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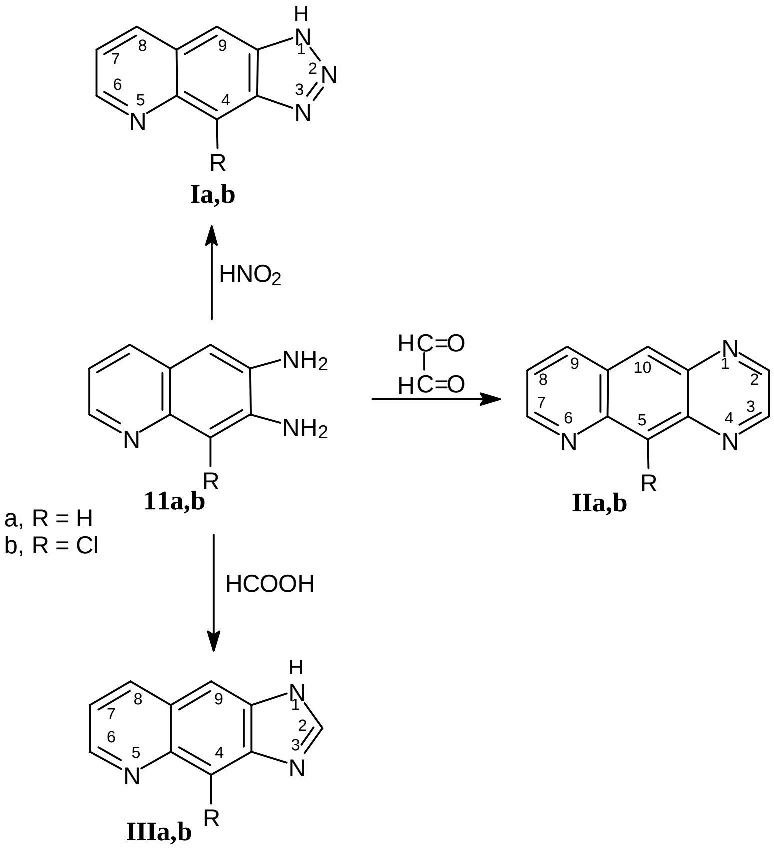
SYNTHESIS OF TWO NOVEL TRICYCLIC RINGS: TRIAZOLO[4,5-*g*]-QUINOLINES AND PYRIDO[2,3-*g*]QUINOXALINES DERIVED FROM 6,7-DIAMINOQUINOLINES

Paolo Sanna,*Antonio Carta, and Giuseppe Paglietti

Dipartimento Farmaco-Chimico-Tossicologico - University of Sassari
via Muroni, 23/a - 07100 Sassari, Italy

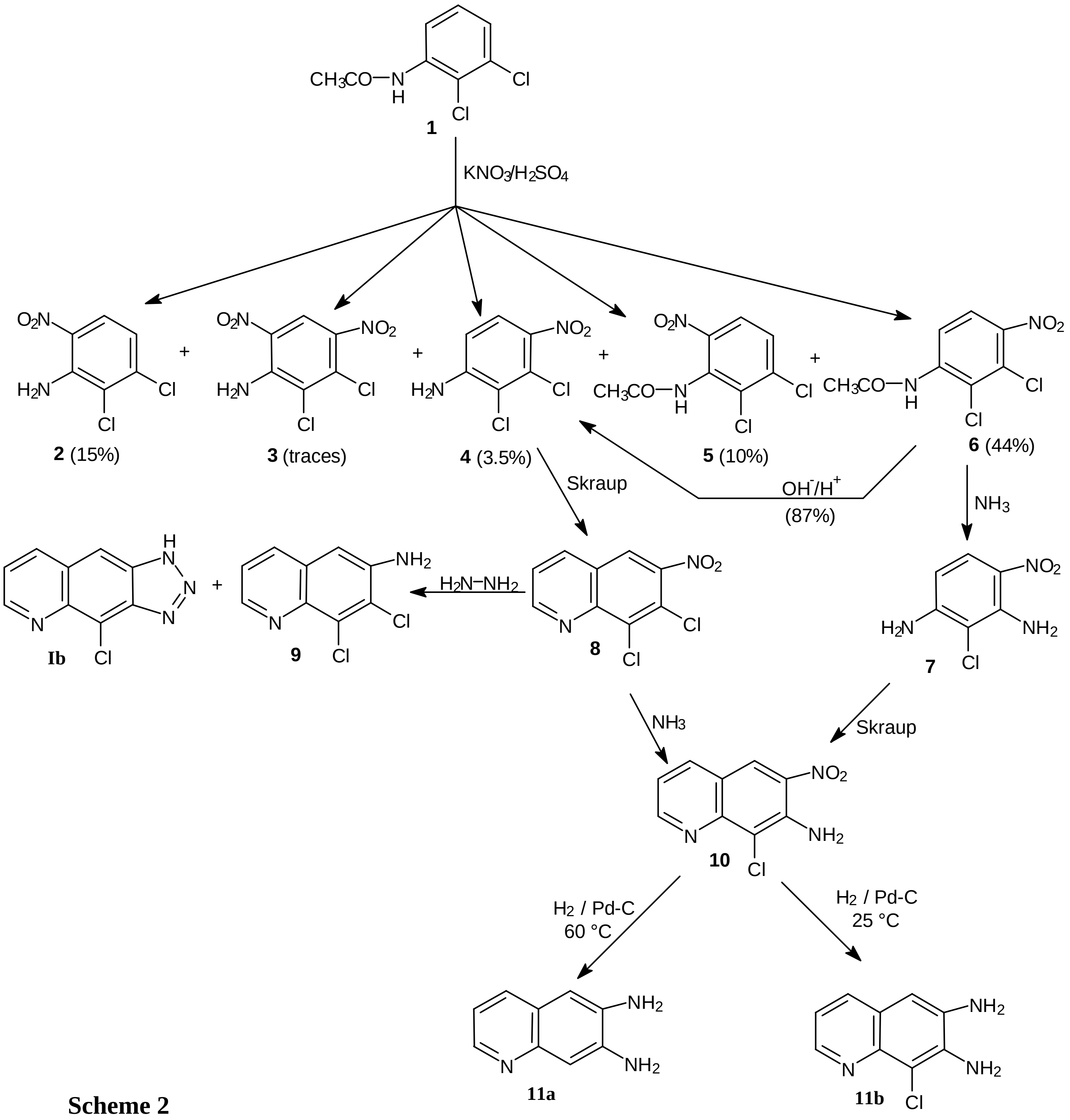
Abstract- A general simple route for the synthesis of triazolo[4,5-*g*]quinolines and pyrido[2,3-*g*]quinoxalines is described. The heterocycles obtained were fully characterised by their spectroscopical properties. A revision of the nitration of the 2,3-dichloroacetanilide is also discussed, since it afforded the request nitro derivative to build up the key intermediate 6,7-diaminoquinolines.

Heterocyclic compounds continue to attract most of the researchers in both University and industry since they dominate ought to the largest number of publications appearing in the literature. According to their importance in various fields of applications,[1] their interest from a medicinal chemistry point of view lies upon the well known properties as antibiotic, neurotropic, cardiovascular and anticarcinogenic agents. Thus, in line with our previous researches in this field, aimed to discover novel pharmacological agents in the series of the triazolo[4,5-*f*]-[2,3] and triazolo[4,5-*h*]quinolines[4] we now planned to design new fundamental heterocyclic nuclei belonging to the class of triazolo[4,5-*g*]quinolines (**Ia**,**b**) and pyrido[2,3-*g*]quinoxalines (**IIa**,**b**) (see Scheme 1) to be further functionalized for a pharmacological evaluation. In this context we also reprepared, using an alternative simpler route, the known imidazo[4,5-*g*]quinolines (**IIIa**,**b**)[5] which in this case were fully spectroscopically (IR, UV and ^{1}H-NMR) characterised. Our previous attempts of preparation of triazolo[4,5-*g*]quinolines starting from 5-aminobenzotriazoles by condensation with activated acetylenic esters,[6,7] suitable β-keto esters,[8] β-diketones[9] or *via* Skraup synthesis[10] led to angular triazolo[4,5-*f*]quinolines; in no way the desired [4,5-*g*] compounds could be obtained. This fact prompted us to devise a new approach that is depicted in the Scheme 1. Thus, we have found that the diamines (**11a**,**b**) underwent ring closure to **Ia**,**b** by diazotization with HNO_2 and cyclization of the corresponding diazonium salts at room temperature. Reaction of **11a**,**b** with glyoxal afforded the pyridoquinoxalines (**IIa**,**b**) *via* an expected nucleophilic addition-elimination mechanism upon the 1,2-dicarbonyl compound under refluxing ethanol. Cyclization to imidazoquinolines (**IIIa**,**b**) occurred with formic acid at 100 °C. In all cases the desired heterocycles were obtained in good yields.



Scheme 1

The necessary diamine (**11a**) is claimed to be formed by hydrogenation of the corresponding parent nitro derivative by Lebenstedt and Schunack[5] who did not isolate and characterize it. Our approach, outlined in Scheme 2, is only partially similar to that used by the cited authors and allowed us to clear the course of the nitration of the starting 2,3-dichloroacetanilide (**1**) according to the indications of the literature.[11] Preparation of the key intermediate (**6**) has been the starting point of the experimental work of this paper. Holleman[11] claimed to have obtained by nitration of **1** the sole mononitro compound (**5**) that upon hydrolysis was coincident with compound (**2**) previously described by Beilstein and Kurbatov,[12] thus concluding that despite the expectations the *ortho* orientation of the acetylamino group was prevailing. This reaction instead proved to be more complicated since from the reaction mixture we were able to isolate, after column chromatography, the requested compound (**6**) in the highest yield (44%) followed by the known compounds: (**2**) (15%),[11,12] (**3**) (traces),[13] (**4**) (3.5%)[14] and (**5**) (10%).[11,15] The presence of the deacetyl compounds (**2**), (**3**) and (**4**) clearly indicates that when the mixture is poured onto ice a partial hydrolysis was occurring, due to exothermal reaction. On the whole the derivatives of *para* substitution of aniline represent nearly 50% of the nitration products whereas a 25% is represented by the *ortho* nitroaniline derivatives and only traces of the dinitro derivative (**3**) were detected. Our results confirm what is generally accepted that both acetylamino and chlorine groups in benzene ring are *ortho*-*para* directing by themselves just producing mixture of isomers, the *para* effect of acetylamino group appearing twice predominant. Consequently in our opinion the Holleman's[11] results are misleading and must be corrected.



Scheme 2

For our purpose we then submitted the intermediate (**4**), also obtained by alkaline hydrolysis of **6**, to Skraup reaction to give the 7,8-dichloro-6-nitroquinoline (**8**) in 53% yield, from which, by nucleophilic substitution with ammonia, the desired intermediate (**10**) (98%) was isolated. Alternatively, compound (**10**) was also prepared starting from **6** *via* **7** after Skraup reaction. However, this conversion appeared to be very disfavored since only a small amount (8%) of **10** was obtained. The latter underwent both hydrogenolysis and reduction to the diamine (**11a**) operating with hydrogen and Palladised charcoal at 60 °C under moderate pressure (3 atm) while the hydrogenation carried out at 25 °C yielded the diamine (**11b**). However, this step is a critical point because the variation of the temperature between 30-50 °C influences the formation ratio of the compounds (**11a**) and (**11b**). As the temperature increases formation of **11a** dominates. This is an improvement in comparison with the results reported by Lebenstedt and Schunack[5] thus offering a possibility to obtain the two diamines by the same intermediate. The availability of the intermediate (**8**) allowed us to extend the investigation of the reaction with hydrazine hydrate that we had previously used on similar compounds in the aim to obtain triazolo[4,5-*f*]quinolines.[10] From this reaction we could observe that hydrazine hydrate mainly reduced the nitro group to amine (**9**) (50%) while the expected nucleophilic displacement of the chlorine in C-7 to give the triazolo[4,5-*g*]quinoline (**Ib**) occurred in lower yield (22%) possibly *via* triazolo *N*-oxide not isolable under these reducing conditions. The result obtained by this route was comparable in terms of overall yield (21%) with that previously described but more immediate avoiding the multisteps leading to the diamine (**11b**). The structures of all compounds described are supported by their analytical and spectroscopical data (IR, UV and ^{1}H-NMR). In particular the UV spectra of compounds (**I**, **II** and **III**) are the most characteristic showing two regions of absorptions respectively in the range 220-260 nm (more intense) and 310-380 nm. In addition the triazolo[4,5-*g*]quinolines (**Ia**,**b**) exhibited a fine structure, very similar to those of the previously reported angular triazolo[4,5-*f*]-[2,3] and [4,5-*h*] analogues,[4] and not present in the other triciclic compounds (**II**) and (**III**). An hypsochromic shift of about 15-20 nm (230 nm compared 245-250 nm of the angular derivatives) was also observed for the intense maxima of **Ia**,**b** in the region 220-260 nm, associated with a batochromic shift of about 50-60 nm for absorptions in the region 310-380 nm.

EXPERIMENTAL

Melting points were determined in open capillaries in a Digital Electrothermal IA9100 melting point apparatus and are uncorrected. In brackets are reported the recrystallization solvents. IR spectra were recorded as nujol mulls with a Perkin-Elmer 781 spectrophotometer. UV spectra are qualitative and were recorded in nm for solutions in ethanol with a Perkin-Elmer Lambda 5 spectrophotometer. ^{1}H-NMR spectra were measured at 200 MHz using a Varian XL-200 spectrometer, using TMS as internal standard.

The chemical shift values are reported in ppm (δ) and coupling constants (J) in Hertz (Hz). Signal multiplicities are represented by s (singlet), d (doublet), dd (double doublet), t (triplet), m (multiplet), and br s (broad singlet). MS spectra were performed on a combined HP 5790-HP 5970 GC/MS apparatus. Silica gel 60 (Merck 70-230 and 230-400 mesh silica gel) was used for column chromatography. The progress of the reactions and the purity of the final compounds were monitored by TLC using Merck F-254 commercial plates. Light petroleum refers to the fraction with bp 40-60 °C. Elemental analyses were performed at the Laboratorio di Microanalisi, Dipartimento di Scienze Farmaceutiche, University of Padua.

Preparation of 2,3-dichloro-4-nitroacetanilide (6). To a solution of 10 g (49.0 mmol) of compound (**1**) prepared as described[12] in concentrated sulfuric acid (50 mL), cooled with an external ice bath, an aqueous solution of potassium nitrate (9.9 g, 98.0 mmol) in concentrated sulfuric acid (15 mL) was slowly added under mechanical stirring so that the inner temperature was always below 10 °C. After the addition was complete, the reaction mixture was stirred below 10 °C for an additional 4 h and then poured into crushed ice (300 g). The resulting precipitate was filtered off, thoroughly washed with water and dried affording 10.8 g of crude reaction product, TLC of which showed to deal with a complex mixture. Separation of the components was accomplished by chromatography on silica gel, eluting at first with a 7:3 mixture of ether-light petroleum, then with ether and eventually with a 8:2 mixture of ether-acetone, to yield in sequence: **2,3-dichloro-6-nitroaniline (2)** (1.56 g, 15%), mp 165-167 °C (lit.,[11,12] 164 °C); **2,3-dichloro-4,6-dinitroaniline (3)** (0.07 g, 0.6%), mp 196-198 °C (lit.,[13] 197-198 °C); **2,3-dichloro-4-nitroaniline (4)** (0.35 g, 3.5%), mp 189-191 °C (lit.,[14] 180-181 °C); **2,3-dichloro-6-nitroacetanilide (5)**: (1.23 g, 10%), mp 218-219 °C (acetone) (lit.,[11] 218 °C, lit.,[15] 222 °C); **2,3-dichloro-4-nitroacetanilide (6)** (5.36 g, 44%), mp 149-151 °C (acetone); IR: 3250, 1680, 1620, 1570 cm^{-1}; UV: λ_{max} 286, 236 sh, 218 nm; ^1H-NMR ($CDCl_3$+DMSO-d_6): δ 8.99 (s, 1H, NH), 8.37 (d, 1H, J = 8.8 Hz, H-5), 7.84 (d, 1H, J = 8.8 Hz, H-6), 2.30 (s, 3H, CH_3); MS: *m/z* 248 (M^+). Anal. Calcd for $C_8H_6N_2O_3Cl_2$: C, 38.58; H, 2.43; N, 11.25; Cl, 28.47. Found: C, 38.24; H, 2.30; N, 11.06; Cl, 28.29.

2,3-Dichloro-4-nitroaniline (4). The title compound was obtained starting from **6** (3.0 g, 12 mmol) in 87% yield (2.17 g) by hydrolysis with concentrated sulfuric acid (20 mL) at 100 °C for 2 h.

7,8-Dichloro-6-nitroquinoline (8). To a mixture of **4** (3.0 g, 14.5 mmol), freshly prepared dry glycerol (5.3 g, 57.7 mmol), and arsenic pentoxide (9.2 g, 40.0 mmol) cooled at 0 °C with an ice bath, 4 mL of concentrated sulfuric acid were added within 30 min under mechanical stirring. After complete addition, the temperature was slowly arised to 150 °C and stirring continued for an additional 2 h. The mixture was then allowed to cool to rt, poured into crushed ice (100 g) and the stirring continued for further 30 min. The resulting precipitate was collected by filtration and purified by chromatography over silica gel, using a 6:4 mixture of ether-light petroleum as eluent, to yield **8** (1.86 g, 53%) as yellowish crystals with mp 156-157 °C (acetone); IR: 1600, 1540, 1520 cm^{-1}; UV: λ_{max} 257, 223 nm; ^1H-NMR ($CDCl_3$+DMSO-d_6): δ 9.21 (d, 1H, J = 4.2 Hz, H-2), 8.84 (s, 1H, H-5), 8.66 (d, 1H, J = 8.4 Hz, H-4), 7.81 (dd, 1H, J = 8.4 and 4.2 Hz, H-3); MS: *m/z* 242 (M^+). Anal. Calcd for $C_9H_4N_2O_2Cl_2$: C, 44.47; H, 1.66; N, 11.53; Cl, 29.17. Found: C, 44.74; H, 1.74; N, 11.32; Cl, 28.89.

7-Amino-8-chloro-6-nitroquinoline (10).

Method A: from **8** using ethanolic ammonia solution.

A solution of **8** (1.65 g, 6.8 mmol) in ethanol (100 mL) saturated with dry gaseous ammonia was heated in a sealed steel vessel at 160 °C under stirring for 22 h. Then the reaction mixture was cooled to rt, the solvent was removed *in vacuo* and the solid residue thoroughly triturated with ether to give **10** (1.49 g, 98%); mp 222 °C (ethanol); IR: 3500, 3350, 1630, 1610, 1580 cm^{-1}; UV: λ_{max} 296, 264, 244 sh, 234, 201 nm; ^1H-NMR ($CDCl_3$): δ 8.96 (dd, 1H, J = 4.2 and 1.6 Hz, H-2), 8.64 (s, 1H, H-5), 8.08 (dd, 1H, J = 8.2 and 1.6 Hz, H-4), 7.23 (dd, 1H, J = 8.2 and 4.2 Hz, H-3), 6.43 (br s, 2H, NH_2); MS: *m/z* 223 (M^+). Anal. Calcd for $C_9H_6N_3Cl$: C, 48.34; H, 2.70; N, 18.79; Cl, 15.86. Found: C, 48.09; H, 2.40; N, 18.52; Cl, 15.67.

Method B: from **7** *via* Skraup synthesis.

To a mixture of **7** (0.5 g, 2.7 mmol), freshly prepared dry glycerol (1.0 g, 11.0 mmol), and arsenic pentoxide (0.8 g, 3.5 mmol) cooled at 0 °C with an ice bath, 2.5 mL of concentrated sulfuric acid were added dropwise over 30 min under mechanical stirring. After the addition was complete, the temperature was slowly arised to 150 °C and the stirring continued for an additional 2 h. The reaction mixture was then allowed to cool to rt, poured into crushed ice (30 g) and the stirring continued for an additional 30 min. The resulting precipitate was filtered off, the filtrate was made alkaline (pH ≅ 12) with concentrated ammonia aqueous solution and extracted with chloroform (5 x 30 mL). The combined extracts, dried on anhydrous sodium sulfate, were evaporated *in vacuo* to yield **10** (0.05; 8%) identical to a specimen obtained under method A.

2-Chloro-4-nitro-1,3-benzenediammine (7). A solution of **6** (1.0 g, 4.0 mmol) in ethanol (100 mL) saturated with dry gaseous ammonia was heated in a sealed steel vessel at 160 °C under stirring for 22 h. After this time the reaction mixture was cooled to rt and the solvent was removed under reduced pressure. The solid residue triturated with ether gave **7** (0.73 g, 97%); mp 164-166 °C (acetone); IR: 3480, 3350, 1640, 1620, 1580 cm^{-1}; UV: λ_{max} 383, 260, 217 nm; ^{1}H-NMR ($CDCl_3$+DMSO-d_6): δ 7.89 (d, 1H, J = 9.4 Hz, H-5), 6.93 (br s, 2H, NH_2), 6.24 (d, 1H, J = 9.4 Hz, H-6), 5.83 (s, 2H, NH_2); MS: *m/z* 187 (M^+). Anal. Calcd for $C_6H_6N_3O_2Cl$: C, 38.41; H, 3.22; N, 22.40; Cl, 18.90. Found: C, 38.13; H, 3.43; N, 22.12; Cl, 18.73.

6,7-Diaminoquinoline (11a). A suspension of **10** (1.0 g, 4.5 mmol) and of 10% palladized charcoal (0.25 g) in ethanol (200 mL) was hydrogenated in Parr at 3 atm and 60 °C for 3.5 h. After filtration of the catalyst, the solvent was removed *in vacuo*. The solid residue was dissolved with water and the resulting solution, made alkaline (pH ≅ 10-11) using a sodium hydroxyde aqueous solution (2 M), was extracted with chloroform (5 x 60 mL). The combined extracts, dried over anhydrous sodium sulfate, evaporated to dryness gave **11a** (0.42 g, 50%), mp 174-175 °C (acetone); IR: 3400, 3200, 1670, 1640, 1630, 1570 cm^{-1}; UV: λ_{max} 342, 235, 204 nm; ^{1}H-NMR ($CDCl_3$+DMSO-d_6): δ 8.45 (d, 1H, J = 4.0 Hz, H-2), 7.75 (d, 1H, J = 8.2 Hz, H-4), 7.16 (s, 1H, H-8), 7.02 (dd, 1H, J = 8.2 and 4.0 Hz, H-3), 6.87 (s, 1H, H-5), 4.77 (br s, 2H, NH_2), 4.58 (br s, 2H, NH_2); MS: *m/z* 159 (M^+). Anal. Calcd for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.17; H, 5.60; N, 26.58.

6,7-Diamino-8-chloroquinoline (11b). A suspension of **10** (1.0 g, 4.5 mmol) and of 10% palladized charcoal (0.20 g) in ethanol (200 mL) was hydrogenated in Parr at 20-25 °C and 3 atm for 3.5 h. After filtration of the catalyst, the solvent was evaporated *in vacuo* and the solid residue was flash chromatographed on silica gel with ether as eluent to afford **11b** (0.77 g, 90%); mp 162-163 °C (ether); IR: 3500, 3300, 1720, 1710, 1690, 1670, 1640 cm^{-1}; UV: λ_{max} 356, 250, 222 nm; ^{1}H-NMR ($CDCl_3$): δ 8.76 (dd, 1H, J = 4.2 and 1.6 Hz, H-2), 7.87 (dd, 1H, J = 8.2 and 1.6 Hz, H-4), 7.20 (dd, 1H, J = 8.2 and 4.2 Hz, H-3), 6.94 (s, 1H, H-5), 4.43 (br s, 2H, NH_2), 3.78 (br s, 2H, NH_2); MS: *m/z* 193 (M^+). Anal. Calcd for $C_9H_8N_3Cl$: C, 55.82; H, 4.16; N, 21.70; Cl, 18.31. Found: C, 56.03; H, 4.19; N, 21.48; Cl, 18.09.

1*H*-1,2,3-Triazolo[4,5-*g*]quinoline (Ia). A solution of sodium nitrite (0.25 g, 3.5 mmol) in water (2 mL) was added dropwise to an ice-cooled stirred solution of **11a** (0.5 g, 3.14 mmol) in 2 M hydrochloric acid solution (10 mL). Then the mixture was allowed to warm at rt and the stirring continued for an additional 7 h. A solid was formed and collected by filtration to give **Ia** (0.22 g, 42%); mp 209-211 °C (acetone); IR: 3450, 1640, 1630, 1610, 1560 cm^{-1}; UV: λ_{max} 360 sh, 350, 332 sh, 320, 312 infl, 230 nm; ^{1}H-NMR (DMSO-d_6): δ 9.42 (d, 1H, J = 4.4 Hz, H-6), 9.31 (d, 1H, J = 8.0 Hz, H-8), 9.12 (s, 1H, H-4), 8.77 (s, 1H, H-9), 7.99 (dd, 1H, J = 8.0 and 4.4 Hz, H-7); MS: *m/z* 170 (M^+). Anal. Calcd for $C_9H_6N_4$: C, 63.52; H, 3.55; N, 32.93. Found: C, 63.34; H, 3.91; N, 33.12.

4-Chloro-1*H*-1,2,3-triazolo[4,5-*g*]quinoline (Ib).

Method A: from **11b** using sodium nitrite.

A solution of sodium nitrite (0.25 g, 3.5 mmol) in water (2 mL) was added dropwise to an ice-cooled stirred solution of **11b** (0.5 g, 2.6 mmol) in 2 M hydrochloric acid aqueous solution (15 mL). After the addition was complete, the mixture was allowed to warm at rt and the stirring continued for additional 7 h, when the pH of the aqueous phase was adjusted to 5 with concentrated ammonia aqueous solution. The resulting precipitate was filtered off obtaining **Ib** (0.23 g, 43%); mp 283-284 °C (acetone); IR: 3450, 1670, 1610 cm^{-1}; UV: λ_{max} 378, 361, 346, 324, 316 sh, 231 nm; ^{1}H-NMR ($CDCl_3$+DMSO-d_6): δ 9.07 (d, 1H, J = 3.6 Hz, H-6), 8.54 (m, 2H, H-8+H-9), 7.54 (dd, 1H, J = 8.4 and 3.6 Hz, H-7); MS: *m/z* 204 (M^+). Anal. Calcd for $C_9H_5N_4Cl$: C, 52.82; H, 2.46; N, 27.38; Cl, 17.33. Found: C, 52.57; H, 2.59; N, 27.18; Cl, 17.11.

Method B: from 7,8-dichloro-6-nitroquinoline (**8**) using hydrazine hydrate.

A mixture of **8** (0.8 g, 3.3 mmol) and hydrazine hydrate (99%, 3.0 g, 60 mmol) in ethanol (70 mL) was heated in a sealed steel vessel at 160 °C under stirring for 10 h. The reaction mixture was then cooled to rt and the solvent was removed *in vacuo*. The solid residue obtained was chromatographed on silica gel column, eluting with a 8:2 mixture of ether-light petroleum, to give: **6-amino-7,8-dichloroquinoline (9)** (0.35 g, 50%); mp 198-200 °C (ether); IR: 3440, 1640, 1610, 1580, 1550 cm^{-1}; UV: λ_{max} 364, 294 sh, 284 sh, 253, 221 nm; ^{1}H-NMR ($CDCl_3$): δ 8.79 (dd, 1H, J = 4.2 and 1.6 Hz, H-2), 7.92 (dd, 1H, J = 8.4 and 1.6 Hz, H-4), 7.35 (dd, 1H, J = 8.4 and 4.2 Hz, H-3), 6.98 (s, 1H, H-5), 4.46 (br s, 2H, NH_2); MS: *m/z* 212 (M^+). Anal. Calcd for $C_9H_6N_2Cl_2$: C, 50.73; H, 2.84; N, 13.15; Cl, 33.28. Found: C, 50.78; H, 3.07; N, 12.94; Cl, 33.09; further elution of the column with ether yielded **4-chloro-1*H*-1,2,3-triazolo[4,5-*g*]quinoline (Ib)** (0.15 g, 22%), identical with an authentic specimen as above described.

Pyrido[2,3-*g*]quinoxaline (IIa). Glyoxal (8.9 g, 61.3 mmol, 40% in water) was slowly dropwise added, under stirring, to a refluxing solution of **11a** (0.6 g, 3.8 mmol) in ethanol (15 mL) and the stirring continued for an additional 2 h. After cooling the resulting solution was evaporated to dryness *in vacuo* to give a solid residue. Purification of this was accomplished by flash chromatography on silica gel using as eluent mixtures of ether-acetone with increasing percentages of acetone, to give **IIa** (0.61 g, 90%) as solid very unstable to air, which decomposes at 140-150 °C; IR: 1670, 1610, 1590 cm^{-1}; UV: λ_{max} 358, 248, 206 nm; ^{1}H-NMR (acetone-d_6): δ 9.14 (dd, 1H, J = 4.0 and 1.4 Hz, H-7), 9.04 (s, 2H, H-2+H-3), 8.85 (s, 1H, H-5), 8.82 (s, 1H, H-10), 8.69 (d, 1H, J = 8.4 Hz, H-9), 7.66 (dd, 1H, J = 8.4 and 4.0 Hz, H-8); MS: *m/z* 181 (M^+). Anal. Calcd for $C_{11}H_7N_3$: C, 72.91; H, 3.89; N, 23.19. Found: C, 73.12; H, 4.21; N, 22.98.

5-Chloropyrido[2,3-*g*]quinoxaline (IIb). To a refluxing solution of **11b** (0.5 g, 2.6 mmol) in ethanol (10 mL), glyoxal (2.4 g, 41.6 mmol, 40% in water) was added dropwise and the reflux continued for an additional 2 h. After removal of the ethanol, the residue was taken up with water (10 mL), made alkaline (pH ≅ 12) with a sodium hydroxide aqueous solution (2 M) and in continuous extracted with chloroform. The organic phase was then dried over anhydrous sodium sulfate and evaporated under reduced pressure to give **IIb** (0.48 g, 86%); mp 175-177 °C (ethanol); IR: 1630, 1620, 1600, 1580 cm^{-1}; UV: λ_{max} 405 sh, 380 sh, 360, 254, 206 nm; ^1H-NMR ($CDCl_3$): δ 9.26 (d, 1H, J = 4.0 Hz, H-7), 9.09 (s, 1H, H-3), 9.02 (s, 1H, H-2), 8.68 (s, 1H, H-10), 8.50 (d, 1H, J = 8.4 Hz, H-9), 7.61 (dd, 1H, J = 8.4 and 4.0 Hz, H-8); MS: *m/z* 215 (M^+). Anal. Calcd for $C_{11}H_6N_3Cl$: C, 61.27; H, 2.80; N, 19.49; Cl, 16.44. Found: C, 61.06; H, 3.05; N, 19.27; Cl, 16.31.

1*H*-Imidazo[4,5-*g*]quinoline (IIIa). A mixture of **11a** (0.6 g, 3.8 mmol) and formic acid (4.9 g, 106 mmol) was stirred at 100 °C for 2 h. After cooling to rt, the solution was made alkaline (pH ≅ 12) with a 50% of sodium hydroxide aqueous solution and allowed to stand at rt for 48 h affording slowly **IIIa** (0.24 g, 37.5%) as solid with mp 219-221 °C (dimethyl sulfoxide) (lit.,[5] 222 °C); IR: 3420, 1640, 1600 cm^{-1}; UV: λ_{max} 320 infl, 309, 221, 206 sh nm; ^1H-NMR ($CDCl_3$): δ 8.90 (dd, 1H, J = 4.2 and 1.4 Hz, H-6), 8.40 (s, 1H, H-4), 8.36 (s, 1H, H-9), 8.33 (d, 1H, J = 8.4 Hz, H-8), 8.17 (s, 1H, H-2), 7.36 (dd, 1H, J = 8.4 and 4.2 Hz, H-7), 4.58 (br s, 1H, NH).

4-Chloro-1*H*-imidazo[4,5-*g*]quinoline (IIIb). In an identical manner reported for preparation of **IIIa**, starting from **11b** (0.6 g, 3.1 mmol) and formic acid (4.9 g, 106 mmol), **IIIb** (0.57 g, 90%) was obtained; mp 300-302 °C (dimethyl sufoxide) (lit.,[5] 304 °C); IR: 3410, 1640, 1600, 1590, 1570 cm^{-1}; UV: λ_{max} 350 sh, 325, 240, 216 nm; ^1H-NMR (DMSO-d_6): δ 8.96 (dd, 1H, J = 4.0 and 1.4 Hz, H-6), 8.67 (s, 1H, H-9), 8.57 (dd, 1H, J = 8.4 and 1.4 Hz, H-8), 8.20 (s, 1H, H-2), 7.52 (dd, 1H, J = 8.4 and 4.0 Hz, H-7).

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