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Short Communication

Synthesis of 2-Acetoxy- and 2-Hydroxy-2,3-dihydronaphtho[1,8-bc]pyran

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Summary. 2-Acetoxy- and 2-Hydroxy-2,3-dihydronaphtho[1,8-bc]pyranes were synthesized by decomposition of 1-hydroperoxy-1,2-dihydroacenaphthylene in acetic acid in the presence of perchloric acid.

Keywords. 2-Acetoxy-2,3-dihydronaphtho[1,8-bc]pyran; 2-Hydroxy-2,3-dihydronaphtho[1,8-bc]-pyran; 1-Hydroperoxy-1,2-dihydroacenaphthylene, decomposition.

Synthese von 2-Acetoxy- und 2-Hydroxy-2,3-dihydronaphtho[1,8-bc]pyran

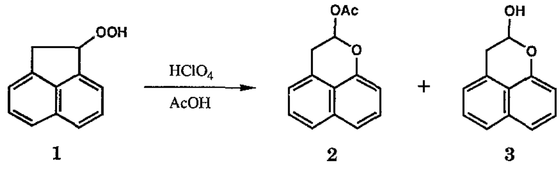
Zusammenfassung. 2-Acetoxy- und 2-Hydroxy-2,3-dihydronaphtho[1,8-bc]pyrane konnten durch Zersetzung von 1-Hydroperoxy-1,2-dihydroacenaphthylen in Essigsäure in Anwesenheit von Perchlorsäure synthetisiert werden.

The 2,3-dihydronaphtho[1,8-bc]pyran ring system can be found in the structure of several natural products [1–3]. Recently, the propranolol analogues containing this ring system were shown to exhibit β-blocking activities [4]. Also the amino derivatives of 2,3-dihydronaphtho[1,8-bc]pyran were investigated during the search for non-toxic antipsychotic agents [5].

The key intermediate in the synthesis of these compounds is 2-hydroxy-2,3-dihydronaphtho[1,8-bc]pyran (**3**) [4, 5]. Compound **3** was obtained by the reduction of 8-hydroxynaphthalene-1-acetic acid lactone (**4**) by means of diisobutylaluminium hydride at low temperatures (−78 °C) [4–6]. The lactone **4** was synthesized using Bayer-Villiger oxidation of acenaphthophenone with peracetic acid [5, 6] or 3-chloroperbenzoic acid [4].

In the present paper a new route for the synthesis of the 2,3-dihydronaphtho[1,8-bc]pyran ring system via acidolysis of 1-hydroperoxy-1,2-dihydroacenaphthylene (**1**) is described.

The decomposition of hydroperoxide **1** in acetic acid in the presence of perchloric acid constitutes a simple (temp. 40 °C, 0.5 h) method of synthesis of 2-acetoxy-2,3-dihydronaphtho[1,8-bc]pyran (**2**) and 2-hydroxy-2,3-dihydronaphtho[1,8-bc]pyran (**3**). The compounds are obtained in a yield of **54**% and 35%, respectively.



Hydroperoxide **1** was obtained by gaseous O_2 oxidation of the readily available reagent 1,2-dihydroacenaphthylene in chlorobenzene [8].

Experimental Part

Melting points – determined in capillary tubes – are uncorrected. Microanalyses were performed using a Perkin–Elmer 240 MC-1 element analyzer. Mass spectra were recorded on a Gas-Chromatograph Mass Spectrometer LKB 2091 with DEI ionization. IR spectra were obtained using a Zeiss Specord 71 IR spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker MSL-300 spectrometer.

2-Acetoxy- (**2**) *and 2-hydroxy-2,3-dihydronaphtho[1,8-bc]pyran* (**3**)

1-Hydroperoxy-1,2-dihydroacenaphthylene (**1**; 0.940 g, 5.05 mmol) was added to a solution of 60% perchloric acid (0.033 g, 0.20 mmol $HClO_4$) in acetic acid (100 ml) at 40° while stirring. The stirring was maintained throughout the reaction (40 °C, 0.5 h). Then K*OAc* (0.021 g, 0.21 mmol) was added and acetic acid was evaporated at 45–50 °C (in vacuum). The residue was dissolved in benzene (40 ml) and the solution washed with water (2 x 10 ml). Benzene was evaporated and the residue chromatographed on a silica gel column (40 x 1.9 cm, 70–230 mesh). Chromatography was monitored by TLC (chloroform was used as a solvent, R_f for **2** and **3** were 0.43 and 0.11, resp.). Elution with hexane/*Et*O*Ac* (10:1) gave **2** in a yield of 0.628 g (54%, m.p. 50.5–51.5 °C, hexane), and **3** in a yield 0.325 g (35%, m.p. 69.5–70.5 °C, hexane) (67–70 °C [6], 69–71 °C [4]).

2: IR ($CHCl_3$): $\bar{\nu} = 1750$ (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$/*TMS*): $\delta = 1.98$ (s, 3 H, CH_3), 3.29 (dd, 1 H, $J = 16.6, 2.8$ Hz, one of CH_2), 3.57 (dd, 1 H, $J = 16.6, 3.6$ Hz, one of CH_2), 6.76 (dd, 1 H, $J = 2.8, 3.6$ Hz, CH), 6.98–7.75 (m, 6 H_{arom}). MS (70 eV): $m/z = 228$ (M^+), 186 (56), 169 (26), 168 (51), 158 (22), 157 (100), 155 (10), 120 (13), 43 (30), 28 (17), 18 (20). Calcd. for $C_{14}H_{12}O_3$: C 73.69, H 5.30; found: C 73.77, H 5.23.

3: IR ($CHCl_3$): $\bar{\nu} = 3598$ (O–H) cm^{-1}. ^{1}H NMR ($CDCl_3$/*TMS*): $\delta = 3.20$ (d, $J = 6.1$ Hz, OH), 3.27 (dd, 1 H, $J = 16.1, 4.6$ Hz, one of CH_2), 3.47 (dd, 1 H, $J = 16.1, 2.9$ Hz, one of CH_2), 5.28 (ddd, 1 H, $J = 6.1, 4.6, 2.9$, CH), 6.96–7.71 (m, 6 H_{arom}). MS (70 eV): $m/z = 186$ (M^+), 158 (21), 157 (100), 155 (12), 129 (22), 128 (13), 127 (11), 28 (32), 18 (32), 18 (15). Calcd. for $C_{12}H_{10}O_2$: C 77.41, H 5.41; found: C 77.33, H 5.45.

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