SYNTHESIS OF 4α-HYDROXY-6,6-DIMETHYL-3-OXABICYCLO [3.1.0]HEX-2-ONE BY OZONOLYSIS OF (1R, *cis*)-4,7,7-TRIMETHYL- -3-OXABICYCLO[4.1.0]HEPT-4-EN-2-ONE

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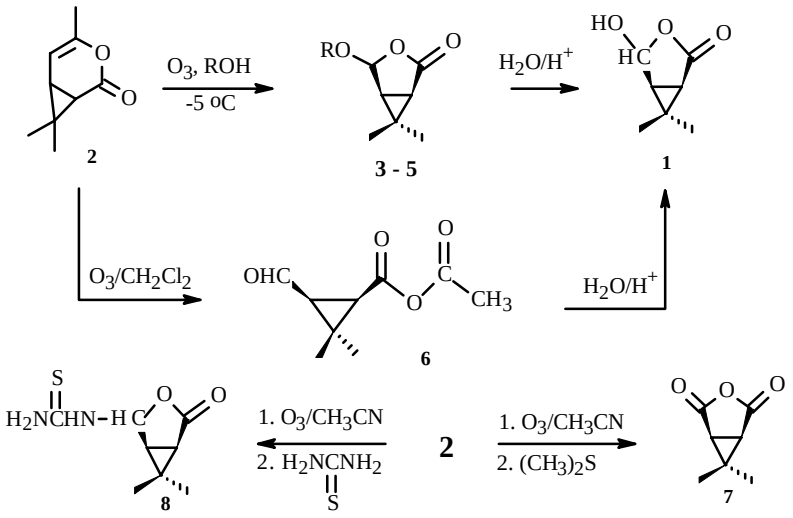
UDC 547.313+542.943.5

4α-Hydroxy-6,6-dimethyl-3-oxabicyclo[3.1.0]hex-2-one (**1**) is an intermediate in the synthetic pathways to many effective pyrethroids with the gem-dimethylcyclopropane ring [1, 2]. One of the approaches to the synthesis of **1** is ozonolysis of (1R,*cis*)-4,7,7-trimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (**2**), which is readily obtained from (+)-3-carene [2].

A detailed investigation of the ozonolysis of enollactone **2** showed that the reaction is exceedingly sensitive to the solvent in which the ozonolysis is performed and the reductant used to decompose the peroxide ozonolysis products. These affect the yield of the desired lactol **1**. The maximum yield is attained with ozonolysis (-5°C) in alcohols. It has been found that the reaction occurs through intermediate alkoxylactols (**3-5**), hydrolysis of which (55 ml of 1% oxalic acid per 0.03 mole of **3-5**, 20°C, 3 h) completes the synthesis of **1**.



R= CH_3 (**3**), C_2H_5 (**4**), C_3H_7 (**5**)

If the ozonolysis is carried out in CH_2Cl_2, the precursor to **1** is a mixed anhydride of acetic and 2,2-dimethyl-3-formylcyclopropylformic acid (**6**), which is successfully converted by hydrolysis into **1**. Use of another aprotic solvent, CH_3CN, for the ozonolysis (-5°C) sharply decreases the yield. Apparently the zwitter ion is stabilized differently and is affected by the structure of the starting substrate and the type of reductant. Use of dimethylsulfide produces a substantial quantity of 6,6-dimethyl-3-oxabicyclo[3.1.0]hex-2,4-dione (**7**). Treatment of the peroxide products with thiourea forms mainly 4α-thioureo-6,6-dimethyl-3-oxabicyclo[3.1.0]hex-2-one (**8**). Both **7** and **8** are not hydrolyzed to **1**.

IR spectrum of **3** (KBr, ν, cm^{-1}): 1780 (C=O). PMR spectrum (300 MHz, $CDCl_3$): δ, 1.16 and 1.18 (6H, s, $2CH_3$), 2.0 (1H, d, J = 5.1 Hz, H-1), 2.04 (1H, dd, J_1 = 5.1, J_2 = 2.0 Hz, H-5), 3.5 (3H, s, CH_3), 5.05 (1H, s, H-4). ^{13}C NMR spectrum (75

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0009-3130/00/3605-0535$25.00

MHz, $CDCl_3$): δ, 15.05 and 25.40 (CH_3), 24.47 (C-6), 29.29 and 35.22 (C-1 and C-5), 56.30 (OCH_3), 102.46 (C-4), 173.39 (C-2).

Spectral properties of **6** are identical to those in the literature [3].

IR spectrum of **7** (KBr, ν, cm^{-1}): 1780, 1840 (C=O). PMR spectrum (300 MHz, $CDCl_3$): δ, 1.31 and 1.40 (6H, s, $2CH_3$), 2.6 (2H, s, H-1 and H-5). ^{13}C NMR spectrum (75 MHz, $CDCl_3$): δ, 16.84 and 25.36 (CH_3), 34.73 (C-6), 34.92 (C-1 and C-5), 167.21 (C=O).

PMR spectrum of **8** (300 MHz, $CDCl_3$): δ, 1.10 and 1.17 (6H, s, $2CH_3$), 1.69 (1H, d, J = 6.0 Hz, H-1) and 2.05 (1H, dd, J_1 = 6.0, J_2 = 2.7 Hz, H-5), 5.20 (1H, d, J = 2.7 Hz, H-4), 5.8 (1H, s, H-N^1), 7.6 and 9.86 (2H, br. s, H_2-N^2). ^{13}C NMR spectrum (75 MHz, $CDCl_3$): δ, 14.55 and 26.11 (CH_3), 26.51 (C-6), 30.47 and 33.95 (C-1 and C-5), 173.65 (C=O), 181.27 (C=S). Found, %: C 48.5, H 6.2, N 13.2, S 15.24. $C_8H_{12}N_2SO_2$. Calc., %: C 48.00, H 5.99, N 14.00, S 16.01.

Spectral properties of **1** are identical to those in the literature [1].

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