Russian Journal of Organic Chemistry, Vol. 37, No. 11, 2001, pp. 1666–1667. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 11, 2001, pp. 1736–1737.

SHORT COMMUNICATIONS

Ozonolytic Hydroxylation of 3-Benzyloxy-(+)-α-Cadinol*

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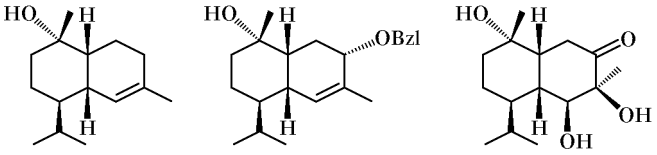
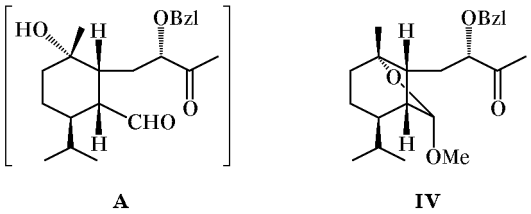
Received August 8, 2001

While developing approaches to formation of the 4,7-oxaeunicellane nucleus (which is a central fragment of eleuthesides [1]) on the basis of (+)-α-cadinol (**I**), we performed ozonolysis of its 3-benzyloxy derivative **II** in CH_2Cl_2 at –78°C, followed by treatment with Me_2S. As a result, "anomalous" ketotriol **III** was obtained.



I **II** **III**



A **IV**

The high stereospecificity of the process suggests a concerted character of transformations in the cyclic structures at the stages of formation and rearrangement of the ozonide [2]. However, the hydrolysis of acetal **IV** (CH_2Cl_2, *i*-PrOH, H_2O–HCl) obtained by ozonolysis of the same 3-benzyloxy derivative **II** in methanol also resulted in formation of ketotriol **III**. Thus we can conclude that ozonolytic hydroxylation of the double bond in **II** is a formal result of stereospecific intramolecular aldol condensation of intermediate **A**.

The NMR spectra were recorded on a Bruker AM-300 instrument at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). The signals were assigned on the basis of the CH correlation spectra. The optical rotations were measured on a Perkin–Elmer 141 polarimeter. We used (+)-α-cadinol with mp 137.8°C, $[\alpha]_D^{20}$ = +100.3° (*c* = 1.0, $CHCl_3$). 3-Benzyloxy derivative **II** was synthesized by the action of SeO_2–AcO_2 on (+)-α-cadinol (**I**) and subsequent benzylation.

(1*R*,3*S*,6*S*,7*R*,10*S*)-3-Benzyloxy-7-isopropyl-4,10-dimethylbicyclo[4.4.0]dec-4-en-10-ol (II). mp 97–99°C, $[\alpha]_D^{22}$ = +54.6°, *c* = 1.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 0.82 d (3H, CH_3, *J* = 6.9 Hz), 0.90 d (3H, CH_3, *J* = 6.9 Hz), 1.15 d.d.d (1H, 8-H, *J* = 3.4, 4.0, 11.2 Hz), 1.28 s (3H, CH_3), 1.48 m (1H, 7-H, *J* = 3.0 Hz), 1.50 m (3H, 9-H_2, 8-H), 1.68 m (1H, 1-H), 1.78 s (3H, CH_3), 1.98 d.q.q (1H, C**H**Me_2, *J* = 3.0, 6.9 Hz), 2.05 m (1H, 6-H), 2.30 m (1H, 2-H, *J* = 10.0 Hz), 2.46 d.d.d (1H, 2-H, *J* = 1.0, 6.3, 10.0 Hz), 3.96 d.d (1H, 3-H, *J* = 6.3, 8.4 Hz), 4.51 d (1H, OC**H**$_2$Ph, *J* = 11.5 Hz), 4.70 d.d (1H, OC**H**$_2$Ph, *J* = 11.5, 10.4 Hz), 5.67 d (1H, 5-H, *J* = 5.4 Hz), 7.38 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 15.24 (CH_3), 19.76 (CH_3), 21.32 (C^8), 21.46 (CH_3), 24.80 (C^2), 26.32 (CH_3), 27.68 (**C**HMe_2), 35.06 (C^9), 36.88 (C^6), 43.68 (C^7), 44.10 (C^1), 70.42 (O**C**H_2Ph), 71.83 (C^{10}), 78.22 (C^3), 128.80 (C^5), 135.48 (C^4), 127.35, 127.66, 128.33, 138.69 (C_{arom}). Found, %: C 80.79; H 9.60. $C_{22}H_{32}O_2$. Calculated, %: C 80.44; H 9.82.

* This study was financially supported by the Russian Foundation for Basic Research (project no. 01-03-32 050).

(1*R*,2*S*,3*R*,6*R*,7*S*,10*R*)-10-Isopropyl-3,7-dimethyl-2,3,7-trihydroxybicyclo[4.4.0]decan-4-one (III). $[\alpha]_D^{20}$ = –10.5° (*c* = 1.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 0.95 d (3H, CH_3, *J* = 6.5 Hz), 0.98 d (3H, CH_3, *J* = 6.5 Hz), 1.15 s (3H, CH_3), 1.28 s (3H, CH_3), 1.35–1.50 m (2H, 10-H, 9-H), 1.55–1.68 m (2H, 8-H, 9-H), 1.70–1.90 m (2H, 8-H, C**H**Me_2), 2.0 br.s (2H, 1-H, 6-H), 2.18 d.d (1H, 5-H, *J* = 3.4, 19.5 Hz), 2.5 br.s (1H, OH), 2.70 d.d (1H, 5-H, *J* = 1.3, 19.5 Hz), 3.70 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 16.65 (CH_3), 19.88 (C^9), 21.25 (CH_3), 21.8 (CH_3), 25.77 (CH_3), 26.70 (**C**Me_2), 33.28 (C^5), 34.09 (C^{10}), 38.52 (C^8), 44.14 (C^6), 44.75 (C^1), 73.64 (C^7), 76.98 (C^3), 77.04 (C^2), 209.79 (C^4). Found, %: C 66.87; H 9.54. $C_{15}H_{24}O_4$. Calculated, %: C 66.64; H 9.69.

(1*R*,4*R*,5*R*,6*R*,8*R*)-8-(2-Benzyloxy-3-oxobutyl)-4-isopropyl-6-methoxy-1-methyl-7-oxabicyclo[3.2.1]-octane (IV). $[\alpha]_D^{20}$ = –55.0° (*c* = 1.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 0.80 d (3H, CH_3, *J* = 6.8 Hz), 0.87 d (3H, CH_3, *J* = 6.8 Hz), 1.18 s (3H, CH_3), 1.25 m (1H, 4-H), 1.35–1.45 m (3H, 2-H_2, 8-H), 1.50–1.62 m (3H, C**H**Me_2, 3-H_2), 1.75 d.d.d (1H, 1′-H_2, *J* = 2.6, 9.6, 11.0 Hz), 2.05 d.d.d (1H, 1′-H_2, *J* = 3.8, 9.9, 11 Hz), 2.12 s (3H, CH_3), 2.40 d (1H, 5-H, *J* = 3.4), 3.30 s (3H, OCH_3), 3.92 d.d (1H, 2′-H, *J* = 2.6, 9.9), 4.30 d (1H, C**H**$_2$Ph, *J* = 10.8 Hz), 4.53 d (1H, OC**H**$_2$Ph, *J* = 10.8 Hz), 4.70 s (1H, 6-H), 7.30 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.65 (CH_3), 22.03 (CH_3), 22.18 (CH_3), 22.29 (C^3), 25.45 (CH_3), 27.61 (**C**HMe_2), 30.60 (C^2), 36.65 ($C^{1'}$), 40.28 (C^4), 43.35 (C^5), 48.03 (C^8), 54.71 (OMe), 72.02 (O**C**H_2Ph), 83.29 ($C^{2'}$), 86.22 (C^1), 109.22 (C^6), 127.84, 127.95, 128.02, 128.20, 128.37, 137.57 (C_{arom}), 204.32 (C=O). Found, %: C 73.53; H 9.24. $C_{23}H_{34}O_4$. Calculated, %: C 73.76; H 9.15.

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