Alkaline Hydrolysis of 4c. Formation of α-Ethyl-β-benzoylpropionic Acid. A mixture of 4c (0.4 g) and 20 ml of 2% NaOH was stirred at 25° for 1 day. The mixture was acidified with 5% HCl, heated on a steam bath for 30 min, and cooled to yield a white solid. Recrystallization from petroleum ether produced white needles of α-ethyl-β-benzoylpropionic acid: mp 86–87° (lit.[28] mp 85°); ir (KBr) 2650, 1680, 757, 688 cm^{-1}; NMR ($CDCl_3$ Me_4Si) δ 1.00 (t, J = 7 Hz, 3 H), 1.68 (q, 2 H), 2.8–3.8 (m, 3 H), 7.3–7.7 (m, 3 H), 7.9–8.1 (m, 2 H), 10.7 (s, 1 H).

Registry No.—2 (R^3 = R^4 = CO_2CH_3), 762-42-5; 2 (R^3 = C_6H_5; R^4 = CO_2CH_3), 4891-38-7; 2 (R^3 = C_6H_5; R^4 = $CO_2C_2H_5$), 2216-94-6; 2 (R^3 = R^4 = C_2H_5), 928-49-4; 2 (R^3 = C_6H_5; R^4 = H), 536-74-3; 2 (R^3 = R^4 = CH_3), 503-17-3; **3a**, 28969-37-1; **3b**, 28969-38-2; **3c**, 28969-39-3; **4a**, 56615-23-7; **4b**, 56615-24-8; **4c**, 56615-25-9; **4e**, 56615-26-0; **4g**, 56615-27-1; **4h**, 56615-28-2; **4i**, 56615-29-3; **5d**, 56615-30-6; **5e**, 56615-31-7; **5f**, 56615-32-8; **5g**, 56615-33-9; **5h**, 56615-34-0; **5i**, 56615-35-1; **10**, 56615-36-2; **11**, 56615-37-3; **12**, 28970-27-6; **13a**, 56615-38-4; **13b**, 56615-39-5; **14a**, 56615-40-8; **14b**, 56615-41-9; **15a**, 56615-42-0; **15b**, 56615-43-1; 1,4-dihydroxy-3,5-diphenylpyrazole, 17953-00-3; *m*-chloroperbenzoic acid, 937-14-4; 1,4-dihydroxy-5-methyl-3-phenylpyrazole, 56615-44-2; α-phenyl-β-benzoylpropionic acid 4370-96-1; α-phenylsuccinic acid, 635-51-8; diazomethane, 334-88-3; α-methyl-β-benzoylpropionic acid, 1771-65-9; α-methylsuccinic acid, 498-21-5; α-ethyl-β-benzoylpropionic acid, 56615-45-3.

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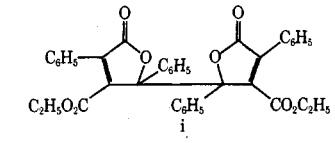

i

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Chemistry of *o*-Amino Aldehydes. Reactions of 2-Aminonicotinaldehyde and Cyclohexanediones

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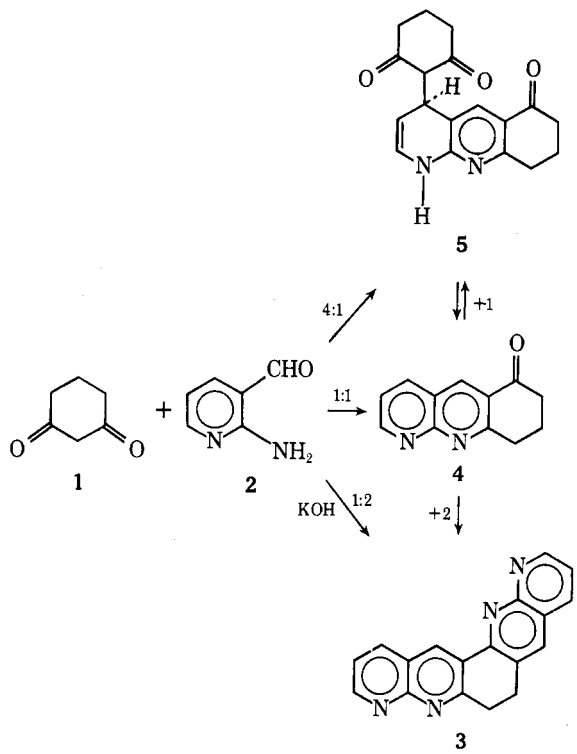
1,3-Cyclohexanedione and 2-aminonicotinaldehyde form 6,7-dihydrodipyrido[2,3-*b*:2,3-*j*]-1,7-phenanthroline (**3**) or 6-oxo-6,7,8,9-tetrahydrobenzo[*b*]-1,8-naphthyridine (**4**) depending on the molar ratio of reagents. Excess 1,3-cyclohexanedione, on the other hand, results in a 2:1 addition product (**5**). Similar reactions with 1,4-cyclohexanedione were not successful; a series of addition–elimination steps in toluene results in the formation of 7-oxo-6,7,8,9-tetrahydrobenzo[*b*]-1,8-naphthyridine (**12**) and 6,7-dihydrodipyrido[3,2-*b*:2,3-*j*]-4,7-phenanthroline (**13**), demonstrating the feasibility of uncatalyzed Friedländer condensations. The isomeric pentacyclic systems are readily dehydrogenated to their fully aromatic analogs. 1,2-Cyclohexanedione gives the highly unreactive 6,7-dihydrodipyrido[2,3-*b*:2,3-*j*]-1,10-phenanthroline (**14**). The mechanism of the actual ring closing step in Friedländer condensation reactions of 2-aminonicotinaldehydes and ketomethylenes is discussed.

The incorporation of the 1,8-naphthyridine heterocyclic system into a polycyclic framework is of interest in view of the unusual stability and properties of "black orlon" obtained from poly(acrylonitrile) by controlled pyrolysis. A linearly annelated sequence of partially oxygenated 1,8-naphthyridine units has been proposed for this remarkable material.[1] The Friedländer condensation of *o*-amino aldehydes seemed a most promising synthetic sequence for the construction of such systems, since fully aromatic substrates without amino or oxo substituents are obtained and the direction of annelation is unequivocally determined by the location of the functional groups in the substrate. This paper deals with the reaction of 2-aminonicotinaldehyde and cyclohexanediones leading to three isomeric pentacyclic systems containing two 1,8-naphthyridine units.

The reaction of 1,3-cyclohexanedione (**1**) and excess 2-

aminonicotinaldehyde (2) in refluxing ethanol containing a few drops of methanolic KOH resulted in the formation of 6,7-dihydrodipyrido[2,3-*b*:2,3-*j*]-1,7-phenanthroline (3) in nearly quantitative yield. On the other hand, refluxing an ethanolic solution of 1 and 2 in a 1:1 molar ratio, in the absence of base, gave the monocondensation product, 6-oxo-6,7,8,9-tetrahydrobenzo[*b*]-1,8-naphthyridine (4) in 90% yield, uncontaminated by 3. This ketone is easily converted into 3 by base-catalyzed (KOH and MeOH) condensation with 2.

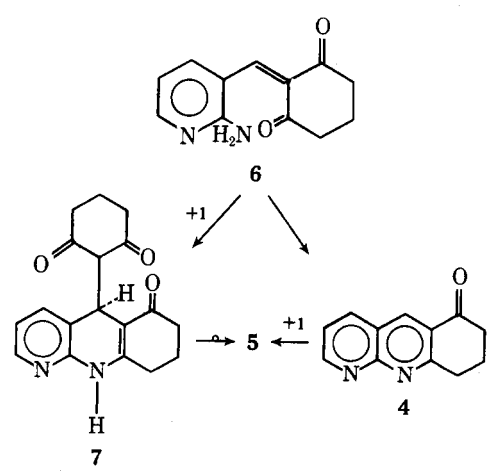


The great reactivity of the central methylene group of 1 seems to favor formation of the monocondensation product under neutral conditions. However, during the course of the reaction leading to 4 a precipitate formed and then slowly disappeared as the reaction progressed. Isolation (maximum yield amounted to 20% under the experimental conditions employed in the synthesis of 4) proved it to be a 2:1 addition product of 1,3-cyclohexanedione and the amino aldehyde, with loss of 2 mol of water. It is not surprising, therefore, that heating an ethanolic solution of 1 and 2 in a 4:1 molar ratio resulted in the formation of the adduct 5 in 90% yield. Its composition is reminiscent of addition products of aldehydes and dimedone; in the present case, the second molecule of water would be eliminated by intramolecular condensation with the amine function. A pronounced molecular ion at *m/e* 310 is observed in the mass spectrometer, with principal fragmentations resulting from either loss of a hydrogen atom or 1,3-cyclohexanedione moiety; the latter fragmentation is more pronounced and is followed by loss of a hydrogen atom with formation of the ion *m/e* 198, identical with the molecular ion obtained from the ketone 4. Such fragmentation pattern is typical for compounds containing a dihydropyridine structure.[2] Characteristic strong absorptions in the ir spectrum for NH and C=O functional groups, observed at 3185 and at 1670, 1640, and 1615–1565 cm^{-1}, are in agreement with a 1,3-cyclohexanedione substituted dihydropyridine structure for 5. Its simple mode of formation and the known tendency of aldehydes to form adducts with 2 mol of 1 seemed to suggest such a dihydro structure for the central pyridine ring of 5. However, its NMR spectrum[3] does not show the characteristic absorptions (doublet of doublets) in the aromatic region for a 2,3-disubstituted pyridine ring. On the contrary, a sharp singlet is observed at δ 8.19, with a proton count of one. A structure wherein the dione moiety resides on the outer pyridine ring is in agreement with this observation.

Absorptions at δ 6.74 (m, 1), 5.70 (m, 1), and 4.4 (m, 1) further substantiate this structure; the latter absorption was assigned to the methine proton on the carbon containing the 1,3-dione moiety, whereas the former are in the characteristic region for vinyl protons. Both the NH and enolic proton of the 1,3-dione moiety are exchanged by dissolving 5 in $CDCl_3$. Addition of a few drops of D_2O to this solution removed the absorption at δ 6.74. The same total exchange of three protons was observed in the spectrum obtained in deuterated acetic acid. Such facile exchange is in agreement with the proposed 1,4-dihydro structure for 5, which contains an enamine structure, in equilibrium with the tautomeric azomethine.

The concurrent formation of 4 and 5 from 2-aminonicotinaldehyde and 1,3-cyclohexanedione seemed to suggest a possible route to the addition product. Indeed, an equimolar solution of 4 and 1, in ethanol at 65°, slowly formed a precipitate (43%) identical in all respects with the addition product isolated from 1 and 2. It is apparent therefore that 5 arises from nucleophilic addition of the 1,3-dione on the outer pyridine ring of 4. As mentioned earlier, 5 is slowly converted to 4 in refluxing ethanol. This elimination is greatly accelerated by the addition of base or by brief treatment with dilute mineral acid. Two reaction mechanisms leading to 4 and ultimately to 5 can be envisioned. Aldol condensation of 1 and 2 followed by dehydration of the aldol results in an α,β-unsaturated carbonyl system (6). Intramolecular Schiff base formation can lead to 4, which then further reacts with a second molecule of 1,3-dione, as discussed earlier.

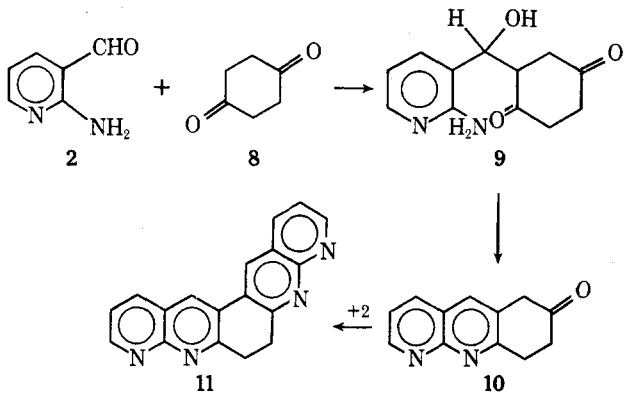
The alternative pathway, based on the known tendency of 1,3-cyclohexanedione to form 2:1 addition products with aldehydes, cannot be excluded. Michael addition of 1 and 6, followed by ring closing, would lead to 7, which would then rearrange to its thermodynamically more stable isomer 5, via dissociation into 4 and 1. The facile elimination



of the 1,3-dione moiety from 5 is indicative of the possibility for such isomerization. However, attempts to isolate 7 from the reaction of 1 and 2 were not successful. The second molecule of 1,3-cyclohexanedione required in both reaction pathways can be readily supplied by retroaldol condensation.

The attempted condensation of 1,4-cyclohexanedione (8) and 2-aminonicotinaldehyde under conditions similar to those utilized in the synthesis of 3 resulted in untractable,

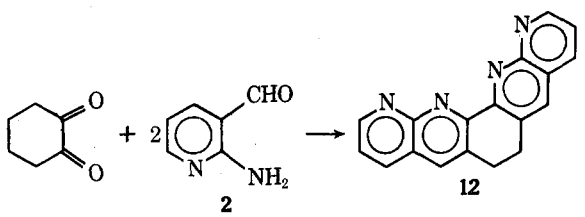
highly colored products. After considerable experimentation a step by step sequence of addition and ring closing reactions proved successful.



2 8 9 11 10

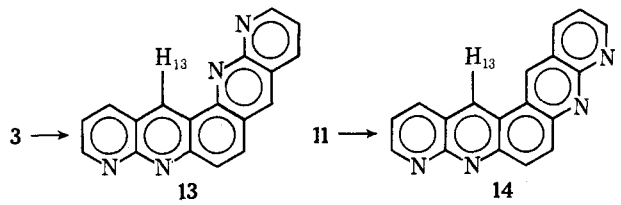
A solution of 2 and 8 (1:1 molar ratio) in ethanol was treated with piperidine at room temperature. A white precipitate was formed slowly and was isolated in 60% yield. Analysis indicated a simple addition product without loss of water, while the infrared spectrum shows the characteristic absorptions for OH and a primary amine (3530, 3450, 3340, and 3220 cm^{-1}). The monoaldol structure 9 is consistent with these data. Its isolation is fortunate since it provides evidence that aldol condensation precedes Schiff base formation in Friedländer condensations of 2 and ketones. The opposite sequence of events has been proposed for condensations of o-aminobenzaldehyde and ketones, although no intermediates analogous to 9 were isolated in condensations utilizing this o-amino aldehyde.[4] Ring closure of 9 could be effected almost quantitatively by dissolving it in boiling toluene; 2 mol of water was eliminated by this treatment with formation of 7-oxo-6,7,8,9-tetrahydrobenzo[b]-1,8-naphthyridine (10). Formation of 6,7-dihydrodipyrido[3,2-b:2,3-j]-4,7-phenanthroline (11) from 2 and 10 was not successful under conventional Friedländer conditions;[5] it was obtained instead in very good yield by refluxing both reagents in toluene with azeotropic removal of water. This condensation is unique in that it represents a first example of a Friedländer reaction in a hydrocarbon solvent. Although 10 could lead to a linear annelation product in the above reaction, this was not observed; the singlet in the NMR spectrum of 11 at δ 8.60 is characteristic of the angular structure (see further).

The base-catalyzed reaction of 2 and 1,2-cyclohexanedione in a 2:1 molar ratio resulted in the formation of 6,7-dihydrodipyrido[2,3-b:2,3-j]-1,10-phenanthroline (12) in moderate yield. Yields could not be increased under a variety of experimental conditions.



2 12

The recognition that Friedländer condensations on cyclohexanediones invariably result in dihydro derivatives of polycyclic systems prompted us to explore the transformation of the three isomeric pentacyclic dihydro compounds into their fully aromatic analogs. Selenium oxide in ethanol proved to be the method of choice for the dehydrogenation of 3 and 11 leading to dipyrido[2,3-b:2,3-j]-1,7-phenanthroline (13) and dipyrido[3,2-b:2,3-j]-4,7-phenanthroline (14), respectively. It is totally ineffective, however, in the dehydrogenation of 12. This is not surprising since 12 does not contain activated carbon–hydrogen bonds.[6] However, dehydrogenation could not be effected even under drastic conditions such as SeO_2 in boiling nitrobenzene, Pd/C in high-boiling hydrocarbon solvents, sulfur, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in acetic acid. Both 13 and 14 are white, crystalline compounds soluble in common organic solvents; 14 is soluble in water.



3 13 11 14

The isomeric pentacyclic compounds described herein all contain two 1,8-naphthyridine units interconnected in different modes, but structured on the same angular building principle. The different magnetic environment on the "bay"[7] side of these molecules provided us with a basis for the interpretation of their NMR spectra (see Experimental Section). The absence of symmetry in 3 and 13 gives rise to rather complicated absorptions for protons H_2–H_{10} and H_3–H_{11}, recognized as two sets of doublets of doublets. As expected, protons on the bay side (four in 11 and 14, two in 3 and 13, none in 12) absorb downfield from identical protons on the opposing side (H-12 and H-4 in 3); protons on the bay side in the proximity of the nitrogen atoms absorb downfield from protons in the same relative position but only under the influence of an aromatic ring (H-13 in 3 and 11).[8] A comparison of the bay protons, especially H-13, in the fully aromatic compounds and their dihydro analogs is of interest. Dehydrogenation of 3 results in a downfield shift for H-13 of 0.85 ppm, while oxidation of 11 produces a similar shift for H-13 of 0.89 ppm. The slightly lower value in going from 3 to 13 is the result of a concurrent upfield shift due to the increased distance separating H-13 and the electron pair on N-14 in 13. The fact that very similar shifts are observed for both systems indicates that the diamagnetic anisotropy of the electron pair of N-14 is already maximized at the dihydro stage, implying a near planar arrangement for the bay side of the dihydro pentacyclic systems. This is substantiated by the ultraviolet spectra of these compounds. It is noteworthy that the three isomers differ in their absorption maximum: 361, 357, and 350 nm for 12, 3, and 11, respectively. This seems to reflect steric interaction between H-13 and the electron pair on N-14 in 3 and between H-13 and H-14 in 11, resulting in decreased conjugation between the two 1,8-naphthyridine moieties.

Experimental Section

General. NMR spectra were recorded with a Varian A-60 and/or Varian XL-100 with FT spectrometer in $CDCl_3$ as solvent using Me_4Si as an internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU6E instrument; infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer and uv spectra on a Cary 15 instrument. All melting points are uncorrected. Microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

6,7-Dihydrodipyrido[2,3-b:2,3-j]-1,7-phenanthroline (3). To a refluxing solution of 2.0 g (17 mmol) of 1,3-cyclohexanedione and 5.0 g (41 mmol) of 2-aminonicotinaldehyde[9] in 50 ml of ethanol was added 10 drops of methanolic KOH (20%). Reflux was continued for 72 hr. The product crystallized upon cooling (4.6 g, 90%): mp 233; ir (Nujol) 1590, 1540, 1470, 1225, 1140, 990, 935, 915, 805, 800, 780, 735, 715 cm^{-1}; NMR δ 9.55 (H-13, 1, s), 9.12 (H-2 and H-10, 2, dd, $J_{\alpha-\beta}$ = 4.3, $J_{\alpha-\gamma}$ = 2 Hz), 8.34 (H-12, 1, dd, $J_{\beta-\gamma}$ = 8.1 Hz), 8.19 (H-4, 1, dd), 8.09 (H-5, 1, s), 7.50 and 7.49 (H-3 and H-11, 2, two sets of dd), 3.54–3.33 (H-6 and H-7, 4, m); uv (MeOH) 357 nm (ϵ 28830), 343 (25260), 236 (46850); mass spectrum M^+ m/e 284.

Anal. Calcd for $C_{18}H_{12}N_4$: C, 76.03; H, 4.25; N, 19.71. Found: C, 75.94; H, 4.17; N, 19.80.

6-Oxo-6,7,8,9-tetrahydrobenzo[*b*]-1,8-naphthyridine (4). A solution of 6.0 g (51 mmol) of **1** and 6.3 g (51 mmol) of **2** in 150 ml of ethanol was heated at 80° for 24 hr and then refluxed for 48 hr. The cooled mixture was filtered and the filtrate evaporated to dryness. Extraction with benzene gave 9.0 g (89%) of product: mp 165° dec; ir (Nujol) 1670, 1590, 1540, 1450, 1410, 1285, 1280, 1250, 1220, 1190, 1175, 1160, 1110, 1020, 1005, 990, 970, 910, 885, 815, 787 cm^{-1}; NMR δ 9.18 (H-2, 1, dd, $J_{\alpha-\beta}$ = 4, $J_{\alpha-\gamma}$ = 2 Hz), 8.81 (H-5, 1, s), 8.30 (H-4, 1, dd, $J_{\beta-\gamma}$ = 8 Hz), 7.50 (H-3, 1, dd), 3.39 (H-9, 2, t, $J_{H-8,H-9}$ = 6 Hz), 2.81 (H-7, 2, t, $J_{H-7,H-8}$ = 6 Hz), 2.31 (H-8, 2, m); uv (MeOH) 327 nm (ϵ 6590), 318 (6520), 276 (6210), 226 (50460); mass spectrum M^+ *m/e* 198 (75%), 170 (100%).

Anal. Calcd for $C_{12}H_{10}N_2O$; C, 72.71; H, 5.08; N, 14.13. Found: C, 72.70; H, 4.95; N, 14.17.

4-(2′,6′-Dioxocyclohexyl)-6-oxo-1,4,6,7,8,9-hexahydrobenzo[*b*]-1,8-naphthyridine (5). Method A. A mixture of 0.250 g (2 mmol) of **2** and 0.920 g (8 mmol) of **1** in 50 ml of ethanol was stirred at 65° for 48 hr. The white precipitate was washed extensively with ethanol to yield 0.540 g (87%) of **5**: mp 203–204°; ir (Nujol) 3185, 1670, 1640, 1615–1565, 1520, 1410, 1320, 1275, 1266, 1225, 1175, 1150, 1110, 1055, 1020, 950, 925, 910, 820, 795, 740–720 cm^{-1}; NMR (CD_3–COOD) δ 8.27 (s, 1, H-5) 6.00 (s, 1, H-2) 4.24 (s, 1, H-4) 3.04 (unresolved triplet, 2, H-9) 2.72–1.92 (unresolved multiplet, 10, remaining aliphatic protons); NMR ($CDCl_3$) δ 8.19 (s, 1, H-5) 6.74 (unresolved m, 1, H-3), 5.70 (distorted dt, 1, H-2, J_{2-3} = 7.2, J_{2-4} = 2.3 Hz), 4.4 (unresolved m, 1, H-4), 2.90 (t, 2, H-9, J_{H8-H9} = 6 Hz), 2.59 (t, 2, H-7, J_{H7-H8} = 6 Hz), 2.46–1.90 (unresolved m, 8, remaining aliphatic protons); mass spectrum M^+ *m/e* 310. Since **5** could not be recrystallized from any solvent without change, an analytical sample was prepared by multiple washings of the crude reaction mixture at room temperature.

Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.65; H, 5.84; N, 9.03. Found: C, 69.33, H, 5.71; N, 9.00.

Method B. A mixture of 0.407 g (2 mmol) of **4** and 0.230 g (2 mmol) of **1** in 15 ml of ethanol was stirred at 65° for 3 days. The white precipitate was collected and characterized as described under method A.

[3-(2-Aminopyridyl)][2′-(1′,4′-dioxocyclohexyl)]methanol (9). To a solution of 8.0 g (65 mmol) of **2** and 6.0 g (54 mmol) of 1,4-cyclohexanedione in 50 ml of ethanol was added 30 drops of piperidine. The mixture was stirred at room temperature for 6 hr. The white precipitate was filtered and washed extensively: yield 6.8 g (59%); mp 125° dec; ir (Nujol) 3530, 3450, 3340, 3220, 3100, 3080, 1690, 1600, 1585, 1520, 1440, 1310, 1300, 1265, 1220, 1140, 1130, 1110, 1090, 1080, 1035, 1005, 980, 940, 820, 805, 780 cm^{-1}. Since **9** could not be recrystallized from any solvent without change, an analytical sample was prepared by multiple washings of the crude reaction product at room temperature.

Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.54; H, 5.98; N, 11.96. Found: C, 61.88; H, 6.06; N, 11.73.

7-Oxo-6,7,8,9-tetrahydrobenzo[*b*]-1,8-naphthyridine (10). **9** (6.8 g) was refluxed in 500 ml of toluene until a clear solution was obtained (~1 hr). The solution was cooled and filtered and the filtrate was evaporated to yield 5.4 g (94%) of product: mp 150° dec; ir (Nujol) 1710, 1625, 1605, 1560, 1480, 1420, 1305, 1290, 1220, 1180, 1160, 1100, 1020, 985, 955, 940, 915, 795, 750, 725 cm^{-1}; NMR δ 9.11 (H-2, 1, dd, $J_{\alpha-\beta}$ = 4, $J_{\alpha-\gamma}$ = 2 Hz), 8.18 (H-4, 1, dd, $J_{\beta-\gamma}$ = 8 Hz), 7.95 (H-5, 1, t, J_{5-6} = 1 Hz), 7.50 (H-3, 1, dd), 3.86 (H-6, 2, d), 3.57 (H-9, 2, t, J_{H8-H9} = 7 Hz), 2.75 (H-8, 2, t); uv (MeOH) 317 nm (ϵ 9510), 307 (9030), 264 (6020); mass spectrum M^+ *m/e* 198.

Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.73; H, 5.30; N, 14.09.

6,7-Dihydrodipyrido[3.2-*b*:2,3-*j*]-4,7-phenanthroline (11). A mixture of 2.0 g (1 mmol) of **10** and 4.0 g (3 mmol) of **2** in 75 ml of toluene was refluxed for 48 hr with continuous water removal. The precipitate was collected to give 2.5 (89%) of product: mp 242; ir (Nujol) 1605, 1538, 1470, 1275, 1225, 1190, 1175, 1150, 1140, 925, 905, 895, 810, 800, 795, 780 cm^{-1}; NMR δ 9.10 (H-3 and H-10, 2, dd, $J_{\alpha-\beta}$ = 4.2, $J_{\alpha-\gamma}$ = 2 Hz), 8.60 (H-13 and H-14, 2, s), 8.27 (H-1 and H-12, 2, dd, $J_{\beta-\gamma}$ = 8.2 Hz), 7.50 (H-2 and H-11, 2, dd), 3.58 (H-6 and H-7, 4, s); uv (MeOH) 350 nm (ϵ 26720), 338 (sh, 24140), 243 (45690), 231 (sh, 41380); mass spectrum M^+ *m/e* 284.

Anal. Calcd for $C_{18}H_{12}N_4$: C, 76.03; H, 4.25; N, 19.71. Found: C, 75.98; H, 4.25; N, 19.64.

6,7-Dihydrodipyrido[2,3-*b*:3,2-*j*]-1,10-phenanthroline (12). To a solution of 2.0 g (16 mmol) of 1,2-cyclohexanedione and 5.0 g (41 mmol) of **2** in 100 ml of ethanol was added 25 drops of methanolic KOH (20%). The solution was refluxed for 48 hr. The precipitate was collected and recrystallized (H_2O) to yield 2.1 g (44%) of **12**: mp 315°; ir (Nujol) 1615, 1590, 1550, 1538, 1450, 1285, 1190, 1125, 1025, 900, 833, 810, 800, 770, 725, 715 cm^{-1}; NMR δ 9.23 (H-2 and H-11, 2, dd, $J_{\alpha-\beta}$ = 4.2, $J_{\alpha-\gamma}$ = 1.9 Hz), 8.18 (H-4 and H-9, 2, dd, $J_{\beta-\gamma}$ = 8.2 Hz), 8.12 (H-5 and H-8, 2, s), 7.50 (H-3 and H-10, 2, dd), 3.31 (H-5 and H-6, 4, s); uv (MeOH) 361 nm (ϵ 26130), 346 (22520), 233 (44140); mass spectrum M^+ *m/e* 284.

Anal. Calcd for $C_{18}H_{12}N_4$: C, 76.03; H, 4.25; N, 19.71. Found: C, 75.96; H, 4.37; N, 19.56.

Dipyrido[2,3-*b*:2,3-*j*]-1,7-phenanthroline (13). A mixture of 1.0 g (3.5 mmol) of **3** and 0.4 g (3.6 mmol) of SeO_2 was refluxed for 3 hr. The reaction mixture was filtered hot and the filtrate evaporated to dryness. The residue was dissolved in chloroform and percolated through a column of alumina to give 0.8 g (87%) of white product: mp 325–326°; ir (Nujol) 1620, 1610, 1590, 1560, 1390, 1175, 925, 910, 820, 810, 765 cm^{-1}; NMR δ 10.40 (H-13, 1, s), 9.32 and 9.30 (H-2 and H-10, 2, two sets of dd, $J_{\alpha-\beta}$ = 4.2, $J_{\alpha-\gamma}$ = 2.1 Hz), 8.69 (H-5, 1, s), 8.55 (H-12, 1, dd, $J_{\beta-\gamma}$ = 8.4 Hz), 8.42 (H-4, 1, dd), 8.11 (H-7, 1, distorted doublet), 8.05 (H-6, 1, distorted doublet, J_{H6-H7} = 9.5 Hz), 7.60 and 7.59 (H-3 and H-11, 2, two sets of dd); mass spectrum M^+ *m/e* 282 (100) and *m/2e* 141 (45); uv (MeOH) 228 nm (ϵ 51887), 278 (18870), 289 (19810), 327 (51890), 342 sh (33000), 377 (2360), 395 (800).

Anal. Calcd for $C_{18}H_{10}N_4$: C, 76.57; H, 3.58; N, 19.86. Found: C, 76.37; H, 3.46; N, 19.80.

Dipyrido[3.2-*b*:2,3-*j*]-4,7-phenanthroline (14). A mixture of 2.0 g (7 mmol) of **11** and 0.78 g (7 mmol) of SeO_2 in 200 ml of ethanol was heated slowly to reflux. At this point heating was continued for 0.5 hr. The cooled mixture was filtered and the filtrate concentrated to give 1.5 g (77%) of **14**, mp 342–344°. An analytical sample was prepared by sublimation (200°, 1 mmHg): ir (Nujol) 1610, 1540, 1495, 1300, 1220, 1040, 930, 835, 810, 780, 730 cm^{-1}; NMR δ 9.49 (H-13 and H-14, 2, s), 9.32 (H-3 and H-10, 2, dd, $J_{\alpha-\beta}$ = 4.2, $J_{\alpha-\gamma}$ = 2 Hz), 8.51 (H-1 and H_{12}, 2, dd, $J_{\beta-\gamma}$ = 8.3 Hz), 8.42 (H-6 and H-7, 2, s), 7.63 (H-2 and H-11, 2, dd); mass spectrum M^+ *m/e* 282; uv (MeOH) 230 nm (ϵ 54500), 274 (24000), 284 (26800), 326 (49000), 341 sh (34000), 357 sh (14000), 372 (5400), 380 (1850), 391 (4200).

Anal. Calcd for $C_{18}H_{10}N_4$: C, 76.57; H, 3.58; N, 19.86. Found: C, 76.35; H, 3.70; N, 19.60.

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References and Notes

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