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SHORT COMMUNICATIONS

Unusual Recyclization of 2(1-Bromostyryl)-4-oxo-1,3-benzoxazinium Perchlorate into 2,3,4,5-Tetrahydro-1,4-benzoxazepine-4,5-dione

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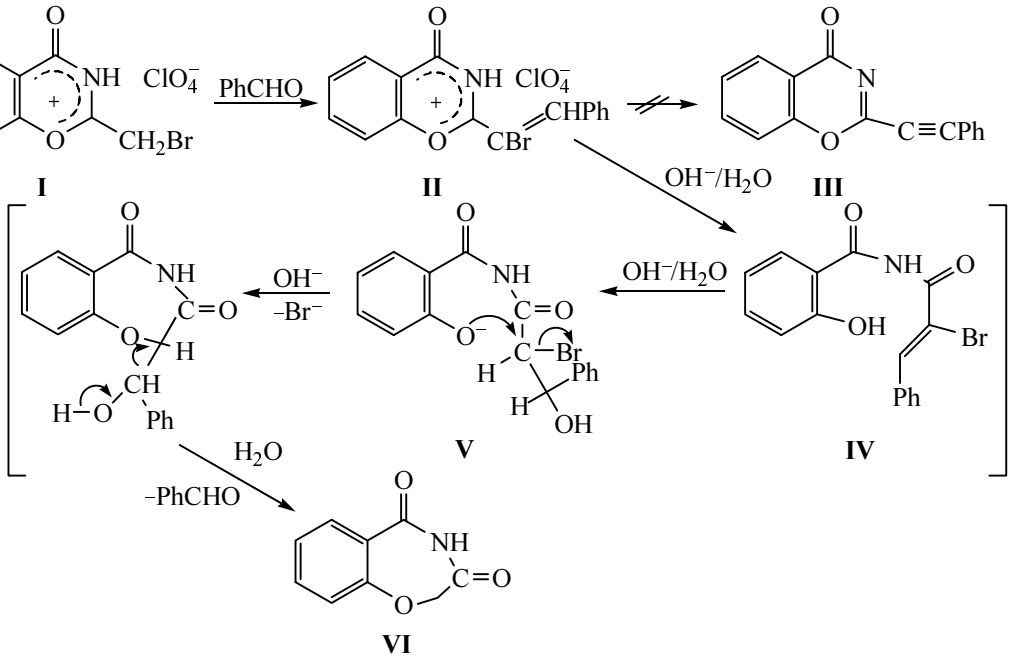
With the goal to investigate the transformations of 2-bromomethyl-4-oxo-1,3-benzoxazinium perchlorate **I** that we had previously synthesized [1] we prepared a product of its condensation with benzaldehyde **II.** We attempted to convert it into 2-phenylethynyl-1,3-benzoxazin-4-one **III** via the corresponding pseudobase by treating with alcohol solution of alkali, but failed, and isolated instead benzoxazepinedione **VI**.



The seven-membered ring of the reaction product **VI** forms presumably by primary ring opening effected by alkali and water addition by Michael reaction to unsaturated imide **IV**. The intramolecular substitution of bromine in the phenolate anion followed by retroaldol cleavage resulted in previously described benzoxazepinedione **VI,** whose composition and structure were proved by elemental analysis, IR, ^{1}H NMR, and mass spectra.

2,3,4,5-Tetrahydro-1,4-benzoxazepine-3,5-dione (VI). Into a solution of 0.08 g (2 mmol) of sodium hydroxide in 10 ml of ethanol was added 0.4 g (1 mmol) of perchlorate **II**. The mixture was boiled for 4 min,

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cooled, and diluted with 6 ml of water. The precipitated reaction product was filtered off, washed with water, and recrystallized from methanol. Yield 0.09 g (51%), colorless powder, mp 156–157°C (publ.: mp 155°C [3]). IR spectrum, ν, cm^{-1}: 3200 (NH), 1710 (C=O), 1660 (C=O), 1620 (C=C), 1600 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.42 s (2H, CH_2), 6.69 m (2H, H^7, H^8), 7.41 d (1H, H^9), 7.73 d (1H, H^6), 10.98 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 177 (58) $[M]^+$, 134 (5), 119 (100), 91 (43), 64 (6), 43 (14), 18 (5). Found, %: C 61.59; H 4.52; N 8.22. $C_9H_7NO_3$. Calculated, %: C 61.02; H 3.95; N 7.91.

IR spectrum of compound **VI** was recorded on spectrophotometer Specord 75IR from mull in mineral oil, ^1H NMR spectrum was registered on spectrometer Varian Unity-300 (300 MHz) at 20°C, mass spectrum was measured on Hitachi M-80 instrument.

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