A solution of 0.20 g (0.74 mmol) of the lower boiling point fraction (5) and 0.65 g (2.4 mmol) of mercuric chloride in 7 mL of 4:1 acetonitrile/water was heated at reflux for 15 h, filtered, and distilled to 130 °C (0.05 mm) to give 0.14 g (80% yield) of the cyclopentyl aldehyde **10**: IR ν_{max} 1735, 1665 cm^{-1}; NMR ($CDCl_3$) δ 10.0 (d, 1 H), 3.8 (s, 6 H), 3.3 (s, 4 H), 2.2 (s, 3 H); *m/e* 226. The product showed a single peak in GLC on a 10-ft methylsilicone column at 200 °C. DNP derivative mp 201–202 °C.

Anal. Calcd for $C_{17}H_{18}N_4O_8$: C, 50.24; H, 4.47; N, 13.79. Found: C, 49.03; H, 4.40; N, 13.93.

4,4-Dicarbomethoxy-2,6-heptanedione (11). A solution of 4.0 g (19 mmol) of dimethyl dipropargylmalonate (1) in 60 mL of acetonitrile and 15 mL of water and 15.6 g (58 mmol) of mercuric chloride was heated at reflux for 12 h. Concentration under vacuum, extraction of the aqueous mixture with ether, washing of the extract with aqueous sodium sulfide, concentration, and distillation gave 4.2 g (90% yield) of the diketone **11**: bp 130 °C (0.5 mm); mp 54–55 °C; IR ν_{max} 1740, 1720 cm^{-1}; NMR ($CDCl_3$) δ 3.8 (s, 6 H), 3.3 (s, 4 H), 2.2 (s, 3 H); *m/e* 244.

Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.10; H, 6.56. Found: C, 54.31; H, 6.69.

5-Carbomethoxy-3-methyl-2-cyclohexenone (13). A. A solution of 2.6 g (11 mmol) of 4,4-dicarbomethoxy-2,6-heptanedione (11) and 0.58 g (11 mmol) of sodium methoxide in 50 mL of methanol was heated at reflux for 15 h. The reaction mixture was acidified with dilute aqueous HCl, concentrated, and partitioned between water and dichloromethane. Distillation of the organic extract at 110 °C (0.05 mm) gave 1.5 g (85% yield) of a single product: IR ν_{max} 1730, 1665, 1620 cm^{-1}; UV λ_{max} 245 nm; NMR ($CDCl_3$) δ 5.9 (s, 1 H), 3.7 (s, 3 H), 3.4–3.7 (m, 5 H), 2.0 (s, 3 H); *m/e* 168; and one peak in GLC at 16.5 min on a 10-ft methylsilicone column at 200 °. DNP derivative mp 126–127 °C (reported[5,6] 149–150 °C).

Anal. Calcd for $C_{15}H_{16}N_4O_6$: C, 51.87; H, 4.32; N, 16.14. Found: C, 51.79; H, 4.55; N, 16.04.

B. A solution of 3.0 g of methallylsuccinic anhydride (14) and 5.0 g of stannic chloride in 25 mL of dichloromethane was stirred at 0 °C for 1 h and at 20 °C for 20 h. Addition of water and dilute aqueous HCl, extraction with dichloromethane, and concentration gave a crude product which was dissolved in aqueous HCl, extraction with dichloromethane, and concentration gave a crude product which was dissolved in aqueous sodium bicarbonate, washed with ether, and recovered by acidification and extraction with dichloromethane, yielding 2.8 of gummy product. Recrystallization from ether–ligroin gave 1.4 g of the acid corresponding to ester **13** with mp 88–90 °C (reported[5,6] mp 92–94 °C). A solution of this compound in ether on reaction with diazomethane gave the ester **13**, identical in all spectroscopic properties with the product obtained above. The mixture melting point of corresponding DNP derivatives was not depressed.

Acknowledgment. This work was supported by the Cancer Institute of the National Institutes of Health, Research Grant PHS CA R01-12010.

Registry No.—**1**, 63104-44-9; **2**(Ar = *p*-tolyl), 63104-45-0; **2** (Ar = Ph), 63133-61-9; **3** (Ar = *p*-tolyl), 63104-46-1; **3** (Ar = Ph), 63104-47-2; **4** (Ar = *p*-tolyl), 63104-48-3; **5** (Ar = *p*-tolyl), 63104-49-4; **5** (Ar = Ph), 63104-50-7; **10**, 63104-51-8; **10** DNP, 63104-42-7; **11**, 63104-52-9; **13**, 63104-53-0; **13** DNP, 63104-43-8; **14**, 18908-20-8; mercuric chloride, 7487-94-7.

References and Notes

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1,9,10-Anthyridines

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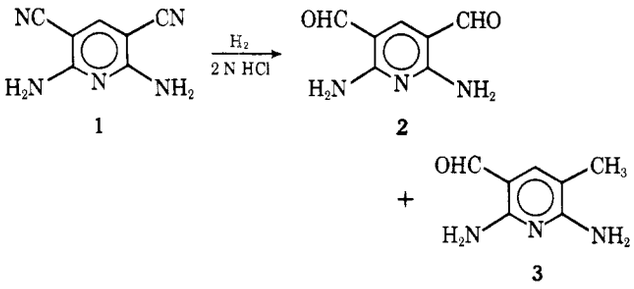
The Friedländer condensation of 2,6-diaminopyridine-3,5-dicarboxaldehyde and ketones was investigated as a possible synthetic route to substituted and fused 1,9,10-anthyridines. Condensation of this bis-*o*-amino aldehyde with acenaphthenone gave the fused, fully aromatic diacenaphtho[1,2-*b*:1′,2′-*i*]1,9,10-anthyridine in 65% yield. Condensations with deoxybenzoin, α-tetralone, and acetophenone, on the other hand, resulted in the formation of the 5,10-dihydro-1,9,10-anthyridine moiety, rather than the expected fully aromatic 1,9,10-anthyridine nucleus. It was demonstrated that base-catalyzed hydride transfer from the solvent on the anthyridine initially formed in the reaction medium resulted in the overall reduction of this heterocyclic system. Oxidation of the dihydroanthyridines with nitrobenzene or nitric acid gave the fully aromatic anthyridines in moderate yield. Prolonged oxidation of 2,8-diphenyl-5,10-dihydro-1,9,10-anthyridine with hot nitric acid gave mainly 2,8-diphenyl-5(10*H*)-1,9,10-anthyridone. Friedländer condensation of 2-amino-5,6-diphenylpyridine-3-carboxaldehyde and deoxybenzoin gave 2,3,6,7-tetraphenyl-1,8-naphthyridine in excellent yield.

The linear fusion of benzene rings leads to the well documented "acene" homologous series.[1] Very little information on the analogous series, containing the pyridine ring as building unit, is available. Contrary to the linear carbocyclic series, introduction of heteroatoms in such polycondensed systems gives rise to an increasing number of isomeric ring structures. The fusion of pyridine rings through their 2,3 bonds is of special interest because such condensed systems have been proposed for the structural unit of pyrolyzed poly(acrylonitrile).[2] In earlier work we have described a new and facile approach to the 1,8-naphthyridine heterocyclic system.[3] We now wish to report a new synthetic method for its next higher homolog, containing three linearly annelated pyridine rings: 1,9,10-anthyridine. Very few compounds containing this fundamental heterocyclic system have been reported.[4] The parent compound was only recently synthesized in a six-step sequence starting from 2,6-diaminopyridine.[5] Our familiarity with the synthetic opportunities present in the *o*-amino aldehyde functional group prompted us to approach the anthyridine skeleton via Friedländer condensation of appropriate *o*-amino aldehydes with ketones.

This synthetic strategy required either 2,6-diaminopyridine-3,5-dicarboxaldehyde **2** or 2-amino-1,8-naphthyridine-3-carboxaldehyde. Hydrogenolysis of *o*-aminonitriles seemed a most promising synthetic method for the elaboration of the *o*-amino aldehyde functional group. Hydrogenation of the readily available[6] 2,6-diamino-3,5-dicyanopyridine **1** suspended in 2 N HCl produced the desired bis-*o*-amino aldehyde

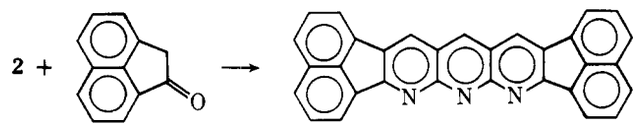
2 in moderate yield together with 2,6-diamino-3-methylpyridine-5-carboxaldhyde 3. The latter apparently is the result of further reduction of 2.



1 2 3

The poor solubility of 1 in 2 N HCl and the excellent solubility of 2 in the reaction medium prevented us from altering the course of the hydrogenation by limiting the hydrogen supply. It was found, however, that treatment of 1 in 2 N HCl with a small amount of copper eliminated this undesirable side reaction, resulting in the formation of 2 in 70% yield. The exact role of copper in this treatment is not well understood. It seems clear, however, that the presence of copper salts deactivate the hydrogenation catalyst. The hydrogenolysis of 2-amino-3-cyano-1,8-naphthyridine[7] under similar conditions did not result in the formation of the corresponding *o*-amino aldehyde. Examination of the reaction products indicated the absence of the fully aromatic 1,8-naphthyridine system and therefore this approach to the 1,9,10-anthyridine skeleton was not further investigated.

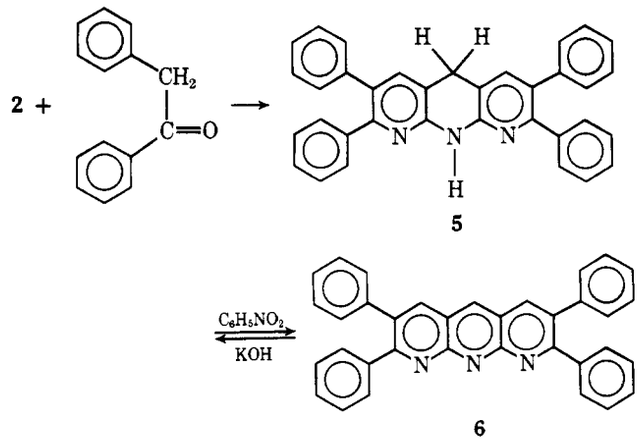
Base-catalyzed condensation of 2 with acenaphthenone in 1-propanol gave the fully condensed polycyclic diacenaphtho[1,2-*b*:1′,2′-*i*]1,9,10-anthyridine 4, orange needles, mp >500 °C, in 65% yield. This fused system represents the first example of the incorporation of the anthyridine system into a polycyclic framework. The lower homolog of 4, diacenaphtho[1,2-*b*: 1′,2′-*g*] 1,8-naphthyridine, was recently synthesized in this laboratory.[3]



4

Condensation of 2 and deoxybenzoin, on the other hand, did not result in the formation of the fully aromatic anthyridine ring system, as evidenced by strong, sharp absorptions at 3410 and 1250 cm^{-1} in the infrared spectrum of the reaction product. This was confirmed by its mass spectrum which showed peaks at *m/e* 485 (15%), 486 (15%), 487 (100%) and 488 (40%). The presence of the NH functional group, the observed molecular ion and its principal fragmentation (loss of hydrogen) seemed to suggest a dihydroanthyridine structure for the reaction product 5 (see further). Analysis is in agreement with this formulation. NMR data could not be obtained due to the very poor solubility of 5. Numerous attempts to alter the outcome of this condensation reaction by changing the solvent, the base employed, and its concentration (KOH in methanol, sodium ethoxide in ethanol) invariably resulted in the same reaction product. Therefore we focused our attention on the transformation of 5 into the desired fully aromatic anthyridine structure. It was found that brief treatment of 5 with boiling nitrobenzene resulted in the formation of 2,3,7,8-tetraphenyl-1,9,10-anthyridine 6 in 45% yield (based on 2), obtained as bright yellow needles (benzene).

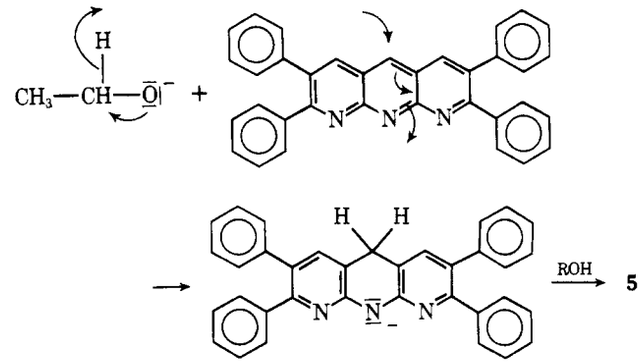
Spectroscopic and analytical data are in agreement with the proposed structure. Comparison of the infrared spectra of 5 and 6 indicated the absence of absorptions at 3410 and 1250 cm^{-1}, characteristic of 5, in the fully aromatic structure 6.



5 6

Oxidation of 5 with nitric acid (30%) was equally successful and resulted in the formation of 6 in 80% yield. Reaction with chromic anhydride in acetic acid was ineffective, due to poor solubility of 5 in the reaction medium.

The formation of fully aromatic heterocyclic systems in condensation reactions of aromatic *o*-amino aldehydes and ketones is well documented and constitutes the basis for the synthetic utility of the Friedländer condensation.[9] The unusual formation of a reduced heterocyclic system (5) in such condensation reaction seemed to suggest that 5, obtained from 2 and deoxybenzoin, could have resulted from further reaction of the fully aromatic tetraphenylanthyridine 6 initially formed in the basic reaction medium. Indeed, refluxing a solution of 6 in 1-propanol containing KOH gave a precipitate (90%), identical in all respects with 5, obtained directly from 2 and deoxybenzoin. However, direct attack of the hydroxyl group cannot account for the formation of the reduced anthyridine moiety in 5. Furthermore, it was found that reaction of 6 with potassium hydroxide in a 3:1 molar ratio resulted in the formation of 5 in nearly 90% yield. Addition of sodium ethoxide to 6 in ethanol resulted in the formation of 5, identical with the product obtained from KOH. It is clear therefore that neither the base nor the solvent is incorporated into the formation of 5 from 6. Apparently hydride transfer from the solvent takes place resulting in the reduction of the heterocyclic system. Hydride attack on the central ring will result in the formation of a stabilized amide anion, which is then protonated by the solvent, with regeneration of an alkoxide ion. The complete reduction of 6 is ensured by the very poor solubility of 5 since this will shift possible equilibria to the right. This base-catalyzed reduction of the anthyridine moiety proved to be a fast reaction. Addition of methanolic KOH to a 10^{-4} M solution of 6 in boiling 1-propanol resulted in the formation of a precipitate (5) within minutes after the addition. It is not surprising therefore that during the base-catalyzed condensation of 2 and deoxybenzoin no anthyridine could be isolated in the reaction mixture.

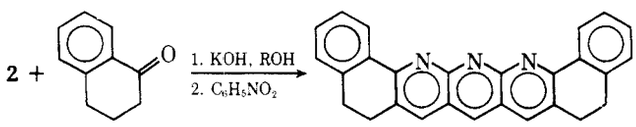


Reduction of 6 with a typical hydride donor such as sodium borohydride gave 5, identical with the product obtained from

6 and potassium hydroxide, confirming the reduction of the anthyridine ring system in the presence of alcoholic potassium hydroxide. A similar base-catalyzed reduction of an electron deficient system was observed in the formation of 3,3′-dimethoxyazoxybenzene from *m*-nitroanisole in ethanol containing sodium ethoxide.[10] Although the position of hydride attack on the anthyridine ring system could not be ascertained due to the insolubility of **5** in NMR solvents, it seems reasonable that such attack would occur on the central pyridine ring. Such enhanced reactivity of the central ring is well documented for linearly fused carbocyclic ring systems.[1]

Although it is conceivable that **5** could arise from initial hydride attack on the pyridine ring of **2**, this was not observed; **2** is stable in base under the reaction conditions employed for the synthesis of **6**. Finally, it should be noted that **6** as well as **5** are stable in boiling 2 N HCl.

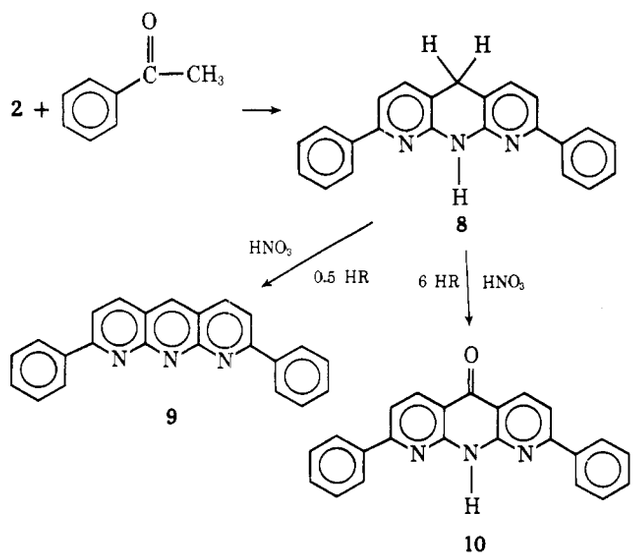
Condensation of **2** with α-tetralone followed by oxidation of the insoluble intermediate dihydro compound gave the fused anthyridine, 5,6,10,11-tetrahydrodinaphtho[1,2-*b*:2′,1′-*i*]1,9,10-anthyridine, **7**, in 50% overall yield.



7

Friedländer condensation of **2** and acetophenone proceeded faster than the condensation with deoxybenzoin. Once again the major product was the dihydroanthyridine **8**, as evidenced by its analysis, infrared, and mass spectrum. However, careful analysis of the reaction mixture revealed the presence of a small amount (~5%) of the fully aromatic 2,8-diphenyl-1,9,10-anthyridine **9**. The dihydroanthyridine **8**, obtained from benzene as a colorless compound, turned bright yellow on standing. Its mass spectrum revealed the appearance of a very intense peak at *m/e* 349, indicative of the presence of the anthyridone moiety (see below). Brief treatment of **8** with hot nitric acid (30%) gave the fully aromatic anthyridine **9** in 65% yield, together with a small amount of 2,8-diphenyl-5(10H)-1,9,10-anthyridone **10**. Longer reaction times resulted in an increase of the anthyridone **10** at the expense of **9**. Oxidation of **8** could also be carried out with boiling nitrobenzene as described earlier for the synthesis of tetraphenylanthyridine. No anthyridone **10** was detected under these reaction conditions.

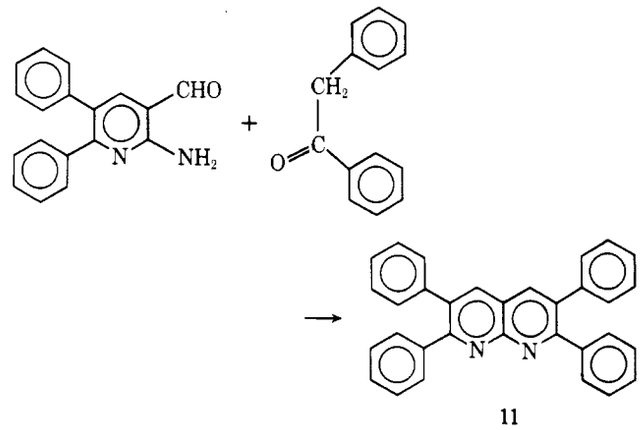
As mentioned earlier, nitric acid oxidation of **5** gave only the fully aromatic tetraphenylanthyridine **6**. The heterogeneous nature of this reaction effectively prevents overoxidation of **6** into the corresponding anthyridone. The conversion of **8** into **9** and **10**, on the other hand, is a homogeneous process.



8 **9** **10**

It is noteworthy that condensations of **2** with the reported ketones in the presence of small amounts of base typically employed in Friedländer reactions (~10 mol %) were not successful; the starting bis-*o*-amino aldehyde was recovered in nearly quantitative yield. The successful, *direct* synthesis of the fully aromatic, fused anthyridine **4** is possible due to its insolubility in the reaction medium, which greatly retards hydride transfer.

Finally, it should be noted that the formation of dihydro derivatives is not observed in the Friedländer condensations of *o*-amino aldehydes leading to the lower homologous 1,8-naphthyridine system, as exemplified by the high yield synthesis of 2,3,6,7-tetraphenyl-1,8-naphthyridine **11** from 2-amino-5,6-diphenylpyridine-3-carboxaldehyde[8] and deoxybenzoin.



11

Experimental Section

General. NMR spectra were recorded with a Varian A-60 and/or Varian XL-100 with FT spectrometer using TMS as an internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU6E instrument; infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer and UV spectra on a Cary-15 instrument. All melting points are uncorrected. Microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Instranal Laboratory, Inc., Rensselaer, N.Y.

2,6-Diaminopyridine-3,5-dicarboxaldehyde 2. A suspension of 4.0 g (0.025 mol) of finely divided 2,6-diamino-3,5-dicyanopyridine[6] 1 in 800 mL of 2 N HCl was stirred with 0.4 g of thin copper wire for 3 h. The copper was removed and the resulting suspension was hydrogenated at 40 °C over Pd/C (5%). The latter was introduced in three successive additions (0.35 g each). Each portion was allowed to react until no more hydrogen was absorbed. Vigorous stirring or shaking was essential for a successful hydrogenolysis. After the theoretical amount of hydrogen was absorbed, the catalyst was filtered and the resulting solution was neutralized (NH_4OH) to yield a thick, white precipitate (3.5 g, 70%). Recrystallizations from dimethylformamide and water gave fibrous needles, mp 295 °C (dec). IR (Nujol): 3400, 3300, 3175, 2740, 1675, 1640, 1610, 1525, 1280, 1180, 1155, 1035, 925, 805, 775, and 735 cm^{-1}; NMR δ (DMSO-d_6) 9.61 (s, 2, CHO), 8.28 (s, 1, H-4), 8.06 (broad, 4, NH_2); mass spectrum M^+ at *m/e* 165.

Anal. Calcd for $C_7H_7N_3O_2$: C, 50.91; H, 4.27; N, 25.44. Found C, 50.79; H, 4.09; N, 25.37.

2,6-Diamino-3-methylpyridine-5-carboxaldehyde 3. The hydrogenation of **1** without prior treatment with copper gave a mixture of **2** and **3** in a 1:2 ratio (as evidenced by the NMR spectrum). Extraction of the crude reaction product with ethanol, followed by concentration of the resulting solution, gave **3** in 40% yield; mp 207 °C (from EtOH); IR (Nujol) 3400, 3080, 2700, 1665, 1590, 1515, 1280, 1220, 1135, 1040, 920, 850, 770, 735, and 725 cm^{-1}; NMR δ (DMSO-d_6) 9.36 (s, 1, CHO), 7.33 (s, 1, H-4), 7.25 (broad, 2, 6-NH_2), 6.63 (broad, 2, 2-NH_2), 2.00 (s, 3, CH_3); mass spectrum M^+ at *m/e* 151.

Anal. Calcd for $C_7H_9N_3O$: C, 55.62; H, 6.00; N, 27.80. Found: C, 55.49; H, 5.89; N, 27.72.

Diacenaphtho[1,2-*b*:1′,2′-*i*]1,9,10-anthyridine 4. To a refluxing

solution of 0.6 g (0.0036 mol) of **2** and 1.6 g (0.01 mol) of acenaphthenone in 50 mL of 1-propanol were added 10 drops of methanolic KOH (20%). Reflux was continued for 24 h. The precipitate was washed with chloroform to yield 1.0 g (65%) of **4**, recrystallized from acetic acid as yellow-orange needles, mp > 500 °C; IR (Nujol) 1635, 1585, 1540, 1430, 1325, 1205, 1190, 1085, 1025, 915, 825, 805, 780, 770, and 735 cm^{-1}; UV ($CHCl_3$) 344 (ε 87 000), 362 (117 400), 405 (22 600), 414 (21 900) and 430 (23 200) nm.

Anal. Calcd for $C_{31}H_{15}N_3$: C, 86.70; H, 3.52; N, 9.78. Found: C, 86.46; H, 3.68; N, 9.62.

2,3,7,8-Tetraphenyl-5,10-dihydro-1,9,10-anthyridine 5. (a) From Deoxybenzoin. To a refluxing solution of 0.99 g (0.006 mol) of **2** and 2.45 g (0.012 mol) of deoxybenzoin in 150 mL of 1-propanol was added 1 mL of methanolic KOH (25%). The mixture was refluxed for 3 days to yield 1.8 g of an orange-colored precipitate **5** (65%), recrystallized from a large volume of *o*-dichlorobenzene, mp > 300 °C (dec). IR (Nujol) 3410, 1590, 1580, 1495, 1435, 1400, 1360, 1300, 1290, 1250, 1190, 1170, 1150, 1070, 1020, 955, 940, 910, 895, 815, 790, 775, 755, 750, 745, 715, 705, and 690 cm^{-1}. Mass spectrum M^+ at *m/e* 487 (100%).

Anal. Calcd for $C_{35}H_{25}N_3$: C, 86.21; H, 5.17; N, 8.62. Found: C, 86.27; H, 4.97; N, 8.72.

(b) From KOH and 6. To a refluxing suspension of 0.5 g of **6** in 100 mL of 1-propanol was added 0.13 mL of methanolic KOH (10%). Reflux was continued for 8 h to yield 0.35 g of **5**, identical in all respects with product obtained above.

2,3,7,8-Tetraphenyl-1,9,10-anthyridine 6. (a) Nitrobenzene. A mixture of 1.6 g of **5** and 30 mL of nitrobenzene was heated until a clear solution resulted. The solution was then refluxed for 30 min. The cooled solution was filtered and set aside for 2 h and filtered again, if necessary. The product was precipitated with petroleum ether and recrystallized from benzene to yield 1.15 g (77%) of **6**, bright yellow crystals, mp 322–323 °C. An analytical sample was prepared by column chromatography (alumina and $CHCl_3$). IR (Nujol) 1605, 1590, 1570, 1510, 1400, 1310, 1300, 1190, 1175, 1145, 1070, 1050, 1015, 995, 950, 930, 915, 810, 780, 765, 750, 730, 715, 700, and 690 cm^{-1}; NMR δ (DMSO-d_6) 9.43 (s, 1, H-5), 8.76 (s, 2, H-4 and H-6), 7.41 (s, 20, phenyl protons). Mass spectrum M^+ at *m/e* 485.

Anal. Calcd for $C_{35}H_{23}N_3$: C, 86.57; H, 4.77; N, 8.65. Found: C, 86.61; H, 4.79; N, 8.60.

(b) Nitric Acid. A suspension of 0.5 g of **5** in 60 mL of nitric acid (30%) was stirred at room temperature for 5 h. The mixture was then heated at 80 °C for 30 min, cooled, and filtered. The precipitate was washed with dilute ammonium hydroxide to yield 0.42 g of **6**, identical with product obtained from nitrobenzene.

5,6,10,11-Tetrahydrodinaphtho[1,2-*b*:2′,1′-*i*]1,9,10-anthyridine 7. To a refluxing solution of 0.5 g (0.003 mol) of **2** and 1.0 g (0.007 mol) of α-tetralone in 75 mL of 1 propanol was added 0.6 mL of methanolic KOH (25%). The mixture was refluxed for 40 h, and the precipitate was collected and washed with acetone to yield 0.82 g (69%) of a product similar to that observed from **2** and deoxybenzoin (IR absorptions at 3400 and 1250 cm^{-1}). The product was refluxed in 10 mL of nitrobenzene for 40 min and was precipitated with petroleum ether. Recrystallization from chloroform gave 0.5 g (70%) of **7**, mp 303 °C. An analytical sample was obtained by column chromatography (alumina, chloroform). IR (Nujol) 1630, 1590, 1520, 1490, 1425, 1390, 1300, 1275, 1250, 1220, 1165, 1140, 1100, 1020, 970, 940, 915, 870, 810, 800, 785, 740, 730, and 690 cm^{-1}.

Anal. Calcd for $C_{27}H_{19}N_3$: C, 84.13; H, 4.97; N, 10.90. Found: C, 84.16; H, 4.98; N, 10.86.

2,8-Diphenyl-5,10-dihydro-1,9,10-anthyridine 8. To a refluxing solution of 0.5 g (0.003 mol) of **2** and 0.84 g (0.007 mol) of acetophenone in 75 mL of 1-propanol was added 1 mL of methanolic KOH (20%). The mixture was refluxed for 3 h. The precipitate was collected and recrystallized immediately from a large volume of boiling benzene (600 mL) to yield 0.450 g (45%) of **8**, white product, mp >270 °C (decomposition). IR (Nujol) 3350, 1590, 1570, 1425, 1260, 835, 810, 760, 750, and 690 cm^{-1}. Mass spectrum M^+ at *m/e* 335.

Anal. Calcd for $C_{23}H_{17}N_3$: C, 82.36; H, 5.11; N, 12.53. Found: C, 82.39; H, 5.01; N, 12.60.

The filtrate was concentrated on the rotary evaporator to approximately 50 mL and set aside to crystallize. The precipitate was filtered and was recrystallized from benzene to give 0.04 g of **9**, identified by its infrared spectrum (see below).

2,8-Diphenyl-1,9,10-anthyridine 9. A mixture of 0.4 g of **8** in 80 mL of nitric acid (30%) was stirred at room temperature for 20 min. The mixture was heated slowly to 80 °C and was kept at this temperature for 30 min. The resulting solution was cooled rapidly, and the crystalline material was filtered and washed extensively with dilute NH_4OH and water. Recrystallization from ethanol yielded 0.25 g (60%) of **9**, pale yellow needles, mp 300–302 °C. IR (Nujol) 1620, 1590, 1575, 1520, 1430, 1315, 1300, 1275, 1230, 1155, 940, 830, 820, 790, 770, 760, 745, and 700 cm^{-1}; NMR δ ($CDCl_3$) 8.75 (s, 1, H-5), 8.48 (m, 4, ortho protons on phenyl rings), 8.40 (d, 2, H-4 and H-6, J_{H3-H4} = 8 Hz), 8.04 (d, 2, H-3 and H-7), 7.61 (m, 6, remaining phenyl protons). Mass spectrum M^+ at *m/e* 333.

Anal. Calcd for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54; N, 12.60. Found: C, 82.94; H, 4.50; N, 12.55.

2,8-Diphenyl-5(10*H*)-1,9,10-anthyridone 10. A mixture of 0.4 g of **8** in 80 mL of nitric acid (30%) was heated at 80 °C for 6 h. The solution was cooled; the crystalline material was filtered, and was washed with dilute NH_4OH and water. Chromatography (alumina, $CHCl_3$) followed by recrystallization from ethanol gave 0.225 g of **10**, mp 279–280 °C. An analytical sample was prepared by sublimation at 165 °C and 1 mmHg. IR (Nujol) 3155, 1610, 1585, 1420, 1265, 1235, 810, 790, 760, and 695 cm^{-1}; NMR δ ($CDCl_3$) 9.36 (broad singlet, 1, H-10), 8.79 (d, 2, H-4 and H-6, J_{H3-H4} = 8 Hz), 8.17 (m, 4, ortho protons on phenyl rings), 7.76 (d, 2, H-3 and H-7), 7.56 (m, 6, remaining phenyl protons). Mass spectrum M^+ at *m/e* 349.

Anal. Calcd for $C_{23}H_{15}N_3O$: C, 79.07; H, 4.33; N, 12.03. Found: C, 79.11; H, 4.35; N, 11.97.

2,3,6,7-Tetraphenyl-1,8-naphthyridine 11. To a refluxing solution of 0.55 g (0.002 mol) of 2-amino-5,6-diphenylpyridine-3-carboxaldehyde[8] and 0.395 g (0.002 mol) of deoxybenzoin in 5 mL of ethanol were added two drops of methanolic KOH (20%). Reflux was continued for 36 h to yield 0.79 g (90%) of **11**, recrystallized from chloroform, mp 301–302 °C; IR (Nujol) 1590, 1570, 1515, 1390, 1250, 1170, 1070, 1045, 1010, 945, 930, 910, 810, 770, 735, 710, 700, and 685 cm^{-1}; NMR δ ($CDCl_3$) 8.20 (s, 2, H-4 and H-5), 7.58 (m, 4, ortho protons on phenyl rings 2 and 7), 7.31 (s, 16, remaining phenyl protons). Mass spectrum M^+ at *m/e* 434.

Anal. Calcd for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10; N, 6.44. Found: C, 88.32; H, 5.05; N, 6.36.

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