Reduction of 4,7-Diphenyl-1,2,5-thia(oxa)diazolo[3,4-*c*]pyridines Affording 2,5-Diphenyl-3,4-diaminopyridines and Ring Closure of the Diamines to Fluorescent Azaheterocycles

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Received June 9, 1982

Reduction of 4,7-diphenyl-1,2,5-thia- (**1a-i**) and 1,2,5-oxadiazolo[3,4-*c*]pyridines (**3a** and **c-e**) gave 3,4-diamino-2,5-diphenylpyridines (**2a-g**), which were converted into the fluorescent triazolo[4,5-*c*]- (**5**), 1,2,5-selenadiazolo[3,4-*c*]- (**6**), imidazolo[4,5-*c*]pyridines (**8**), and pyrido[5,6-*c*]pyridines (**11**). In the reduction of **3a, c** and **e**, 4,5-dihydro[1,2,5]oxadiazolo[3,4-*c*]pyridines (**4a-c**) were obtained.

J. Heterocyclic Chem., **19**, 1481 (1982).

It has been reported (1,2) that the ring opening of 1,2,5-thia(oxa)diazoles with suitable reducing agents afforded vicinal diamines (**1, 2**), which are useful starting materials of azaheterocycles.

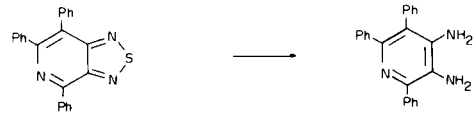
Recently, we have prepared a variety of pyridine-fused five membered heterocyclic compounds by the reaction of vicinally diaroyl-substituted heterocycles with methylamine derivatives (3-5). All of these heterocycles are fluorescent in daylight. Thus, the reduction of 1,2,5-thia(oxa)diazolo[3,4-*c*]pyridines is expected to afford 3,4-diaminopyridines and these diamines are also expected to be converted into fluorescent pyridine-fused heterocycles.

From the above point of view, we carried out the reduction of 1,2,5-thia(oxa)diazolopyridines and the consequent cyclization of the obtained diamines to azaheterocycles, which are reported herein.

Results and Discussion.

Reduction.

Reduction of 4,6,7-triphenyl-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**1a**) by sodium metal in ethanol and by sodium borohydride in refluxing ethanol was unsuccessful and unchanged **1a** was recovered in 98 and 90% yields, respectively. The compound **1a** was reduced by lithium aluminum hydride to 2,5,6-triphenyl-3,4-diaminopyridine (**2a**) in 87% yield with recovery of **1a** in 8% yield. Reduction by Raney nickel alloy in refluxing ethanol in the presence of potassium hydroxide at 50° also afforded **2a** in 77% yield.



1a 2a

meta-Di(thiadiazolopyridino)benzene (*1b*) was also reduced by Raney nickel alloy affording the corresponding tetramine **2b** in 44% yield, however, **1c** was not reduced under the same conditions because of its insolubility in ethanol and **1c** was recovered.

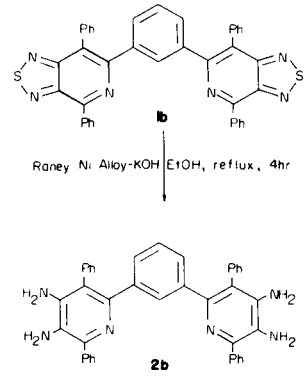
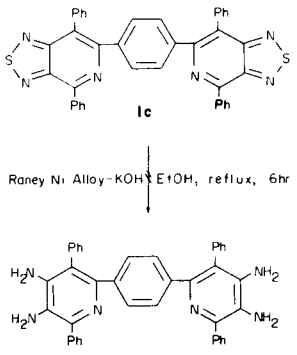


Table 1

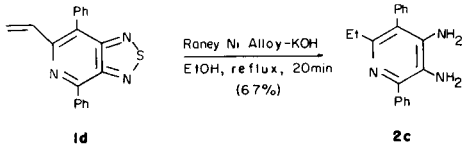
Reduction of 4,6,7-Triphenyl-1,2,5-thiadiazolo[3,4-*c*]pyridine (**1a**)

Run	Reducing Agent (Molar Ratio) (a)	Reaction Conditions (Solvent/temperature/time)	Yield of **2a** (%) (b)	Recovery of **1a** (%)
1	Sodium-Ethanol	Ethanol/room temperature/3 hours	—	98
2	Sodium Borohydride (4)	Ethanol/reflux/2 hours	2	90
3	Lithium Aluminum Hydride (2)	THF/room temperature/20 minutes	87	8
4	Raney-Ni-Alloy-Potassium Hydroxide	Ethanol/50°/2 hours	77	2

(a) Molar ratio; reducing agent/**1a**. (b) Yields of isolated products are given.



The compound **1d** was not reduced by sodium borohydride in refluxing ethanol and by lithium aluminum hydride in tetrahydrofuran at room temperature and **1d** was recovered. Raney nickel alloy in refluxing ethanol reduced both the vinyl group and the 1,2,5-thiadiazole ring of **1d** to give the ring opened 6-ethyl-2,5-diphenyl-3,4-diaminopyridine (**2c**) in 67% yield.



As is shown in Table 2, sodium borohydride reduction of **1e** and **3a** in ethanol gave different products depending upon the reaction conditions. The ethoxycarbonyl group of **1e** was reduced by sodium borohydride at room temperature for 24 hours to afford hydroxymethylthiadiazolopyridine **1f** as a major product with a small amount of diaminopyridine **2d**. On the other hand, **2d** was obtained in 57% yield together with 2% yield of **1f** when the reduction was carried out in refluxing ethanol for 10 minutes. The ethoxycarbonyl group of **2d** was slowly reduced in refluxing ethanol and, after 24 hours, **2e** was obtained in 19% yield with a decrease of **2d**.

The reduction of **3a** by sodium borohydride in ethanol at room temperature proceeded stepwise, as follows; (1) when the reduction was carried out for 1 hour, dihydropyridine **4a** was formed in 41% yield with recovery of some **3a**; (2) when the reduction was conducted for 3 hours, the yield of **4a** decreased with an increase of the yield of **3b**; and (3) after 18 hours, hydroxymethyldiaminopyridine **2e** was obtained in 21% yield with 2% yield of **3b**. On the contrary, the oxadiazole ring of **3a** was first reduced in refluxing ethanol to give **2d** in 39% yield. When heated at reflux for 12 hours, reduction of ester group of **2d** took place and **2e** was the sole product isolated. Thus, the ethoxycarbonyl group of oxa(thia)diazole ring of **1e** (**3a**) could be selectively reduced by a choice of the reaction conditions. The structure of **4a** will be mentioned later.

Lithium aluminum hydride in tetrahydrofuran at room temperature reduced both the ethoxycarbonyl group and the thiadiazole ring (ring opening) of **1e** to afford **2e** in 68% yield, while the ethoxycarbonyl group of **3a** was reduced under the above mentioned conditions to give **3b** as a major product with a 10% yield of **2e**.

Sodium borohydride reduction of **1g** afforded cyanodiaminopyridine **2f**. When **3c** was reduced by sodium borohydride at room temperature for 1 hour, dihydropyridine **4b** was obtained in 65% yield together with **2f** in 4% yield. In ethanol, **2f** was obtained in 79% yield. The results are summarized in Table 3.

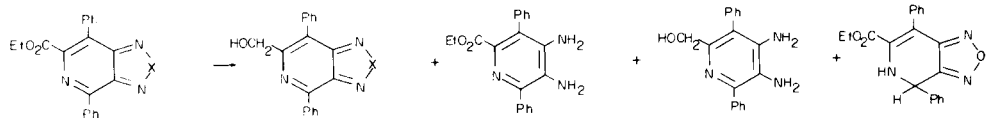
From the nmr spectra, three isomeric dihydrooxadiazo-

Table 2

Reduction of Ethyl 4,7-Diphenyl-1,2,5-thia(oxa)diazolo[3,4-c]pyridine-6-carboxylate (**1f**, **3f**)

Run	Substrate	X	Reducing Agent (Molar Ratio (a))	Reaction Conditions (Solvent/temperature/time)	Products Yield (%) (b)	Recovery of **1e**, **3a** (%)
1	**1e**	S	Sodium Borohydride (30) (c)	Ethanol/room temperature/24 hours	**1f** (41) **2d** (15)	—
2	**1e**	S	Sodium Borohydride (2)	Ethanol/reflux/10 minutes	**2d** (16)	68
3	**1e**	S	Sodium Borohydride (5)	Ethanol/reflux/10 minutes	**1f** (2) **2d** (27)	3
4	**1e**	S	Sodium Borohydride (10)	Ethanol/reflux/10 minutes	**1f** (1) **2d** (47) **2e** (2)	1
5	**1e**	S	Sodium Borohydride (30)	Ethanol/reflux/12 hours	**1f** (6) **2d** (29) **2e** (19)	—
6	**3a**	O	Sodium Borohydride (30) (c)	Ethanol/room temperature/18 hours	**3b** (2) **2e** (21)	—
7	**3a**	O	Sodium Borohydride (10)	Ethanol/room temperature/3 hours	**3b** (15) **4a** (10)	10
8	**3a**	O	Sodium Borohydride (10)	Ethanol/room temperature/1 hour	**3b** (3) **4a** (41)	37
9	**3a**	O	Sodium Borohydride (5)	Ethanol/reflux/10 minutes	**2d** (39) **2e** (6)	3
10	**3a**	O	Sodium Borohydride (30)	Ethanol/reflux/12 hours	**2e** (55)	—
11	**1e**	S	Lithium Aluminum Hydride	THF/room temperature/1 hour	**1f** (22) **2e** (68)	—
12	**3a**	O	Lithium Aluminum Hydride	THF/room temperature/1 hour	**3b** (62) **2e** (10)	—

(a) Molar ratio; reducing agent/**1e** or **3a**. (b) Yields of isolated products are given. (c) Ten times the molar quantity of sodium borohydride at first and each 5 times the molar quantity of sodium borohydride was added for 4 times at 2-3 hour intervals.



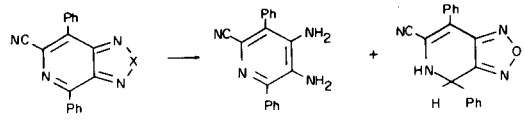
1e, X = S **1f**, X = S **2d** **2e** **4a**, X = O
3a, X = O **3b**, X = O

lopyridines are possible for the strucutres of **4a** and **4b**. In order to clarify the structure of **4** by means of nmr spectra, **4c** was prepared as follows; (i) hydrolysis of ethyl oxadiazolopyridine-6-carboxylate (**3a**) under basic conditions and subsequent decarboxylation of the resulting carboxylic acid **3d** afforded **3e**, and (ii) the desired **4c** was obtained in 64% yield with recovery of **3e** in 20% yield in the reduction of **3e** with sodium borohydride at room temperature while the compound **3e** afforded diamine **2g** in 65% yield when reduced in refluxing ethanol. In the nmr spectrum of **4c**, methine and olefinic protons were observed at 6.05 ppm and 7.11 ppm, respectively, as a doublet which couples with amino hydrogen at 5.75 ppm. Thus, the structures of **4a** and **4b** were determined as 4,5-dihydro derivatives (**4a-A** and **4b-A**).

The dihydropyridine **4a** was reduced with sodium borohydride in refluxing ethanol to give **2d, 2e, 3a** and **3b** in 34, 15, 4 and 2% yields, respectively. Dihydropyridines **4b**

Table 3

Reduction of 6-Cyano-4,7-diphenyl-1,2,5-thia(oxa)diazolo[3,4-*c*]pyridine (**1g, 3c**) by Sodium Borohydride (a)



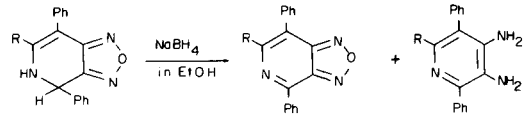
1g, X = S **2f** **4b**
3c, X = O

Run	Substrate	X	Reaction Conditions (Solvent/temperature/time)	Products Yield (%) (b)	Recovery of **1g, 3c** (%)
1	**1g**	S	Ethanol/room temperature/24 hours	**2f** (15)	66
2	**1g**	S	Ethanol/reflux/10 minutes	**2f** (89)	—
3	**3c**	O	Ethanol/room temperature/1 hour	**2f** (4) **4b** (65)	19
4	**3c**	O	Ethanol/reflux/10 minutes	**2f** (79)	—

(a) Molar ratio; reducing agent/**1g** or **3c** = 10. (b) Yields of isolated products are given.

Table 4

Reduction of 6-Substituted-4,7-diphenyl-4,5-dihydro-1,2,5-oxadiazolo[3,4-*c*]pyridine with Sodium Borohydride



4a-c

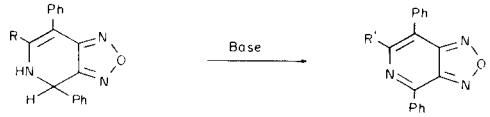
3a, R' = CO_2Et **2d**, R' = CO_2Et
3b, R' = CH_2OH **2e**, R = CH_2OH
3c, R' = CN **2f**, R = CN
3e, R' = H **2g**, R = H

Run	Substrate	Molar Ratio (Sodium Borohydride/**4**)	Reaction Conditions (temperature/time)	Products Yields (%))a)
1	**4a**	5	reflux/10 minutes	**3a** (4) **3b** (2) **2d** (34) **2e** (15)
2	**4b**	10	room temperature/24 hours	**3c** (1) **2f** (51)
3	**4c**	5	reflux/10 minutes	**3e** (13) **2g** (81)

(a) Yields of isolated products are given.

Table 5

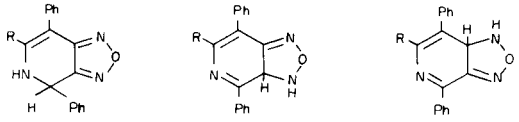
Treatment of 6-Substituted-4,7-diphenyl-4,5-dihydro-1,2,5-oxadiazolo[3,4-*c*]pyridines With Base



4a-c **3**

Run	Substrate	R	Base (Molar Ratio (a))	Reaction Conditions (Solvent/temperature/time)	Products Yield (%) (b)	R'
1	**4a**	CO_2Et	Sodium Hydroxide (10)	Ethanol/room temperature/90 minutes	**3d** (77)	CO_2H
2	**4a**	CO_2Et	DBU (1)	Benzene/room temperature/4 hours	**3a** (85)	CO_2Et
3	**4b**	CN	Sodium Hydroxide (10)	Ethanol/room temperature/90 minutes	**3c** (50)	CN
4	**4c**	H	Sodium Hydroxide (10)	Ethanol/room temperature/90 minutes	**3e** (71)	H
5	**4c**	H	DBU (1)	Benzene/room temperature/4 hours	**3e** (82)	H

(a) Molar ratio; base/**4**. (b) Yields of isolated products are given.



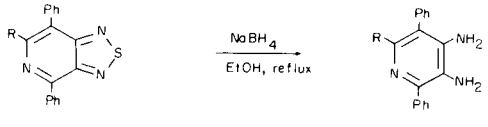
4a-A, R = CO_2Et **4a**-B **4a**-C
4b-A, R = CN **4b**-B **4b**-C
4c-A, R = H **4c**-B **4c**-C

and **4c** also afforded the corresponding diaminopyridines **2f** and **2g** in the yields shown in the Table 4, together with aromatized **3c** and **3e**.

In order to study the possibility of the oxidation of **4** during work-up, compounds **4a-c** were treated with bases under the conditions shown in Table 5 and the oxidation products **3d, a, c** and **e** were obtained in good yields.

Table 6

Reduction of **1** with Sodium Borohydride in Refluxing Ethanol



1 **2**

Substrate	R-	Molar ratio **1**:Sodium Borohydride	Reaction time	Yield (%) of **2** (a)	Recovery of **1** (%)
1h	HO_2C- ($Na^+O_2C^-$)	1:5	2 hours	—	48
1d	CH_2=CH-	1:5	2 hours	—	90
1a	Ph-	1:4	2 hours	**2a** (2)	90
1f	$HOCH_2$-	1:5	2 hours	**2e** (30)	50
1i	H-	1:5	2 hours	**2h** (60)	29
1e	EtO_2C-	1:5	10 minutes	**2d** (57)	—
1g	NC-	1:5	10 minutes	**2f** (89)	—

(a) Yields of isolated products are given.

It should be noted that the 1,2,5-thiadiazole ring of **1** bearing strongly electron-withdrawing group (**1e** and **1g**) was easily reduced to give the expected diamines in good yields, while the reduction of that of **1** bearing phenyl and vinyl group (**1a** and **1d**) proceeded very slowly or not at all, as shown in Table 6.

Ring Closure Reaction.

The ring-closure reaction of the above prepared diaminopyridines were carried out according to the usual manner and the results are summarized in Table 7-10. Triazolo- (**5**) and selenadiazolopyridines (**6**) were prepared in good yields. The reaction of **2a** and **2d** with formic acid (**7a**) at reflux gave the corresponding imidazolopyridines **8a** and **8d** and the reaction of **2a** with acetic acid at reflux also afforded **8b**, however, the reaction with acetic anhydride at reflux resulted in predominant formation of the tetraacetylated pyridine **9**. Tetraphenylimidazolopyridine (**8c**) was obtained in 48% yield by heating **2a** in **7d** at 280° for 1 hour.

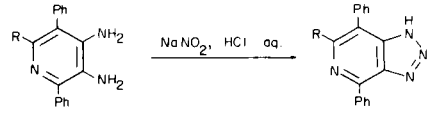
Pyridopyrazines **11** were obtained in the reaction of **2a, 2d**, and **2e** with diacetyl (**10a**), benzil (**10b**) and acenaphthenquinone (**10c**). Cyanopyridine **2f** did not give the expected pyridopyrazine in refluxing ethanol and **2f** was recovered in 94% yield. The above obtained heterocycles-condensed 1,4-diphenylpyridines are all fluorescent in daylight as expected.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were measured on a Nippon Bunko IR-A-102 spectrophotometer as potassium bromide pellets. The pmr spectra were recorded on a Nippon Denshi JEOL FT-100 using TMS as an internal standard in deuteriochloroform unless otherwise stated. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

Table 7

Preparation of 4,7-Diphenyltriazolo[4,5-*c*]pyridines (**5**)

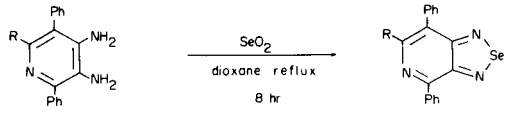


2 **5**

Run	Substrate	R	Product **5** Yield (%)
1	**2a**	Ph	**5a** (88)
2	**2d**	CO_2Et	**5b** (81)
3	**2e**	CH_2OH	**5c** (97)
4	**2f**	CN	**5d** (83)

Table 8

Preparation of 4,7-Diphenyl-1,2,5-selenadiazolo[3,4-*c*]pyridines



2 **6**

Run	Substrate	R	Product **6** Yield (%)
1	**2a**	Ph	**6a** (93)
2	**2d**	CO_2Et	**6b** (36)
3	**2e**	CH_2OH	**6c** (66)
4	**2f**	CN	**6d** (90)

Reduction of **1a** with Raney Nickel Alloy.

A mixture of **2a** (2.83 g), Raney nickel alloy (Ni, 50%, 14.1 g) and potassium hydroxide (14.1 g) in ethanol (140 ml) was heated at 50° for 2 hours. The reaction mixture was filtered and washed with benzene. The combined filtrate and washings were poured into water and extracted with benzene. The extract was dried over sodium sulfate and evaporated *in vacuo* to afford the residue which was column chromatographed. Unreacted **1a** (0.057 g) was eluted with benzene and **2a** (2.00 g) with chloroform and ethanol.

3,4-Diamino-2,5,6-triphenylpyridine (**2a**).

This compound was obtained as colorless needles (ethanol), mp 210.5-212°; ir: 3460, 3390, 3300, 3230 cm^{-1}; pmr (deuteriodimethylsulfoxide): δ 7.72-6.75 (m, 15H), 4.82, 4.44 (each br, 2H, exchanged with deuterium oxide); ms: m/e (relative intensity) 337 (M^+, 85), 336 (100), 77 (38).

Anal. Calcd. for $C_{23}H_{19}N_3$: C, 81.87; H, 5.67; N, 12.45. Found: C, 81.57; H, 5.79; N, 12.52.

Preparation of **1b** and **1c**.

A mixture of 3,4-dibenzoyl-1,2,5-thiadiazole (0.30 g), *m*-xylilenediamine (0.69 g) and DBU (0.16 g) in toluene (20 ml) was heated at reflux for 1 hour and evaporated *in vacuo* to leave the residue which, on column chromatography with benzene, afforded **1b** (0.23 g).

m-Bis(4,7-diphenyl-1,2,5-thiadiazolo[3,4-*c*]pyridino)benzene.

This compound was obtained as yellow powder (hexane), mp 303-310°.

Anal. Calcd. for $C_{40}H_{24}N_6S_2$: C, 73.60; H, 3.71; N, 12.87. Found: C, 73.20; H, 3.94; N, 12.61.

A mixture of 3,4-dibenzoyl-1,2,5-thiadiazole (0.30 g), *p*-xylilenediamine (0.69 g) and DBU (0.16 g) in toluene (20 ml) was heated at reflux for 1 hour and the solvent was evaporated *in vacuo* to afford **1c** (0.20 g).

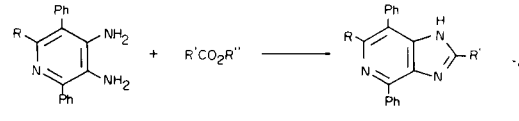
p-Bis(4,7-diphenyl-1,2,5-thiadiazolo[3,4-*c*]pyridino)benzene.

This compound was obtained as yellow powder (xylene), mp 402-408°.

Anal. Calcd. for $C_{40}H_{24}N_6S_2$: C, 73.60; H, 3.71; N, 12.87. Found: C, 73.62; H, 3.96; N, 12.78.

Table 9

Preparation of 4,7-Diphenylimidazolo[4,5-*c*]pyridines (**8**)



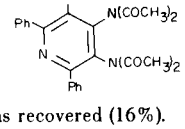
2 **7** **8**

Run	**2** (R =)	**7** (R′ = , R″ =)	Reaction Conditions (Solvent/temperature/time)	Products Yield (%) (a)
1	**2a** (Ph)	**7a** (H, H)	Neat/reflux/48 hours	**8a** (72)
2	**2a** (Ph)	**7b** (CH_3, H)	Neat/reflux/48 hours	**8b** (79)
3	**2a** (Ph)	**7c** (CH_3, $COCH_3$)	Neat/reflux/24 hours	**8b** (18) **9** (49)
4 (c)	**2a** (Ph)	**7d** (Ph, Ph)	Neat/280°/1 hour	**8c** (48)
5	**2e** (CO_2Et)	**7a** (H, H)	Neat/reflux/24 hours	**8d** (90)

(a) Yields of isolated products are given.

(b)

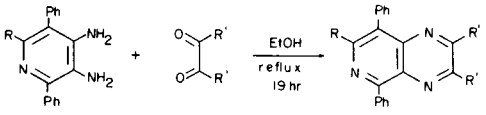
9



(c) Substrate **2a** was recovered (16%).

Table 10

Preparation of 5,8-Diphenylpyrido[3,4-*b*]pyrazines



2 10 11

Run	2	R	10	R'	Product 11 Yield (%)	Recovery of 2 (%)
1	**2a**	Ph	**10a**	CH_3	**11a** (36)	32
2	**2a**	Ph	**10b**	Ph	**11b** (79)	10
3	**2a**	Ph	**10c**		**11c** (95)	—
3	**2d**	CO_2Et	**10b**	Ph	**11d** (76)	—
4	**2e**	CH_2OH	**10b**	Ph	**11e** (48)	45
5	**2f**	CN	**10b**	Ph	—	94

Reduction of **1b** with Raney Nickel Alloy.

A mixture of **1b** (0.30 g), Raney nickel alloy (1.50 g) and potassium hydroxide (6.00 g) in ethanol (50 ml) was heated at reflux and additional Raney nickel alloy (1.50 g × 3) was added for every one hour. The reaction mixture was treated as described above to afford **2b** (0.12 g).

m-Bis(3,4-diamino-2,5-diphenyl-6-pyridino)benzene (**2b**).

This compound was obtained as colorless prisms (benzene), mp 334-347°; ir: 3480, 3390, 3300, 3230 cm^{-1}; ms: m/e (relative intensity) 596 (M^+, 100), 595 (99).

Anal. Calcd. for $C_{40}H_{32}N_6$: C, 80.51; H, 5.41; N, 14.09. Found: C, 80.71; H, 5.45; N, 13.73.

Preparation of 4,7-Diphenyl-6-vinyl-1,2,5-thiadiazolo[3,4-*c*]pyridine (**1d**).

A mixture of 3,4-dibenzoyl-1,2,5-thiadiazole (0.30 g), allylamine hydrogen chloride (0.29 g) in 10 mol% methanolic potassium hydroxide solution was heated at reflux for 2 hours and poured into water to give **1d** (0.31 g). This compound was obtained as orange prisms (hexane), mp 139-141°; pmr: δ 5.55 (dd, 1H, J = 3, 5, 9.5 Hz), 6.74 (dd, 1H, J = 3.5, 17 Hz), 7.00 (dd, 1H, J = 9.5, 17 Hz), 7.35-7.60 (m, 8H), 8.55-8.75 ppm (m, 2H); ms: m/e (relative intensity) 315 (M^+, 100), 314 (99).

Anal. Calcd. for $C_{19}H_{13}N_3S$: C, 72.52; H, 4.23; N, 13.16. Found: C, 72.36; H, 4.15; N, 13.32.

Reduction of **1d** with Raney Nickel Alloy.

A mixture of **1d** (0.30 g), Raney nickel alloy (3.00 g) and potassium hydroxide (3.00 g) in ethanol (30 ml) was heated at reflux for 20 minutes and the reaction mixture was treated as described above to afford **2c** (0.18 g).

3,4-Diamino-6-ethyl-2,5-diphenylpyridine (**2c**).

This compound was obtained as a 1:1-adduct with methanol on recrystallization from methanol as pale brown prisms, mp 148.5-151°.

Anal. Calcd. for $C_{20}H_{23}N_3O$: C, 74.74; H, 7.21; N, 13.07. Found: C, 74.50; H, 7.13; N, 12.71.

Compound **2c** was made free from methanol on being heated at 100° under vacuum for 24 hours as pyellow prisms, mp 129-130°; ir: 3480, 3440, 3380, 3290, 3210 cm^{-1}; pmr: δ 7.69-7.10 (m, 10H), 3.80 (br s, 2H), 3.3-2.6 (br s, 2H), 2.49 (q, 2H), 1.80 ppm (t, 3H); ms: m/e (relative intensity) 289 (M^+, 61), 288 (100).

Anal. Calcd. for $C_{19}H_{19}N_2$: C, 78.86; H, 6.62; N, 14.52. Found: C, 79.10; H, 6.55; N, 14.53.

Sodium Borohydride Reduction of **1e** and **3a**.

A mixture of **1e** and **3a** (0.30 g) and sodium borohydride in ethanol (30 ml) was treated under the conditions mentioned in Table 2. The reaction mixture was poured into water, extracted with benzene, and dried over sodium sulfate. Benzene was evaporated *in vacuo* to leave the residue which was column chromatographed. Unreacted **1e** and **3a**, and the products, **4a** and **1f** or **3b** were eluted with benzene. The compound **2d** was eluted with chloroform and **2e** with ethanol. The yields are given in Table 2.

4,7-Diphenyl-6-hydroxymethyl-1,2,5-thiadiazolo[3,4-*c*]pyridine (**1f**).

This compound was obtained as yellow plates (hexane), mp 152-153° (lit 152-153°) (3).

Ethyl 4,5-Diamino-3,6-diphenylpyridine-6-carboxylate (**2d**).

This compound was obtained as colorless crystals, mp 98-99°; ir: 3470, 3370, 3300, 3220, 1730 cm^{-1}; pmr: δ 7.75-7.24 (m, 10H), 4.02 (q, 2H), 3.90, 3.65 (each br, 2H, exchange with deuterium oxide), 0.96 ppm (t, 3H); ms: m/e (relative intensity) 333 (M^+, 33), 261 (29), 260 (M^+-CO_2Et, 100).

Anal. Calcd. for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.76; H, 5.88; N, 12.42.

4,7-Diphenyl-6-hydroxymethyl-1,2,5-oxadiazolo[3,4-*c*]pyridine (**3b**).

This compound was obtained as yellow needles (hexane), mp 136-137°; ir: 3400 cm^{-1}; pmr: δ 8.72-8.48 (m, 2H), 7.64-7.26 (m, 8H), 4.83 (s, 2H), 3.53 ppm (very br, 1H, OH, exchange with deuterium oxide); ms: m/e (relative intenstiy) 303 (M^+, 100), 302 (22), 286 (27), 274 (60).

Anal. Calcd. for $C_{18}H_{13}N_3O_2$: C, 71.27; H, 4.32; N, 13.86. Found: C, 71.52; H, 4.39; N, 13.69.

3,4-Diamino-2,5-diphenyl-6-hydroxymethyl pyridine (**2e**).

This compound was obtained as pale yellow leaves (ethanol), mp 247-249°; ir: 3500, 3400, 3310, 3220 cm^{-1}; pmr: δ 7.74-7.08 (m, 10H), 4.29 (s, 2H), 3.89 (br, 1H), 3.3 ppm (br, 4H); ms: m/e (relative intensity) 291 (M^+, 100), 290 (98), 272 (26), 262 (34), 260 (45), 77 (13).

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.33; H, 5.93; N, 14.13.

Ethyl 4,5-Dihydro-4,7-diphenyl[1,2,5]oxadiazolo[3,4-*c*]pyridine-6-carboxylate (**4a**).

This compound was obtained as pale yellow needles (hexane), mp 120-121°; ir: 3350, 1705 cm^{-1}; pmr: δ 7.80-7.30 (m, 10H), 6.07 (d, 1H, J = 3 Hz), 5.41 (br s, 1H), 4.00 (q, 2H), 0.87 ppm (t, 3H); ms: m/e (relative intensity) 347 (M^+, 100).

Anal. Calcd. for $C_{20}H_{17}N_3O_3$: C, 69.15; H, 4.93; N, 12.10. Found: C, 69.36; H, 4.97; N, 11.94.

Reduction of **1e** and **3a** with Lithium Aluminum Hydride.

A mixture of **1e** or **3a** (0.30 g) and 10 times molar ratio of lithium aluminum hydride in anhydrous tetrahydrofuran (30 ml) was stirred at room temperature for 1 hour under nitrogen atmosphere. A mixture of ethanol (0.5 ml) and water (0.5 ml) was added to the reaction mixture and the solvent was removed *in vacuo* to leave the residue which was extracted with benzene. The extract was condensed and column chromatographed. The compound **1f** or **3b** was eluted with benzene and **2e** with ethanol in the yields given in Table 2.

Reduction of **1g** and **3c** with Sodium Borohydride.

A mixture of **1g** or **3c** (0.30 g) and sodium borohydride in ethanol (30 ml) was treated under the conditions shown in Table 3 and worked up as described above. Unreacted **1g** or **3c** and the product **4c** were eluted with benzene and **2f** with chloroform. Their yields are given in Table 3.

6-Cyano-3,4-diamino-2,5-diphenylpyridine (**2f**).

This compound was obtained as orange needles (ethanol), mp

244.5-246°; ir: 3450, 3380, 3280, 2225 cm^{-1}; pmr: δ 7.69-7.27 (m, 10H), 3.97, 3.82 ppm (each br, 2H); ms: m/e (relative intensity) 286 (M^+, 76), 285 (100).

Anal. Calcd. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.70; H, 4.97; N, 19.28.

6-Cyano-4,5-dihydro-4,7-diphenyl[1,2,5]oxadiazolo[3,4-*c*]pyridine (**4b**).

This compound was obtained as yellow needles (hexane), mp 158.5-159.5°; ir: 3350, 2250 cm^{-1}; pmr: δ 7.72-7.26 (m, 10H), 6.09 (d, 1H, J = 2 Hz), 4.67 ppm (br s, 1H); ms: m/e (relative intensity) 300 (M^+, 100).

Anal. Calcd. for $C_{18}H_{12}N_4O$: C, 71.99; H, 4.03; N, 18.66. Found: C, 72.01; H, 4.02; N, 18.65.

Preparation of **3e**.

A mixture of **1e** (4.00 g) and sodium hydroxide (2.00 g) in ethanol (200 ml) was stirred at room temperature for 24 hours and poured into water (300 ml). The mixture was made acidic with dilute hydrochloric acid solution and extracted with chloroform (100 ml × 2). The extract was dried over sodium sulfate and evaporated *in vacuo* to afford **3d** which, on being heated at 220-230° for 10 minutes, gave **3e** (2.77 g).

4,7-Diphenyl-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylic Acid (**3d**).

This compound was obtained as yellow prisms (benzene-hexane), mp 219-220°; ir: 3200, 1760, 1330 cm^{-1}; pmr: δ 8.68-8.46 (m, 2H), 7.71-7.38 ppm (m, 8H); ms: m/e (relative intensity) 317 (M^+, 64), 273 (M^+-CO_2Et, 35), 243 (100).

Anal. Calcd. for $C_{15}H_{11}N_3O_3$: C, 68.14; H, 3.49; N, 13.24. Found: C, 68.62; H, 3.60; N, 13.06.

4,7-Diphenyl-1,2,5-oxadiazolo[3,4-*c*]pyridine (**3e**).

This compound was obtained as yellow plates (benzene-hexane), mp 149-150.5°; pmr: δ 8.67 (s, 1H), 8.74-8.46 (m, 2H), 8.12-7.85 (m, 2H), 7.66-7.30 ppm (m, 6H); ms: m/e (relative intensity) 273 (M^+, 100).

Anal. Calcd. for $C_{17}H_{11}N_3O$: C, 74.71; H, 4.06; N, 15.38. Found: C, 74.87; H, 4.15; N, 14.98.

Reduction of **3e** with Sodium Borohydride.

(i) A mixture of **3e** (0.20 g) and sodium borohydride (0.28 g) in ethanol (20 ml) was stirred at room temperature for 4 hours and treated as described earlier. Unreacted **3e** (0.04 g) and dihydropyridine **4c** (0.13 g) were eluted with benzene.

(ii) A mixture of **3e** (0.10 g) and sodium borohydride (0.07 g) in ethanol (10 ml) was heated at reflux for 10 minutes and treated as usual. Unreacted **3e** (0.02 g) was eluted with benzene and diamine **2g** (0.06 g) with chloroform.

4,5-Dihydro-4,7-diphenyl[1,2,5]oxadiazolo[3,4-*c*]pyridine (**4c**).

This compound was obtained as pale yellow plates (methanol), mp 123-125°; ir: 3430 cm^{-1}; pmr: δ 7.75-7.16 (m, 10H), 7.11 (d, 1H, J = 6.2 Hz), 6.05 (d, 1H, J = 1.8 Hz), 5.75 ppm (br d, 1H, J = 6.2 Hz); ms: m/e (relative intensity) 275 ($M,^+$, 37), 274 (23), 273 (100).

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.16; H, 4.76; N, 15.26. Found: C, 74.09; H, 4.84; N, 14.93.

3,4-Diamino-2,5-diphenylpyridine (**2g**).

This compound was obtained as colorless plates (benzene-hexane), mp 191-193°; ir: 3460, 3400, 3340 cm^{-1}; pmr: δ 7.95 (s, 1H), 7.68-7.20 (m, 10H), 4.10 (br, 2H), 3.3 ppm (very br, 2H, exchange with deuterium oxide); ms: m/e (relative intensity) 261 (M^+, 68), 260 (100).

Anal. Calcd. for $C_{17}H_{15}N_3$: C, 78.13; H, 5.79; N, 16.08. Found: C, 77.96; H, 5.86; N, 15.66.

Reduction of **4a**, **4b** and **4c** with Sodium Borohydride.

A mixture of **4a**, **4b** or **4c** (0.20 g) and sodium borohydride in ethanol (20 ml) was treated under the conditions shown in Table 4 and worked up as usual. The products were separated through column chromatography.

Treatment of **4** With Base.

(i) A mixture of **4a** (0.20 g) and sodium hydroxide (0.23 g) in ethanol (20 ml) was stirred at room temperature for 90 minutes. The reaction mixture was poured into water (100 ml), acidified with dilute hydrochloric acid solution, and extracted with chloroform (30 ml × 3). Evaporation of the extract afforded carboxylic acid **3a** (0.14 g).

(ii) A mixture of **4b** or **4c** (0.20 g or 0.10 g) and sodium hydroxide (0.27 g or 0.15 g) in ethanol (20 ml) was stirred at room temperature for 90 minutes. The mixture was poured into water and extracted with benzene. The extract was evaporated *in vacuo* to leave the residue which, on column chromatography with benzene, afforded **3c** (0.10 g) or **3e** (0.07 g).

(iii) A mixture of **4a** (0.11 g) or **4c** (0.10 g) and DBU (0.05 g or 0.06 g) in benzene (10 ml) was stirred at room temperature for 4 hours and evaporated *in vacuo* to leave the residue which, on column chromatography with benzene, afforded **3a** (0.095 g) or **3e** (0.082 g).

Reduction of **1a**, **d**, **e**, **f**, **g**, **h** and **i** With Sodium Borohydride.

A mixture of **1** (0.20 g) and sodium borohydride in ethanol (20 ml) was treated under the conditions shown in Table 6 and worked up as usual.

Preparation of Triazolopyridine (**5**).

To a mixture of **2a** (0.20 g) and ice (2.5 g) in concentrated hydrochloric acid (2.5 ml) and water (10 ml) was added dropwise a solution of sodium nitrite (0.05 g) in water (0.5 ml).Then the reaction mixture was stirred at room temperature for 2 hours and made alkaline by sodium bicarbonate to give **5a** (0.18 g).

4,6,7-Triphenyltriazolo[4,5-*c*]pyridine (**5a**).

This compound was obtained as colorless needles (methanol), mp 199-201°; ir: 3400 cm^{-1}; pmr: δ 12.22 (br, 1H), 8.93-8.64 (m, 2H), 7.64-7.02 ppm (m, 13H); ms: m/e (relative intensity) 348 (M^+, 80), 320 (M^+-N_2, 76), 319 (M_2^+-HN_2, 100).

Anal. Calcd. for $C_{23}H_{16}N_4$: C, 79.29; H, 4.63; N, 16.08. Found: C, 79.56; H, 4.94; N, 15.63.

Ethyl 4,7-diphenyltriazolo[4,5-*c*]pyridine-6-carboxylate (**5b**).

This compound was obtained as colorless crystals (benzene-hexane), mp 153-155°; ir: 3440, 3120, 1733, 1708 cm^{-1}; pmr: δ 8.64-8.38 (m, 2H), 7.52-7.10 (m, 8H), 4.16 (q, 2H), 1.03 ppm (t, 3H); ms: m/e (relative intensity) 344 (M^+, 21), 244 (68), 243 (67), 242 (M^+-CO_2Et, HN_2, 100).

Anal. Calcd. for $C_{20}H_{16}N_4O_2$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.66; H, 4.87; N, 15.78.

4,7-Diphenyl-6-hydroxymethyltriazolo[4,5-*c*]pyridine (**5c**).

This compound was obtained as colorless needles (benzene-ethanol), mp 235-238°; ir: 3400, 3100 cm^{-1}; pmr (deuteriodimethylsulfoxide): δ 8.88-8.64 (m, 2H), 7.70-7.36 (m, 8H), 5.23 (br, 1H), 4.58 ppm (s, 2H); ms: m/e (relative intensity) 302 (M^+-CHO or HN_2, 32), 256 (62), 255 (69).

Anal. Calcd. for $C_{18}H_{14}N_4O$: C, 71.51; H, 4.67; N, 18.53. Found: C, 71.60; H, 4.71; N, 18.45.

6-Cyano-4,7-diphenyltriazolo[4,5-*c*]pyridine (**5d**).

This compound was obtained as colorless prisms (benzene), mp 232-234°; ir: 3430, 3140, 2240 cm^{-1}; pmr (deuteriodimethylsulfoxide): δ 8.77-8.48 (m, 2H), 7.86-7.40 ppm (m, 8H); ms: m/e (relative intensity) 297 (M^+, 55), 269 (40), 268 (M^+-HN_2, 100).

Anal. Calcd. for $C_{18}H_{11}N_5$: C, 72.71; H, 3.73; N, 23.56. Found: C, 72.75; H, 3.77; N, 23.16.

Preparation of Selenadiazolopyridine (**6**).

Typical Procedure.

A mixture of **2d** (0.10 g) and selenium dioxide (0.04 g) in dioxane (1 ml) was heated at reflux for 8 hours. The mixture was poured into water (20 ml), extracted with benzene (10 ml × 3) and evaporated *in vacuo* to leave the residue which, on column chromatography with benzene, afforded **6b** (0.044 g).

4,6,7-Triphenyl-1,2,5-selenadiazolo[3,4-*c*]pyridine (**6a**).

This compound was obtained as yellow needles (benzene), mp

247.5-249.5°; pmr: δ 8.65-8.40 (m, 2H), 7.62-7.05 ppm (m, 13H); ms: m/e (relative intensity) 415 (M^+, 19), 414 (28), 413 (M^+, 83), 412 (47), 411 (M^+, 46), 410 (M^+, 36), 409 (M^+, 21), 77 (Ph, 100).

Anal. Calcd. for $C_{23}H_{15}N_3Se$: C, 66.99; H, 3.67; N, 10.19. Found: C, 67.27; H, 3.84; N, 9.83.

Ethyl 4,7-Diphenyl-1,2,5-selenadiazolo[3,4-*c*]pyridine-6-carboxylate (**6b**).

This compound was obtained as yellow plates (benzene-hexane), mp 176-179°; ir: 1732 cm^{-1}; pmr: δ 8.57-8.35 (m, 2H), 7.62-7.26 (m, 8H), 4.20 (q, 2H), 1.05 (t, 3H); ms: m/e (relative intensity) 411 (M^+, 11), 410 (13), 409 (M^+, 44), 407 (M^+, 24), 406 (M^+, 10), 405 (M^+, 9), 337 (46), 335 (38), 257 (100).

Anal. Calcd. for $C_{20}H_{15}N_3O_2Se$: C, 58.83; H, 3.70; N, 10.29. Found: C, 59.13; H, 3.93; N, 9.82.

4,7-Diphenyl-6-hydroxymethyl-1,2,5-selenadiazolo[3,4-*c*]pyridine (**6c**).

This compound was obtained as yellow needles (benzene), mp 247-249°; ir: 3440 cm^{-1}; pmr: δ 8.56-8.30 (m, 2H), 7.64-7.25 (m, 8H), 4.75 (br d, 2H), 4.00 ppm (br, 1H); ms: m/e (relative intensity) 369 (M^+, 6), 367 (M^+, 26), 366 (13), 365 (M^+, 14), 364 (M^+, 9), 363 (M^+, 6), 77 (100).

Anal. Calcd. for $C_{18}H_{13}N_3OSe$: C, 59.03; H, 3.58; N, 11.47. Found: C, 58.83; H, 3.61; N, 11.03.

6-Cyano-4,7-diphenyl-1,2,5-selenadiazolo[3,4-*c*]pyridine (**6d**).

This compound was obtained as yellow crystals (benzene), mp 282-284.5°; ir: 2240 cm^{-1}; pmr: δ 8.60-8.42 (m, 2H), 7.85-'7.30 ppm (m, 8H); ms: m/e (relative intensity) 364 (M^+, 5), 282 (100).

Anal. Calcd. for $C_{18}H_{10}N_4Se$: C, 59.84; H, 2.79; N, 15.51. Found: C, 60.10; H, 2.97; N, 15.14.

Preparation of Imidazolopyridine (**8**).

A mixture of **2** and **7a** or **6** was treated under conditions mentioned in Table 9. The mixture was poured into water, made alkaline with sodium bicarbonate, extracted with benzene, and evaporated *in vacuo* to leave the residue. Product **8a**, **8d** and **8e** were obtained on trituration of the residue with ether, and product **8b** and **8f** were isolated through column chromatography using chloroform as an eluent.

4,6,7-Triphenylimidazolo[4,5-*c*]pyridine (**8a**).

This compound was obtained as colorless prisms (benzene-hexane), mp 218-220°; ir: 3400 cm^{-1}; pmr: δ 10.2 (very br, 1H), 8.58-8.30 (br, 2H), 7.60 (s, 1H), 7.52-6.95 ppm (m, 13H); ms: m/e (relative intensity) 347 (M^+, 70), 346 (100).

Anal. Calcd. for $C_{24}H_{17}N_3$: C, 82.97; H, 4.93; N, 12.10. Found: C, 82.84; H, 5.02; N, 12.18.

4,6,7-Triphenyl-2-methylimidazolo[4,5-*c*]pyridine (**8b**).

This compound was obtained as colorless prisms (ethanol), mp 294-295°; ir: 3470 cm^{-1}; pmr: δ 9.3 (very br, 1H, exchange with deuterium oxide), 8.70-8.47 (br, m, 2H), 7.60-7.10 (m, 13H), 3.65 ppm (s, 3H); ms: m/e (relative intensity) 361 (M^+, 60), 360 (100).

Anal. Calcd. for $C_{25}H_{19}N_3$: C, 83.07; H, 5.30; N, 11.63. Found: C, 82.90; H, 5.39; N, 11.81.

Ethyl 4,7-Diphenylimidazolo[4,5-*c*]pyridine-6-carobxylate (**8d**).

This compound was obtained as colorless plates (ethanol-water), mp 151-152.5°; ir: 3380, 1715 cm^{-1}; pmr: δ 10.48 (very br, 1H), 8.66-8.00 (br, 2H), 7.88 ppm (s, 3H); ms: m/e (relative intensity) 343 (M^+, 23), 271 (100), 270 (M^+-CO_2Et, 37).

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 72.95; H, 5.33; N, 11.96.

Reaction of **2a** With Acetic Anhydride.

A mixture of **2a** (0.20 g) and **7c** (2 ml) was treated as described in Table 9 and poured into water (20 ml). After being allowed to stand at room temperature overnight, the mixture was made alkaline by sodium bicarbonate. Precipitates formed were collected by filtration and subjected to column chromatography with chloroform as an eluent to give **8b** (0.04 g) and **9** (0.15 g).

3,4-Di(diacetylamino)-2,5,6-triphenylpyridine (**9**).

This compound was obtained as colorless plates (ethanol), mp 223-225°; ir: 1738, 1728, 1707 cm^{-1}; pmr: δ 7.70-6.90 (m, 15H), 2.16 ppm (s, 12H); ms: m/e (relative intensity) 505 (M^+, 11), 43 (100).

Anal. Calcd. for $C_{31}H_{27}N_3O_4$: C, 73.64; H, 5.38; N, 8.31. Found: C, 73.56; H, 5.43; N, 8.19.

Preparation of **8c**.

An equimolecular mixture of **2a** (0.20 g) and **7d** (0.12 g) was heated at 280° for 1 hour. After being cooled to room temperature, the solid reaction mixture was triturated with benzene to give **8d** (0.12 g).

2,4,6,7-Tetraphenylimidazolo[4,5-*c*]pyridine (**8c**).

This compound was obtained as colorless needles (benzene), mp 287-290°; ir: 3400 cm^{-1}; pmr: δ 9.3 (br, 1H), 8.95-8.73 (br, m, 2H), 8.12-7.94 (m, 2H), 7.96-7.15 (m, 16H); ms: m/e (relative intensity) 423 (M^+, 85), 422 (100).

Anal. Calcd. for $C_{30}H_{21}N_3$: C, 85.08; H, 5.00; N, 9.62. Found: C, 85.27; H, 5.02; N, 10.08.

Preparation of Pyridopyrazine (**11**).

An equimolecular mixture of **2** and **10** in ethanol was heated at reflux for 24 hours and evaporated *in vacuo* to leave the residue which, on column chromatography using benzene as an eluent, afforded **11** in the yields given in Table 10.

2,3-Dimethyl-5,7,8-triphenylpyrido[3,4-*b*]pyridine (**11a**).

This compound was obtained as pale yellow needles (benzene-hexane), mp 258-260°; pmr: δ 8.36-8.10 (m, 2H), 7.56-7.00 (m, 13H), 2.72, 2.65 ppm (each s, 3H); ms: m/e (relative intensity) 387 (M^+, 94), 386 (100).

Anal. Calcd. for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.95; H, 5.41; N, 10.52.

2,3,5,7,8-Pentaphenylpyrido[3,4-*b*]pyridine (**11b**).

This compound was obtained as pale yellow prisms (benzene-hexane), mp 285-286°; pmr: δ 8.48-8.20 (m, 2H), 7.68-7.00 ppm (m, 23H); ms: m/e (relative intensity) 511 (M^+, 100), 510 (72).

Anal. Calcd. for $C_{37}H_{25}N_3$: C, 86.86; H, 4.93; N, 8.21. Found: C, 86.87; H, 4.99; N, 8.14.

8,10,11-Triphenylacenaphtho[1,2,-*b*]pyrido[4,3-*e*]pyridine (**11c**).

This compound was obtained as yellow needles (benzene-hexane), mp 285-287°; pmr: δ 8.47-6.92 ppm (m, 21H); ms: m/e (relative intensity) 483 (M^+, 100), 482 (80).

Anal. Calcd. for $C_{35}H_{21}N_3$: C, 86.93; H, 4.38; N, 8.69. Found: C, 86.89; H, 4.46; N, 8.46.

Ethyl 2,3,5,8-Tetraphenylpyrido[3,4-*b*]pyridine-7-carboxylate (**11d**).

This compound was obtained as pale yellow crystals (ethanol), mp 183-183.5°; pmr: δ 8.38-8.15 (m, 2H), 7.66-7.04 (m, 18H), 4.19 (q, 2H), 1.05 ppm (t, 3H); ms: m/e (relative intensity) 507 (M^+, 49), 435 (100), 434 (M^+-CO_2Et, 49), 432 (56).

Anal. Calcd. for $C_{34}H_{25}N_3O_2$: C, 80.45; H, 4.96; N, 8.28. Found: C, 80.35; H, 4.98; N, 8.21.

7-Hydroxymethyl-2,3,5,8-tetraphenylpyrido[3,4-*b*]pyridine (**11e**).

This compound was obtained as yellow needles (ethanol), mp 203-205°; ir: 3430 cm^{-1}; pmr: δ 8.42-8.20 (m, 2H), 7.65-7.10 (m, 18H), 4.82 (br d, 2H, J = 4 Hz), 4.62 ppm (br d, 1H, J = 4 Hz); ms: m/e (relative intensity) 465 (M^+, 100), 464 (56), 436 (M^+-CHO, 28).

Anal. Calcd. for $C_{32}H_{23}N_3O$: C, 82.56; H, 4.98; N, 9.03. Found: C, 82.44; H, 4.99; N, 8.92.

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