. Analogously **19** (2.58 g, 10.3 mmol) afforded **3** (2.4 g) that was used without further purification.

IR spectrum (ν, cm^{-1}): 1650 (N=O), 1605 (Ar), 1080, 820, 750 (O–N).

3. Analogously **20** (2.20 g, 15.3 mmol) afforded **4** (1.61 g) that was used without further purification.

IR spectrum (ν, cm^{-1}): 1645 (N=O), 1085, 820 (O–N).

Photolysis of Nitrites. 1. A solution of a mixture of **2** and **21** (0.40 g) in benzene (70 mL) was placed in a thermostatted Pyrex glass cell and irradiated (Ar, 27°C) for 1.5 h. The solvent was evaporated. The solid (0.36 g) was chromatographed (PE:*t*-BuOMe, 15:1) to isolate and identify a mixture of **6** and **7** (0.08 g), **15** (0.20 g), and **22** (0.01 g).

1-Acetoxy-3-nonanone (22). IR spectrum (ν, cm^{-1}): 1740 (OC=O), 1714 (C=O).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.90 (3H, t, J = 6.8, CH_3), 1.20-1.40 (6H, m, $3CH_2$), 1.50-1.65 (2H, m, H-5), 2.05 (3H, s, OAc), 2.42 (2H, t, J = 7.4, H-4), 2.72 (2H, t, J = 6.3, H-2), 4.32 (2H, t, J = 6.3, H-1).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 13.98 (q, C-9), 20.85 (q, C–CO), 22.44 (t, C-8), 23.53 (t, C-5), 29.00 (t, C-6), 31.54 (t, C-7), 41.20 (t, C-2), 43.22 (t, C-4), 59.38 (t, C-1), 170.90 (s, CO_2), 208.08 (d, C-3).

2. Photolysis of **3** (0.40 g) by the method described above gave a mixture of products (0.40 g), column chromatography of which isolated and identified **19** (0.13 g), **23** (0.06 g), **15** (0.02 g), and **24** (0.16 g).

3*R*-Benzyloxynonanal (23). IR spectrum (ν, cm^{-1}): 1720 (C=O), 1650 (Ar).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.90 (3H, t, J = 6.7, CH_3), 1.20-1.45 (6H, m, $3CH_2$), 1.50-1.65 (2H, m, H-5), 1.65-1.75 (2H, m, H-4), 2.60 (1H, ddd, J = 16.5, J = 4.9, J = 2.0, H_a-2), 2.67 (1H, ddd, J = 16.5, J = 7.2, J = 2.6, H_b-2), 3.95-4.00 (1H, m, H-3), 4.45-4.60 (2H, m, CH_2-Ph), 7.25-7.38 (5H, m, Ph), 9.81 (1H, t, J = 2.2, CHO).

2-Phenyl-4*R*-hexyl-1,3-dioxane (24), $[\alpha]_D^{20}$ +15.7° (*c* 0.02, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 1640 (Ar), 1155, 1125, 1040 (O–C–O),.

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.87 (3H, t, J = 7.02, CH_3), 1.25-1.40 (6H, m, $3CH_2$), 1.40-1.75 (5H, m, H-1′, H-2′, H_e-5), 1.82 (1H, dtd, J = 14.0, J = 11.4, J = 4.8, H_a-5), 3.83 (1H, dddd, J = 11.4, J= 7.1, J = 4.8, J = 2.4, H_a-4), 3.95 (1H, td, J = 11.4, J = 2.3, H_a-6), 4.28 (1H, ddd, J = 11.4, J = 4.8, J = 1.2, H_e-6), 5.52 (1H, s, H-2), 7.25-7.55 (5H, m, Ph).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 14.04 (q, C-6′), 22.58 (t, C-5′), 24.92 (t, C-2′), 29.23 (t, C-3′), 31.34 (t, C-4′), 31.77 (t, C-1′), 36.01 (t, C-5), 67.09 (d, C-6), 77.41 (t, C-4), 101.09 (d, C-2), 125.99, 128.13, 128.56, 138.93 (m, Ph).

3. Photolysis of **4** (0.40 g) by the method descibed above gave a mixture of products (0.27 g), column chromatography of which isolated and identified **25** (0.02 g), **20** (0.08 g), and **26** (0.15 g).

3-Nonanone (25). IR spectrum (ν, cm^{-1}): 1714 (C=O).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 0.90 (3H, t, J = 6.6, H-9), 1.15 (3H, t, J = 7.5, H-1), 1.20-1.35 (6H, m, $3CH_2$), 1.59 (2H, quintet, J = 7.3, H-5), 2.39 (2H, t, J = 7.4, H-2), 2.42 (2H, q, J = 7.3, H-4).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.77 (q, C-1), 13.95 (q, C-9), 22.56 (t, C-8), 24.87 (t, C-5), 29.64 (t, C-6), 31.82 (t, C-3), 35.76 (t, C-2), 42.37 (t, C-4), 211.85 (s, C-3).

Dimer of 6-nitroso-3*S*-nonanol (26), $[\alpha]_D^{20}$ +5.5° (*c* 0.01, CH_2Cl_2).

IR spectrum (ν, cm^{-1}): 3400 (OH), 1378, 1240, (N=O), 1174 (C–O).

PMR spectrum ($CDCl_3$, δ, ppm): 0.80-1.00 (6H, m, $2CH_3$), 1.20-2.00 (11H, m, $5CH_2$, OH), 3.40-3.55 (1H, m, H-3), 5.35-5.50 (1H, m, H-6).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 9.85 (q, C-1), 13.60 (q, C-9), 19.08 (t, C-8), 28.17 (t, C-5), 29.96 (t, C-2), 32.74 (t, C-4), 34.14 (t, C-7), 66.59 (d, C-6), 72.22 (d, C-3).

6-Oximino-3*S*-nonanol (27). Dimer **26** was heated at 60°C for 48 h to produce in quantitative yield an oily product that was a chromatographically inseparable equal mixture of the *syn*- and *anti*-isomers of **27**, $[\alpha]_D^{20}$ -6.2° (*c* 0.02, CH_2Cl_2).

IR spectrum (ν, cm^{-1}): 3500 (OH), 1660 (C=N), 1120 (C–O), 960 (N–O).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): *syn*: 0.90-1.00 (6H, m, H-1,9), 1.45-1.60 (4H, m, H-2,8), 3.53 (1H, tdd, ^3J = 6.3, ^3J = 3,5, ^3J = 9.5, H-3), 1.60-1.70 (2H, m, H-4), 2.25 (1H, ddd, ^3J = 5.3, ^3J = 7.5, ^2J = 13.0, H_a-5), 2.70 (1H, td, ^3J = 8.6, ^2J = 13.0, H_b-5), 2.15 (2H, t, ^3J = 7.4, H-7), 1.20-1.70 (2H, br.s, OH).

anti: 0.90-1.00 (6H, m, H-1,9), 1.45-1.60 (4H, m, H-2,8), 3.42 (1H, tdd, ^3J = 6.3, ^3J = 3.5, ^3J = 9.5, H-3), 1.60-1.70 (2H, m, H-4), 2.25 (1H, ddd, ^3J = 5.3, ^3J = 7.5, ^2J = 13.0, H_a-5), 2.40 (1H, td, ^3J = 8.6, ^2J = 13.0, H_b-5), 2.35 (2H, t, ^3J = 7.7, H-7), 1.20-1.70 (2H, br.s, OH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): *syn*: 10.04 (C-1), 30.06 (C-2), 72.10 (C-3), 33.04 (C-4), 23.46 (C-5), 161.85 (C-6), 35.88 (C-7), 19.04 (C-8), 14.30 (C-9).

anti: 10.11 (C-1), 29.70 (C-2), 71.99 (C-3), 32.68 (C-4), 29.76 (C-5), 161.85 (C-6), 30.45 (C-7), 19.71 (C-8), 13.79 (C-9).

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