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Acid-catalyzed rearrangement of 3-(β-2-aminostyryl)quinoxalin-2(1*H*)ones—a new and efficient method for the synthesis of 2-benzimidazol-2-ylquinolines

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ABSTRACT

A highly efficient, one-step, versatile method for the synthesis of 2-benzimidazol-2-ylquinolines has been developed on the basis of an acid-catalyzed rearrangement proceeding via a novel ring contraction of 3-(β-2-aminostyryl)quinoxalin-2(1*H*)ones.

The benzimidazole[1] moiety is an important pharmacophore that has proved to be useful for a number of biologically relevant targets. Compounds possessing a benzimidazole moiety exhibit significant activity towards several viruses, such as HIV,[1d,e] Herpes (HSV-1),[1d,f] human cytomegalovirus (HCMV),[1b,d,f] and influenza.[1g] On the other hand, nitrogen-containing heterocyclic systems, in which nitrogen atoms are intimately related to the bond connecting the nuclei, are of interest due to their ability to form complexes with metal ions. Since the report on organic light emitting diodes (OLED) by Tang and VanSlyke,[2] LEDs based on organic or polymeric materials have generated considerable interest and have enabled the development of low-cost, full-color, flat-panel displays along with other emissive products.[3–6] Organic electronic devices (OEDs) have made excellent progress over the past few years and investigations into synthesizing new active organic materials for applications in organic thin film transistors have recently attracted much attention.[7] The best-known electroluminescent (EL) metal chelate is Alq_3, where q is the 8-hydroxyquinolinato ligand, which is not only a good emitter, but is also a highly efficient electron-transporting material.[8,9] Attachment of a benzimidazole group at the 2-position would allow this ligand to form stable complexes with metal ions in a way similar to 8-hydroxyquinoline.

The preparation of benzimidazole derivatives in general, and 2-benzimidazol-2-ylquinolines in particular, is usually straightforward and a number of synthetic methods are available.[10,11] However, these methods have disadvantages, such as low yields, harsh reaction conditions, for example, high reaction temperatures (~200 °C), use toxic reagents, such as $POCl_3$, TMS-Cl, and polyphosphoric acid, and the following catalyst/oxidizing agents: $Pb(OAc)_4$, $Py(Cr_2O_7)_2$, and $Cu(OAc)_2$, and continuous O_2 bubbling over the course of the reaction.

In the present work, we report a direct, efficient, and convenient approach to the synthesis of 2-benzimidazol-2-ylquinolines. The method[12] is based on a new acid-catalyzed quinoxaline-benzimidazole rearrangement of 3-(β-2-aminostyryl)quinoxalin-2(1*H*)ones which occurs via reduction of the corresponding, easily available, 3-(β-2-nitrostyryl)quinoxalin-2(1*H*)ones **1a–i** when exposed to $Na_2S_2O_4$. As is evident from the structures of products **2**, the C(2)–C(3) fragment and the β-2-nitrostyryl group at position 3 of the starting quinoxalin-2(1*H*)one system, are involved in constructing two new heterocyclic systems (Scheme 1).

This reaction also proceeded with a compound possessing two 3-(β-2-nitrostyryl)quinoxalin-2(1*H*)one fragments, with the formation of a benzimidazole-monopodand with terminal quinoline fragments at the 2 and 2′ positions of the benzimidazole ring system (Scheme 2).

The structures of compounds **2a–i** were deduced from their elemental analyses and ^{1}H NMR data.[12] The mass spectra of these

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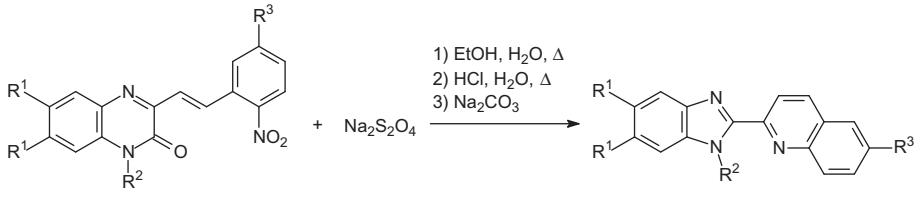
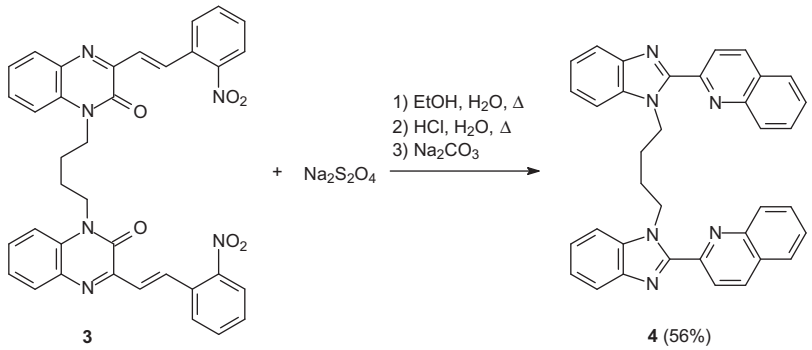


1a-i 2a-i

R^1	R^2	R^3	Product (yield)	M.p., °C	R_f[a]
H	H	H	**2a** (80%)	93-95	–
H	Me	H	**2b** (76%)	108-110	–
H	Et	H	**2c** (74%)	86-88	–
H	*n*-Pr	H	**2d** (53%)	< 70	–
H	*n*-Bu	H	**2e** (69%)	–	0.39
H	$(CH_2)_4CH_3$	H	**2f** (70%)	–	0.49
H	$(CH_2)_5CH_3$	H	**2g** (54%)	–	0.50
Me	H	H	**2h** (79%)	225-227	–
H	H	Cl	**2i** (59%)	168-170	–

[a]Eluent: hexane – EtOAc (3:1)

Scheme 1. An efficient method for the synthesis of 2-benzimidazol-2-ylquinolines from 3-(β-2-nitrostyryl)quinoxalin-2(1*H*)ones (**2a**–**i**).



3 **4** (56%)

Scheme 2. Synthesis of 1,4-bis-[2-(quinolin-2-yl)benzimidazol-1-yl]butane (**4**).

compounds displayed molecular ion peaks at appropriate *m/z* values. Initial fragmentation involved scission of the benzimidazole and quinoline ring systems.[12]

In the ^{1}H NMR spectra of compounds **2b–i**, along with signals due to the two aromatic fragments, in the region of δ 7.70–8.61 and δ 7.32–7.83, two doublet signals for the AB-system were seen. The chemical shift of this AB system was not only shifted downfield (δ 8.55–8.61 and δ 8.48–8.54) compared with the chemical shifts of the signals of the AB protons of the styryl fragment (δ 8.30–8.36 and δ 7.61–7.66, $^3J \approx 16.0$ Hz) of the starting compounds **1**, but also had a small $^3J \approx 8.6$ Hz coupling constant, characteristic of the *cis*-configuration of the vinyl protons. This indicated that closure of the pyridine ring had occurred with formation of the quinoline system of the 2-benzimidazol-2-ylquinolines **2b–i**. The chemical shifts of the protons of the N–CH_2 fragments of the substituent at position 1 of the 2-benzimidazol-2-ylquinolines **2c–g** moved downfield by about ~0.7 ppm compared with the chemical shifts of the same protons of the starting compounds **1c–g**. It should be pointed out that the protons of the benzimidazole fragment in compounds **2b–g** resonate as two doublets and two triplets, whereas in compound **2a** they resonate as AA′BB′-system multiplets.

The molecular structure of compound **2c** was established unambiguously by single crystal X-ray analysis (Fig. 1).[13]

To investigate the reaction mechanism, we performed the reduction of 3-(β-2-nitrostyryl)-6,7-dimethylquinoxalin-2(1*H*)-one (**1h**) with hydrogen using 10 mol % Pd/$CaCO_3$ as the catalyst in methanol and obtained the corresponding 3-(β-2-aminostyryl)-6,7-dimethylquinoxalin-2(1*H*)-one (**5h**).[14] When boiled in AcOH for 3 h the latter was transformed into 2-benzimidazol-2-ylquinoline **2h** (Scheme 3).[15]

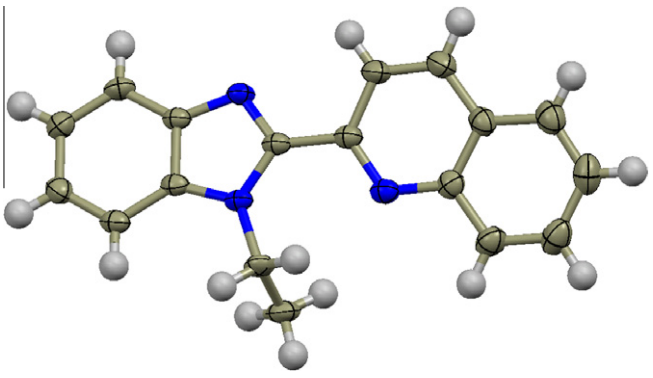
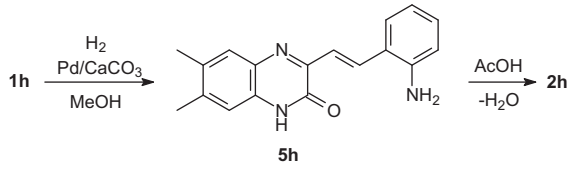
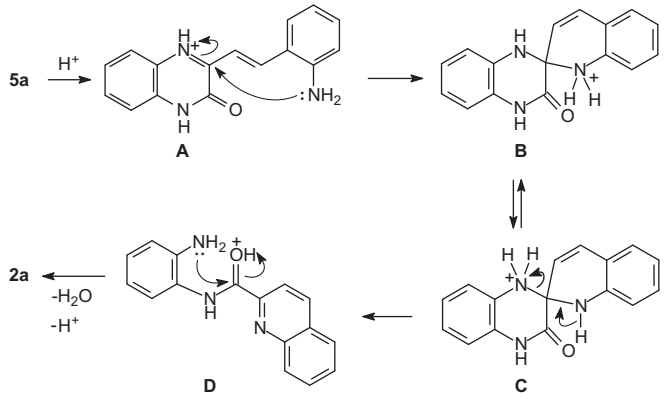


Figure 1. ORTEP plot of compound **2c**. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by spheres of arbitrary radii.

On the basis of the known chemistry of aniline,[16] azadienes,[17] and quinoxalinones,[18] it is reasonable to assume that the first stage of this reaction involves the nucleophilic attack of the amine group



Scheme 3. The formation of 2-benzimidazol-2-ylquinoline (**2h**) from 3-(β-2-aminostyryl)quinoxalin-2(1*H*)one (**5h**).



Scheme 4. A plausible mechanism for the formation of 2-benzimidazol-2-ylquinolines.

at C(3) of the quinoxalin-2(1*H*)-one of **A** to form the spiro-quinoxaline derivative **B**. Rearrangement of the spiro-quinoxaline is then assumed to occur according to Scheme 4 by cascade reactions involving: (a) acid-catalyzed ring-opening with cleavage of the C(3)–N(4) bond in the spiro-compound **C** leading to formation of the quinoline derivative **D**, and (b) intramolecular nucleophilic attack by the amino group on the carbamoyl carbonyl group with formation of the final product **2** following elimination of water (Scheme 4).

In conclusion, we have developed a synthetic strategy for the preparation of substituted 2-benzimidazol-2-ylquinolines **2** that have not as yet been described in the literature. This protocol includes a novel acid-catalyzed rearrangement of 3-(β-2-aminostyryl)quinoxalin-2(1*H*)ones. The simplicity of the reaction design and the possibility of introducing a variety of substituents at any position of both the benzimidazole and quinoline ring systems makes this method a useful tool for constructing these medicinally and technically (organic emitting materials) relevant compounds. The reaction is readily applicable to large-scale synthesis. Application of this method to the synthesis of other heterocyclic ring systems is currently under investigation and the results will be published in due course.

Acknowledgment

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12. *Typical procedure for the preparation of* **2**. A solution of 0.30 g (0.9 mmol) of 1-ethyl-3-(β-2-nitrostyryl)-quinoxalin-2(1*H*)-one (**1c**) and 0.77 g (3.7 mmol) of 85% $Na_2S_2O_4$ in 5 mL of EtOH and 5 mL of H_2O was heated under reflux for 3 h. Next, 5 mL of HCl and 5 mL of H_2O were added, and the mixture was heated under reflux for 2 h. After cooling to room temperature, the reaction mixture was neutralized by addition of aqueous Na_2CO_3. The product was extracted with $CHCl_3$ (3 × 20 ml), and the organic extracts dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel with hexane–EtOAc (15:1) as eluent to give 0.19 g (74%) of an analytically pure sample of 2-(1-ethylbenzimidazol-2-yl)quinoline (**2c**): IR (KBr) ν 3046, 2955, 2925, 2854, 1615, 1599, 1563, 1496, 1466, 1437, 1398, 1375, 1329, 1258, 1190, 1117, 1067, 828, 761, 740 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.56 (3H, t, J = 7.0 Hz); 5.07 (2H, q, J = 7.0 Hz); 7.34 (1H, dd, J = 8.2; 6.8 Hz); 7.42 (1H, dd, J = 7.9; 7.2 Hz); 7.70–7.80 (2H, m); 7.83 (1H, d, J = 8.2 Hz); 7.91 (1H, dd, J = 7.9; 7.2 Hz); 8.11 (1H, d, J = 8.2 Hz); 8.18 (1H, d, J = 8.2 Hz); 8.54 (1H, d, J = 8.5 Hz); 8.59 (1H, d, J = 8.5 Hz). MS (EI$^+$), m/z I (%): 274 (17), 273 (87) $M^{+\cdot}$, 272 (42), 259 (20), 258 (100), 246 (37), 245 (32), 136 (13), 129 (11), 128 (24), 77 (10). *(The peaks of ions with relative intensity less than 10% are not specified.) MALDI mass spectrum m/z: 274 MH^+.
1,4-Bis-[2-(quinolin-2-yl)benzimidazol-1-yl]butane (**4**). Mp 264–267 °C. IR (KBr) ν 3077, 3048, 2954, 2925, 2855, 1673, 1597, 1496, 1461, 1437, 1427, 1397, 1367, 1329, 1284, 1259, 1159, 1121, 1074, 842, 758, 736, 719 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.20 (4H, br s); 5.09 (4H, br s); 7.29–7.40 (4H, m); 7.56–7.68 (4H, m); 7.74 (2H, d, J = 7.6 Hz); 7.75–7.81 (4H, m); 8.05 (2H, d, J = 7.9 Hz); 8.49 (2H, d, J = 8.6 Hz); 8.53 (2H, d, J = 8.6 Hz). MS (EI$^+$), m/z I (%): 545 (28), 544 (75) $M^{+\cdot}$, 416 (19), 415 (19), 412 (14), 300 (14), 299 (65), 298 (11), 286 (22), 272 (100), 258 (66), 246 (34), 171 (46). *(The peaks of ions with relative intensity less than 10% are not specified.) MALDI mass spectrum m/z: 545 MH^+.
13. The X-ray diffraction data for crystals of **2c** were collected on a Bruker AXS Smart Apex II CCD diffractometer at 296 K. Crystallographic data for **2c**. $C_{18}H_{15}N_3$, pink prisms, formula weight 273.33, orthorhombic, $Pca2_1$, a = 21.506(2), b = 4.9627(5), c = 13.1575(13) Å, V = 1404.3(3) Å^3, Z = 4, ρ_{calc} = 1.293 g cm^{-3}, $\mu(\lambda MoK_\alpha)$ = 0.78 cm^{-1}. $F(0\,0\,0)$ = 576, reflections collected = 8128, unique = 2940, R(int) = 0.0885, full-matrix least-squares on F^2, parameters = 191, restraints = 1. Final indices R_1 = 0.0546, wR_2 = 0.0766 for 1952 reflections with $I > 2\sigma(I)$; R_1 = 0.0922, wR_2 = 0.0851 for all data, goodness-of-fit on F^2 = 0.974, largest difference in peak and hole (0.149 and −0.177 eÅ^{-3}). Crystallographic data (excluding structure factors) for the structure **2c** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 778693. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
14. *3-(β-2-Aminostyryl)-6,7-dimethylquinoxalin-2(1H)one* (**5h**). A suspension of 0.50 g (1.6 mmol) of 3-(β-2-nitrostyryl)-6,7-dimethylquinoxalin-2(1*H*)-one

(**1h**) and 0.05 g of $Pd/CaCO_3$ in 20 mL of MeOH was stirred under a H_2 atmosphere for 3 d. The precipitated crystals were collected by filtration and washed with 40 ml of DMF. The DMF layer was diluted with 70 ml of H_2O, and the precipitated crystals were collected by filtration to afford 0.30 g (67%) of an analytically pure sample of 3-(β-2-aminostyryl)-6,7-dimethylquinoxalin-2(1*H*)-one (**5h**): IR (KBr) *ν* 3444, 3229, 3063, 2918, 1659, 1614, 1508, 1489, 1456, 1438, 1390, 1255, 1154, 741, 595 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) *δ* 2.30 (3H, s); 2.31 (3H, s); 5.39 (2H, br s); 6.61 (1H, dd, *J* = 7.6; 7.3 Hz); 6.74 (1H, d, *J* = 7.9 Hz); 7.06 (1H, dd, *J* = 7.9; 7.3 Hz); 7.06 (1H, s); 7.43 (1H, d, *J* = 15.9 Hz); 7.47 (1H, d, *J* = 7.6 Hz); 7.55 (1H, s); 8.12 (1H, d, *J* = 15.9 Hz); 12.27 (1H, br s). MS (EI*), *m*/*z* I (%): 292 (10), 291 (55) $M^{+\cdot}$, 290 (32), 289 (11), 274 (19), 273 (25), 272 (18), 264 (12), 263 (61), 262 (27), 248 (23), 247 (100), 246 (10), 147 (10), 145 (25), 135 (13), 131 (33), 129 (24), 128 (14), 123 (10), 118 (12), 117 (16). (The peaks of ions with relative intensity less than 10% are not specified.) MALDI mass spectrum *m*/*z*: 292 MH^+.

15. *2-(5,6-Dimethylbenzimidazole-2-yl)quinoline* (**2h**). A solution of 0.30 g (1.0 mmol) of 3-(β-2-aminostyryl)-6,7-dimethylquinoxalin-2(1*H*)-one (**5h**) in 8 mL of AcOH was heated under reflux for 3 h. After cooling to room temperature, the precipitated crystals were collected by filtration and 0.21 g (75%) of an analytically pure sample of 2-(5,6-dimethylbenzimidazol-2-yl)quinoline (**2h**) was obtained: IR (KBr) *ν* 3501, 3052, 2964, 2939, 2317, 1717, 1701, 1652, 1618, 1600, 1563, 1506, 1448, 1413, 1324, 1277, 1261, 1234, 1111, 1003, 865, 856, 834, 757 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) *δ* 2.38 (6H, s); 7.42 (1H, br s); 7.56 (1H, br s); 7.70 (1H, dd, *J* = 7.6; 7.0 Hz); 7.89 (1H, dd, *J* = 8.2; 7.0 Hz); 8.09 (1H, d, *J* = 8.0 Hz); 8.19 (1H, d, *J* = 8.2 Hz); 8.48 (1H, d, *J* = 8.6 Hz); 8.55 (1H, d, *J* = 8.6 Hz). MS (EI*), *m*/*z* I (%): 274 (21), 273 (100) M^+, 272 (45), 258 (27), 128 (15), 60 (11). (The peaks of ions with relative intensity less than 10% are not specified.) MALDI mass spectrum *m*/*z*: 274 MH^+.
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