An Anomalous Course of the Reduction of 2-(3-Oxo-3,4-dihydroquinoxalin-2-yl)benzene Diazonium Salt. Synthesis of a New Quinoxalino[1,2-*c*][1,2,3]benzotriazine System [1].

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By diazotization of 3-(2-aminophenyl)quinoxaline-2(1*H*)-one **1a** and 3-(2-aminophenyl)-6,7-dimethylquinoxaline-2(1*H*)-one **1b** followed by the reaction with sodium sulphite new quinoxalino[1,2-*c*]-[1,2,3]benzotriazins **4a** and **4b** were prepared, respectively.

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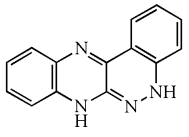
Arylhydrazines have been prepared most suitable from the reaction of diazonium salts with an excess of alkaline sulfite [2]. In this reaction, azo copulation occurs at first forming arylazo sulfonates, which are further reduced by sulfite to the corresponding hydrazino sulfonates, and these are converted to arylhydrazine by an acid hydrolysis.

Recently, we have applied this method to the preparation of 5-(*o*-hydrazinophenyl)-6-azauracil and its derivatives, which are cyclized to [1,2,4]triazino[5,6-*c*]cinnolins [3-5]. We were intersted in the synthesis of cinnoline nucleus A (Figure) in the same way from quinoxalin-2(1*H*)-ones **1**.



A

Figure

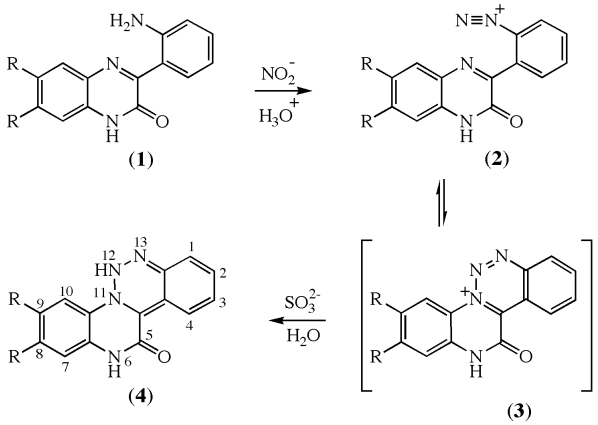
However, we found that the above reaction proceeded in a different way, as shown in Scheme. Diazotization of 3-(2-aminophenyl)quinoxaline-2(1*H*)-one **1a** and 6,7-dimethyl derivative **1b** would give the diazonium salts **2a** and **2b**, whose reaction with an excess of sodium sulfite afforded 12*H*-quinoxalino[1,2-*c*][1,2,3]benzotriazine-5(6*H*)-one **4a** and its 8,9-dimethyl derivative **4b**, respectively.

This unusual course of reaction can be explained by the formation of the benzotriazines **3a** and **3b**, whose reduction provided compounds **4a** and **4b**, respectively.

The structure of compounds **4a** and **4b** was determined by C, H, N elementary analysis, mass spectrometry and ^{1}H-, ^{13}C- and ^{15}N-NMR spectra.

The N-12 (δ 177.6 ppm) is single bond coupled (doublet, J = 107 Hz) with the atom H-12 and weak long-range interaction (*via* four bonds) with the atom H-10 was observed. Atom N-11 (δ 126.7 ppm) is scalar coupled with the H-4, H-6, and H-10. For N-6 signal, single bond interaction (J = 98 Hz) with H-6 and multiple bond interactions with H-7, H-8, and H-10 were likewise observed. The only multiple bond correlation of N-13 with H-12 resonance was detected.

Scheme



a) R = H
b) R = CH_3

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. Infrared spectra were measured in KBr disks and scanned on an ATI Unicam Genesis FTIR instrument and values are described in cm $^{-1}$. Elemental analyses were performed by using an EA 1108 Elemental Analyzer (Fison Instrument). The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded using a Bruker Avance DRX 500 and Avance 300 spectrometers. All ^{1}H- and ^{13}C-NMR signals were assigned on the basis of ^{13}C APT, H,H-COSY, 2D GHMQC [9], and 2D HMBC [7,8] experiments. Gradient-enhanced 2D inverse detected heteronuclear experiments (^{1}H-^{13}C correlation) were obtained on a Avance 300 spectrometer with 5 mm triple-resonance broadband inverse probehead and QNP (Quattro Nucleus) probehead, respectively. The chemical shifts were referenced to tetramethylsilan (TMS). Directly detected ^{15}N NMR spectrum was observed for a sample

prepared by dissolving 160 mg of the compound in 2.5 ml of deuteriodimethyl sulfoxide inside of a 10 mm NMR tube and using Avance DRX 500 with BBO (Broadband-Observe) probehead. The duration of this measurement was 44 hours. The chemical shifts were referenced indirectly to the signal of liquid ammonia (0 ppm). All ^{15}N NMR signals were assigned on the basis of ^{1}H-^{15}N chemical shift correlations [10]. Gradient-enhaced ^{1}H-^{15}N GHMBC experiment was recorded using Bruker Avance 300 spectrometer with 5 mm BBI (Broadband Decoupling Inverse 1H Probe). The sample for measurement in 5 mm tube was prepared by dissolving 40 mg of compound in 0.5 ml of deuteriodimethyl sulfoxide. The temperature of the measurements was 308 K. MS spectra were measured on ZAB-EQ (VG Analytical Ltd., England). Electronic spectra were measured in ethanol solutions on a UV-VIS spectrometer Unicam Helios α in 1 cm cuvettes.

12*H*-Quinoxalino[1,2-*c*][1,2,3]benzotriazin-5(6*H*)-one (**4a**).

The suspension of 3-(2-aminophenyl)quinoxaline-2(1*H*)-one [6] (241.3 mg, 1.02 mmol) in a mixture of water (32 ml) and sulfuric acid (0.5 ml, 95%) was heated until solution was formed which was quickly cooled to room temperature. The suspension was than cooled on an ice bath to the temperature 0-5 °C. During the course of 10 minutes the solution of sodium nitrite (75.6 mg, 1.10 mmol) in ice-cold water (6 ml) was added to the mixed suspension while the temperature was maintained between 0-5 °C. The reaction mixture was mixed on an ice-bath until the solution was formed (about 1 hour). This solution was poured into the solution of sodium sulfite (2.00 g, 15.87 mmoles) in ice-cold water (12 ml). After allowing the reaction mixture to stand at room temperature for 30 minutes it was refluxed for 2 hours on boiling a water-bath. The solution was left overnight at room temperature and than the solid precipitate was collected by suction, thoroughly washed with water and dried in air. Yield of monohydrate is 230.2 mg (84 %), mp = 307-310 °C (decomposition) (toluene); ^{1}H nmr (deuteriodimethyl sulfoxide): δ 13.32 (s, 1H, NH-12), 11.27 (s, 1H, NH-6), 7.65 (d, 1H, 10-H, J = 8.5 Hz), 7.46 (m, 1H, 9-H, J = 8.5 Hz,), 7.18 (m, 1H, 8-H, J = 8.2 Hz), 7.74 (d, 1H, 7-H, J = 8.2 Hz), 7.16 (m, 1H, 4-H, J = 1.1, 8.3 Hz), 7.12 (dd, 1H, 3-H, J = 1.0, 7.9 Hz), 7.04 (ddd, 1H, 2-H, J = 1.1, 7.9, 8.3 Hz), 7.16 (d, 1H, 1-H, J = 8.3 Hz); ^{13}C nmr (deuteriodimethyl sulfoxide): δ 136.6 (C-4b), 153.1 (C=O, C-5), 116.6 (C-6a), 141.1 (C-10a), 110.6 (C-10), 126.8 (C-9), 120.6 (C-8), 120.6 (C-7), 130.1 (C-13a), 128.8 (C-4a), 109.3 (C-4), 122.0 (C-3), 120.9 (C-2), 109.2 (C-1); ^{15}N nmr **(**deuteriodimethyl sulfoxide) [ref. NH_3(l)]: δ 177.6 (NH, N-12, $J_{N,H}$ = 107 Hz), 126.7 (N-11), 119.5 (NH, N-6, $J_{N,H}$ = 98 Hz), 301.5 (N-13); m/s (m/z) (relative intensites): 251.3 (40), 523 (100) ir (ν, cm^{-1}): 3100, 1740, 1676, 1655, 1597, 1509, 1456, 1416, 1371, 1321, 1293, 1247, 1192, 1160, 1076, 1016, 976, 760, 691, 594, 573, 547, 479; UV-VIS λ_{max} (log ε) (ethanol): 304 (4.66), 439 (4.78). By drying in a vacuum at 150 °C we have recorded the weight loss corresponding to the loss of 1 molecule of water.

Anal. Calcd. For $C_{14}H_{10}N_4O$ (250.25): C, 67.19; H, 4.03; N, 22.39; Found: C, 66.98; H, 3.95; N, 22.16

8,9-Dimethyl-12*H*-quinoxalino[1,2-*c*][1,2,3]benzotriazin-5(6*H*)-one (**4b**).

This compound was prepared by the same method as that of compound (**4a**) using amino derivative (**1b**) [11] (536.7 mg, 2.02 mmoles), hydrochloric acid (3 ml, 37%) and water (90 ml) in (73 %) yield; ms : m/z 279; ir (ν, cm^{-1}): 3197, 3155, 3100, 1735, 1655, 1579, 1539, 1489, 1433, 1380, 1338, 1263, 1237, 1199, 1155, 1000, 966, 745, 590, 588, 547; ^{1}H nmr (deuteriodimethyl sulfoxide): δ 13.25 (s, 1H, NH-12), 11.03 (s, 1H, NH-6), 7.68 (m, 1H, ArH), 7.46 (m, 1H, ArH), 7.38 (m, 1H, ArH), 7.20 (m, 1H, ArH), 7.12 (m, 1H, ArH), 7.10 (m, 1H, ArH), 7.04 (m, 1H, ArH), 7.16 (m, 1H, ArH), 2.23 (s, 6H, CH_3).

Anal. Calcd. For $C_{16}H_{14}N_4O$•1/2H_2O (287.32): C, 66.89; H, 5.26; N, 19.50 Found: C, 66.66; H, 5.00; N, 9.33

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