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SHORT COMMUNICATIONS

Synthesis of (1*R*,6*S*)-*cis*-7,7-Dimethyl-4-formyl-3-oxabicyclo[4.1.0]hept-4-en-2-one

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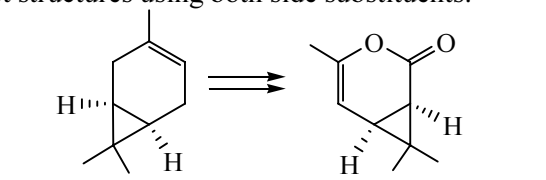
Natural substances with a *cis*-disubstituted *gem*-dimethylbicyclopropane fragment are found mainly among terpenoids (phorbol [1], lathyrol [2], bertyadionol [3], jolkinol C [4], casbene [5], ingenol [6], virtrenal [7], aromadendrenes [8], jatrophone, milliamines [9], chrysantemic acid and pyrethroids [10], tigliane [11] etc.). Synthetic approaches to these structures [12–14] can be based on commercially available (+)-3- and (–)-2-carenes. The latter by standard operations of an oxidative cleavage of the double bonds can be converted in a single stage into chiral α,ω-bifunctional *gem*-dimethylbicyclopropane blocks suitable for subsequent designing of the target structures using both side substituents.



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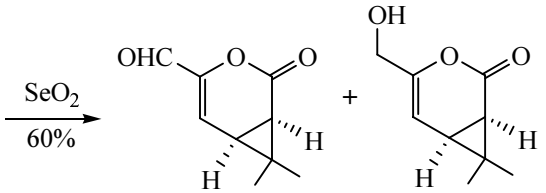

II **III**

We report here on a new multipurpose functionalized *gem*-dimethylbicyclopropane synthons **II** obtained by the oxidation with selenium dioxide of "carene" enololactone **I** employed in the pyrethroids synthesis [15].

The minor product of this reaction is alcohol **III** obtained in certain experiments in variable yields in 5–10% range. Alcohol **III** can be converted into aldehyde **II** by oxidizing with MnO_2. The attempts to carry out an oxidative bromination of compound **I** with NBS led to the formation of a complex mixture of decomposition products. Obviously the chemical potential of compound **II** due to its "orthogonal functionalization" is high, and the promising aspects of its application to the synthesis are easily predictable.

Reaction of (1*R*,6*S*)-*cis*-4,7,7-trimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (I) with SeO_2. To a solution of 0.5 g (3.3 mmol) of compound **I** in 15 ml of anhydrous toluene at reflux under an argon atmosphere was added by small portions within 60 min 0.75 g (6.6 mmol) of SeO_2. The reaction mixture was boiled at reflux for 1.5 h, then cooled to room temperature and filtered. The red-brown filtrate was cooled to 0°C, and *m*-chloro-perbenzoic acid was added till the solution got light-yellow (~0.6 g). The reaction mixture was stirred for 5 min at 0°C, then it was poured into a water solution of K_2CO_3, the reaction product was extracted first into toluene (2×20 ml), then into $CHCl_3$ (3×20 ml). The combined organic solutions were washed with a saturated K_2CO_3 solution, dried with $MgSO_4$, evaporated, and subjected to column chromatography on SiO_2 (eluent EtOAc–petroleum ether, 1:2) to obtain 0.28 g (~45%) of compound **II** as colorless crystals and 0.1 g (~15%) of inseparable mixture of compounds **II** and **III** in a ratio ~ 4:3 (^{1}H NMR data).

(1*R*,6*S*)-*cis*-7,7-Dimethyl-2-oxo-3-oxabicyclo-[4.1.0]hept-4-en-4-carbaldehyde (II), mp 119–121°, $[\alpha]_D^{20}$ +68.5° (*C* 0.97, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.99 s and 1.33 s (3H each, *gem*-CH_3), 2.04 d.d (1H, H^6, *J* 5.3 and 7.0 Hz), 2.14 d (1H, H^1, *J* 6.9 Hz), 6.46 d (1H, H^5, *J* 5.2 Hz), 9.17 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 15.39 and 26.51 (*gem*-CH_3), 25.59 (C^7), 29.66 and 31.09 (C^1, C^6), 121.96(C^5), 148.07 (C^4), 163.94 (C^2), 182.86 (CHO).

(1*R*,6*S*)-*cis*-7,7-Dimethyl-4-hydroxymethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one (III). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 s and 1.29 s (3H each, *gem*-CH_3), 1.79 d.d (1H, H^6, *J* 5.0 and 7.3 Hz), 1.87 d (1H, H^1, *J* 7.4 Hz), 4.2 s (2H, OCH_2), 5.41 d (1H, H^5, *J* 5.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 15.59 and 26.76 (*gem*-CH_3), 23.42 (C^7), 28.62 and 28.99 (C^1, C^6), 61.31 (CH_2OH), 99.51 (C^5), 149.97 (C^4).

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-300 at operating frequencies 300.13 and 75.47 MHz respectrively, internal reference TMS. The optical rotation was measured on a Perkin-Elmer-141 instrument.

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