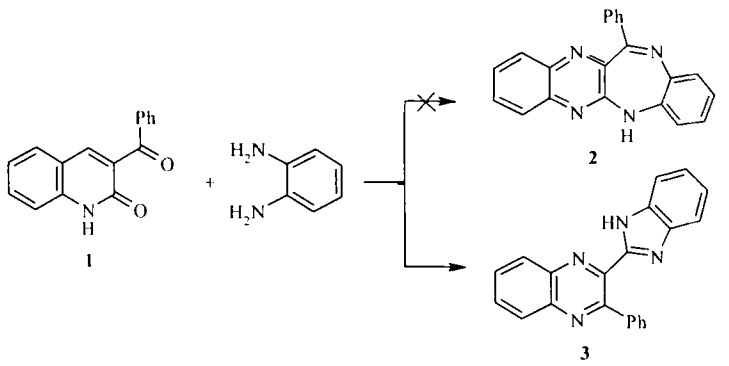
Chemistry of Heterocyclic Compounds, Vol. 36, No. 7, 2000

UNEXPECTED QUINOXALINO–BENZIMIDAZOLE REARRANGEMENT

A. A. Kalinin, V. A. Mamedov, and Ya. A. Levin

Keywords: 2-benzimidazolyl-3-phenylquinoxaline, quinoxalino–benzimidazole rearrangement.

We have found that when *o*-phenylenediamine reacts with 3-benzoyl-1,2-dihydro-2-oxoquinoxaline (**1**) in boiling acetic acid, cleavage of two water molecules occurs but the compound formed of composition $C_{21}H_{14}N_4$ is not the expected quinoxalinobenzodiazepine (**2**) but rather its structural isomer 2-benzimidazolyl-3-phenylquinoxaline (**3**). Evidence for this comes from the results of an investigation of its structure by comprehensive spectral methods, in particular from the fact that the ^{13}C NMR spectrum includes 19 signals from 21 carbon nuclei, and six of them (belonging to the benzo moiety of the benzimidazole system) appear as broad singlets due to the occurrence of benzimidazole tautomerism. Structure **2** does not give such a ^{13}C NMR spectrum.



The structure of compound **3** has also been confirmed by X-ray diffraction analysis (the results will be published separately).

We suggest that in structure **3**, the $C_{(2)}$ atom of the benzimidazole ring is the $C_{(2)}$ atom of the starting quinoxalinone **1**, and that over the course of the reaction a quinoxalino–benzimidazole rearrangement occurs, and construction of the new quinoxaline ring occurs using the *o*-phenylenediamine and also the ketone and imine carbon atoms of benzoylquinoxalinone **1**.

2-(2'-Benzimidazolyl)-3-phenylquinoxaline (3). A solution of benzylquinoxalinone **1** (1.20 g, 4.80 mmol) and *o*-phenylenediamine (0.60 g, 5.55 mmol) was boiled for 2 h in acetic acid (12 ml). The reaction mixture was cooled and poured into water; the crystals precipitated were filtered off and washed with water

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Science Center, Russian Academy of Sciences, Kazan 420088, Russia; e-mail: mamedov@iopc.kcn.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 995-996, July, 2000. Original article submitted December 22, 1999.

 0009-3122/00/3607-0882$25.00©2000 KluwerAcademic/Plenum Publishers

(2×10 ml) and *i*-PrOH (2×5 ml). Yield 1.52 g (97%); mp 301-303°C (DMSO). IR spectrum (thin layer, vaseline oil): 700, 755, 770, 960, 1095, 1220, 1415, 1480, 3000-3300 cm^{-1}. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.19-7.64 (9H, m, Ph, quinoxaline); 7.87-8.25 (4H, m, benzimidazole); 13.24 (1H, s, HN). $^{13}C\{^1H\}$ NMR spectrum (DMSO + acetone-d_6, 9:1), δ, ppm: benzimidazole moiety – 112.05, 118.87, 122.12, 123.49, 134.58, 143.25 (6 br. s, $C_{(3a')}$, $C_{(4')}$, $C_{(6')}$, $C_{(7')}$, $C_{(7a')}$), 149.57 (s, $C_{(2')}$); phenyl – 127.72 (dd, J = 159.2, 7.4 Hz, *m*-C_{Ph}); 129.13 (ddd, 160.6, 7.3, 1.2 Hz, *p*-C_{Ph}); 129.50 (d, 160.5 Hz, *o*-C_{Ph}); 138.82 (dd, J = 8.4, 7.6 Hz, *ipso*-C_{Ph}); quinoxaline moiety – 128.82 and 128.89 (2d, J = 163.9 and 162.7 Hz, $C_{(6)}$ and $C_{(7)}$; 130.84 and 131.40 (2 dd, J = 162.5, 8.3 and 161.9, 8.1 Hz, $C_{(5)}$ and $C_{(8)}$); 138.98 and 141.21 (2m, $C_{(4a)}$ and $C_{(8a)}$); 143.95 (s, $C_{(2)}$); 152.50 (s, $C_{(3)}$). Found, %: C 78.60; H 4.27; N 17.46. $C_{21}H_{14}N_4$. Calculated, %: C 78.24; H 4.38; N 17.38.