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CYCLODEHYDRATION OF 3-[α-(2'-AMINOPHENYLAMINO)-BENZYLIDENE]-2-OXO-1,4-DIHYDROQUINOXALINE INTO 2,2'-BISBENZIMIDAZOLE WITH ELIMINATION OF THE BENZYLIDENE FRAGMENT

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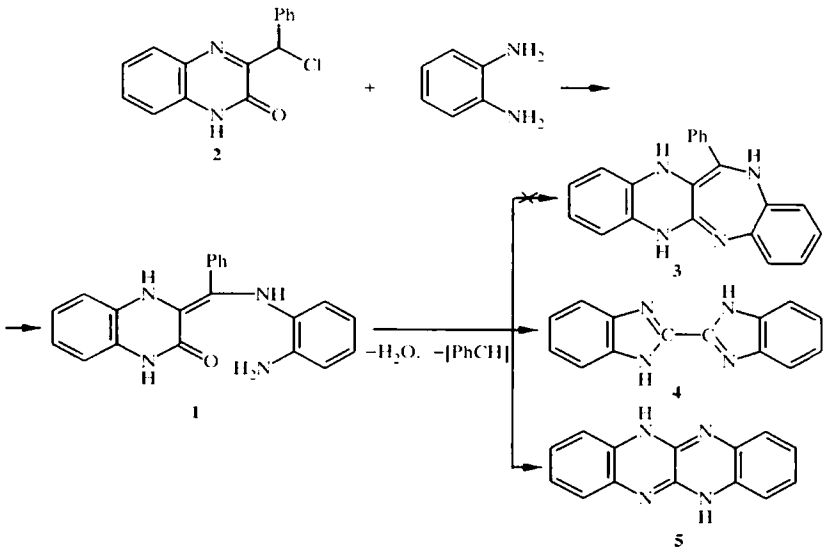
When attempting the cyclodehydration of product **1**, obtained by the reaction of 3-(α-chlorobenzyl)-2-oxo-1,2-dihydroquinoxaline (**2**) with *o*-phenylenediamine, into the benzodiazepinoquinoxaline **3** we discovered that unexpectedly fission of a C–C bond with elimination of the benzylidene fragment, and the formation of 2,2'-bisbenzimidazole in good yield (**4**) are occurred. This conversion proceeds well both on melting compound **1** and also on boiling it in acetic acid.



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The product obtained was identical in electronic spectrum with the known compound **4** [1]. Its structure was confirmed by mass spectrometric data, and by ^{1}H and ^{13}C NMR spectra. Contamination by dihydroquinoxalino[2,3-*b*]quinoxaline (**5**), which is isomeric with bisbenzimidazole **4**, was present in the unrecrystallized product, judging by the absorption band in the visible region of the spectrum and the yellow-green fluorescence of solutions [2].

3-[α-(2'-N-Aminophenylamino)benzyliden]-2-oxo-1,4-dihydroquinoxaline (1). A solution of quinoxaline **2** (1.00 g, 3.70 mmol) and *o*-phenylenediamine (0.44 g, 4.07 mmol) in DMSO (10 ml) was kept at room temperature for 7 days, poured into water, and treated with aqueous Na_2CO_3 solution. The precipitated crystals were filtered off, washed with water, and with ether. Yield 0.99 g (78%); mp >200°C (decomp., from 2-PrOH). IR spectrum (nujol, cm^{-1}): 1600, 1663, 3040, 3240, 3342. ^{1}H NMR spectrum (DMSO-d_6): 4.88 (1H, s, NH); 6.59-8.24 (13H, m, C_6H_5, $2C_6H_4$); 9.92 (1H, s, NH); 13.22 ppm (1H, br. s, NH). Found, %: C 73.93; H 5.33; N 15.97. $C_{21}H_{18}N_4O$. Calculated, %: C 73.67; H 5.30; N 16.36.

2,2'-Bisbenzimidazole (4). A. A solution of compound **1** (0.30 g, 0.88 mmol) in AcOH (5 ml) was boiled for 2 h. The precipitated crystals were filtered off, and washed with 2-PrOH (2 × 5 ml). Yield 0.17 g (83%); mp >360°C (AcOH). ^{1}H NMR spectrum (DMSO-d_6): 6.00-6.38 (4H, m); 6.45-6.83 (4H, m). ^{13}C{^{1}H} NMR spectrum (DMSO-d_6 + acetone-d_6, 9 : 1): 143.25 (s, $C_{(2)}$, $C_{(2')}$); 139.74 (br. s, $C_{(3a)}$, $C_{(3a')}$, $C_{(7a)}$, $C_{(7a')}$); 122.72 (dd, J = 159.80, 8.20 Hz, $C_{(4)}$, $C_{(4')}$, $C_{(7)}$, $C_{(7')}$); 115.31 ppm (br. dt, J = 161.91, 5.4 Hz, $C_{(5)}$, $C_{(5')}$, $C_{(6)}$, $C_{(6')}$). In the mass-spectrum there was a peak for the molecular ion at *m/z* 234 (100%), the accurate mass corresponded to the composition $C_{14}H_{10}N_4$.

B. A melt of compound **1** (0.30 g, 0.88 mmol) was heated for 5 min at 250-260°C, cooled, dioxane (5 ml) was added, the mixture brought to boiling, and left for 1 h. The crystals were then filtered off and washed with acetone. Yield 0.15 g (73%) of a substance identical with that obtained in acetic acid.

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