Furopyridines. XXIX [1]. Reactions of Furo[2,3-*b*:4,5-*c*']-, -[3,2-*b*:-4,5-*c*']-, -[2,3-*c*:4,5-*c*']- and -[3,2-*c*:3,2-*c*']dipyridine

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Furo[2,3-*b*:4,5-*c*']- **1a**, -[3,2-*b*:4,5-*c*']- **1b**, -[2,3-*c*:4,5-*c*']- **1c** and -[3,2-*c*:4,5-*c*']dipyridine **1d** were derived to the *N*-oxides **2a-d**, *N'*-oxides **2'b**, **2'c** or *N,N'*-dioxide **3b-d** by *N*-oxidation with *m*-chloroperbenzoic acid. Chlorination of these *N*-oxides, *N'*-oxide and *N,N'*-dioxides with phosphorus oxychloride afforded compounds chlorinated at the α-position(s) to the ring nitrogen **4a-d, 4'c, 14b-d** and **14'b**. Acetoxylation of *N*-oxides **2a-d** and **2'c** with acetic anhydride gave the corresponding pyridone compounds **6a-d** and **6'c** in good yields, while the acetoxylation of *N,N'*-dioxides gave a complex mixture from which no compound could be isolated. Cyanation of **2a-d**, **2'c** and **3b-d** with trimethylsilyl cyanide yielded the cyano compounds **7a-d**, **7'c**, cyano-*N*-oxides **15b-d** and dicyano compounds **15'c** and **15'd**. Monocyano compounds **7a-d** and **7'c** were converted to the imino esters **8a-d** and **8'c** by treatment with sodium ethoxide. Imino esters were derived to the carboxylic esters **9a-d** and **9'c**, from which the corresponding aldehydes **10a-d** and **10'c** were obtained by reduction with diisobutylaluminum hydride. Dicyanide **15'c** was converted to dialdehyde **19** by the treatment with sodium ethoxide, and the subsequent hydrolysis of the imino ester and reduction of the carboxylic ester with diisobutylaluminum hydride.

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In a previous paper we reported the synthesis and some spectral aspects of furo[2,3-*b*:4,5-*c*']- **1a**, -[3,2-*b*:4,5-*c*']- **1b**, -[2,3-*c*:4,5-*c*']- **1c** and -[3,2-*c*:4,5-*c*']dipyridine **1d** [2]. In order to extend the chemistry of furopyridines, we intend to examine the chemical reactivity of these new tricyclic heterocycles. In this paper we report the *N*-oxidation of **1a-d** and chlorination, acetoxylation and cyanation of the *N*-oxides **2a-d** and **2'c** and *N,N'*-dioxides **3b-d**.

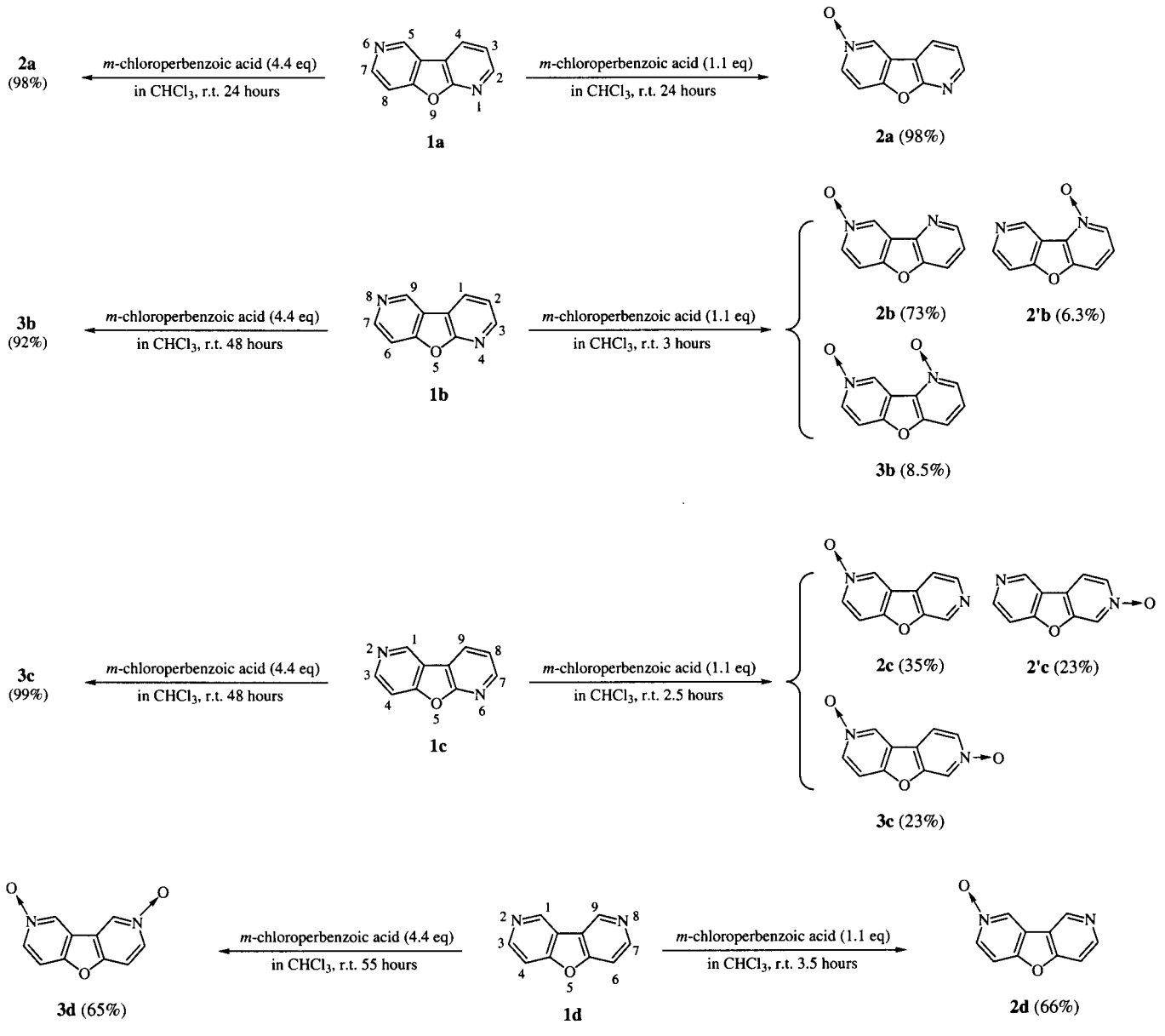
Table I

PMR Spectal Data of Furodipyridines and their *N*-Oxides [a]

	H-2	H-3	H-4	H-5	H-7	H-8
1a [b]	8.49	7.40	8.33	9.20	8.69	7.54
2a	8.60	7.49	8.32	8.90	8.39	7.59
	(J = 1.7, 4.9)	(J = 4.9, 7.8)	(J = 1.7, 7.8)	(J = 0.5, 2.0)	(J = 2.0, 7.1)	(J = 0.5, 7.1)
	(+0.11)	(+0.09)	(-0.01)	(-0.30)	(-0.30)	(+0.05)
	H-2	H-3	H-4	H-9	H-7	H-6
1b [b]	8.63	7.38	7.82	9.44	8.71	7.49
2b	8.75	7.53	7.95	9.10	8.40	7.55
	(J = 1.5, 4.7)	(J = 4.7, 8.5)	(J = 1.5, 8.5)	(J = 0.6, 1.8)	(J = 1.8, 7.3)	(J = 0.6, 7.3)
	(+0.12)	(+0.15)	(+0.13)	(-0.34)	(-0.31)	(+0.06)
2'b	8.34	7.40	7.56	9.86	8.84	7.58
	(J = 1.2, 6.2)	(J = 6.2, 8.5)	(J = 1.2, 8.5)	(J = 1.0)	(J = 5.9)	(J = 1.0, 5.9)
	(-0.29)	(+0.02)	(-0.26)	(+0.42)	(+0.13)	(+0.09)
	H-6	H-8	H-9	H-1	H-3	H-4
1c [b]	9.06	8.69	7.96	9.35	8.79	7.61
2c	9.09	8.72	7.87	8.94	8.43	7.54
	(J = 0.8)	(J = 5.3)	(J = 0.8, 5.3)	(J = 1.8)	(J = 1.8, 7.3)	(J = 7.3)
	(+0.03)	(+0.03)	(-0.09)	(-0.41)	(-0.36)	(-0.07)
2'c	8.69	8.31	7.85	9.26	8.76	7.59
	(J = 1.2)	(J = 1.2, 6.7)	(J = 6.7)	(s)	(J = 5.9)	(J = 5.9)
	(-0.37)	(-0.38)	(-0.11)	(-0.09)	(-0.03)	(-0.02)
	H-6	H-7	H-9	H-1	H-3	H-4
1d [b]	7.58	8.74	9.35	9.35	8.74	7.58
2d	7.59	8.80	9.26	8.93	8.38	7.54
	(J = 0.9, 5.9)	(J = 5.9)	(J = 0.9)	(J = 1.8)	(J = 1.8, 7.0)	(J = 7.0)
	(+0.01)	(+0.06)	(-0.09)	(-0.42)	(-0.36)	(-0.04)

[a] The numerical data in the parentheses are differences between the chemical shifts of protons in furodipyridines and those of the corresponding protons in their *N*-oxides. [b] See reference [2].

Scheme 1



N-Oxidation of compound **1a** with 1.1 or 4.4 molar equivalents of *m*-chloroperbenzoic acid in chloroform afforded the *N*-oxide **2a** in 98% yield. Treatment of **1b** with 1.1 equivalents of *m*-chloroperbenzoic acid gave *N*-oxide **2b** (73%), *N'*-oxide **2'b** (6%) and *N,N'*-dioxide **3b** (8%); treatment with 4.4 equivalents of *m*-chloroperbenzoic acid afforded *N,N'*-dioxide **3b** in 94% yield. The reaction of **1c** with 1.1 equivalents of *m*-chloroperbenzoic acid gave *N*-oxide **2c** (35%), *N'*-oxide **2'c** (23%) and *N,N'*-dioxide **3c** (23%); the same reaction with 4.4 equivalents of *m*-chloroperbezoic acid gave *N,N'*-dioxide **3c** (99%). *N*-Oxidation of **1d** with 1.1 equivalents of *m*-chloroperbenzoic acid gave *N*-oxide **2d** (66%), and the reaction with 4.4 equivalents of *m*-chloroperbenzoic acid gave *N,N'*-dioxide **3d** (65%). These results apparently reflect the base strength of both ring nitrogen atoms in each furodipyridine [2]; the more basic one is more easily *N*-oxidized. The pmr spectral data for these *N*-oxides of furodipyridines are recorded in Table I for comparison with the data of the parent furodipyridines [2]. All of the signals are clearly distinguishable and were easily assigned from their chemical shift values, coupling patterns and constants in comparison with those of the parent furodipyridines [2]. Determination of the positions of the *N*-oxidized nitrogen atom in **2a-d** and **2'c** was based on the fact that the pmr signal of the proton at α- or γ-position to the *N*-oxidized nitrogen is found at higher field than that of the parent pyridine [3], quinoline [3] and furopyridines [2]. Signal for H-9 for **2'b** falls espe-

cially far downfield because the proton occupies an angular position [2,4] in the phene-type structure and is affected by the anisotropic effect of the *N*-oxide oxygen.

Treatment of the *N*-oxides **2a-d** and **2'c** with phosphorus oxychloride in absolute chloroform under reflux afforded the corresponding α-chloropyridine derivatives **4a** (95%), **4b** (85%), **4c** (85%), **4'c** (85%) and **4d** (82%). Compounds **4a-d** were identified by comparison of the ir and pmr spectra of each compound with those of an authentic sample which is the intermediate for the synthesis of each furodipyridine [2]. The pmr spectrum of **4'c** showed two pairs of doublets at δ 8.84 (J = 5.9 Hz) and 7.68 (J = 5.9, 0.9 Hz) and at δ 8.46 (J = 5.0 Hz) and 7.91 (J = 5.0 Hz) and a doublet at δ 9.35 (J = 0.9 Hz) indicating the position of the chlorine atom in **4'c** to be the 6-position. When the chlorination of compounds **2a** and **2b** were carried out in commercial chloroform containing about 1% of ethanol, the *N*-ethylpyridone derivatives **5a** (25%) and **5b** (31%) were obtained besides the formation of the α-chloro compounds **4a** (73%) and **4b**

Scheme 2

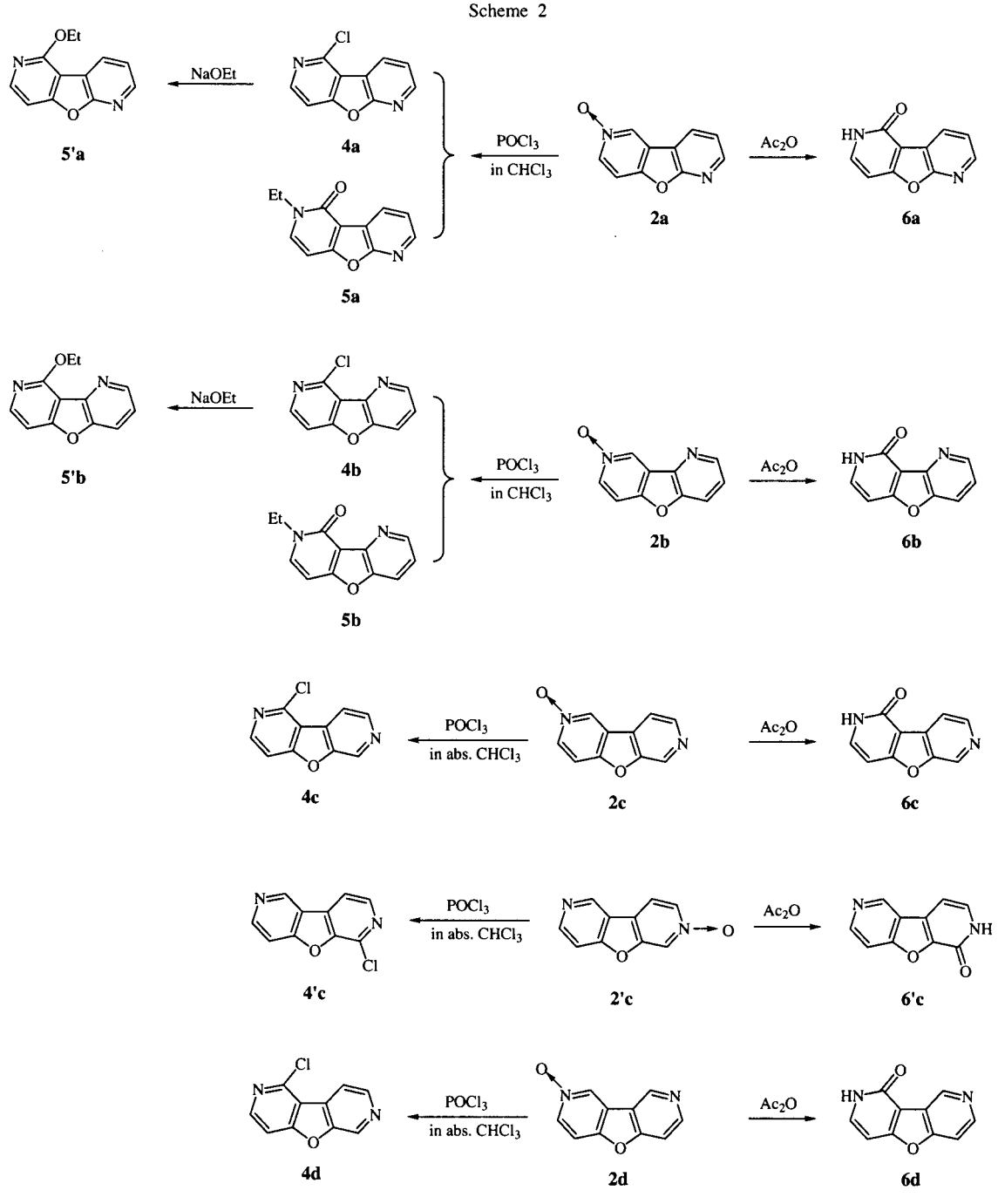
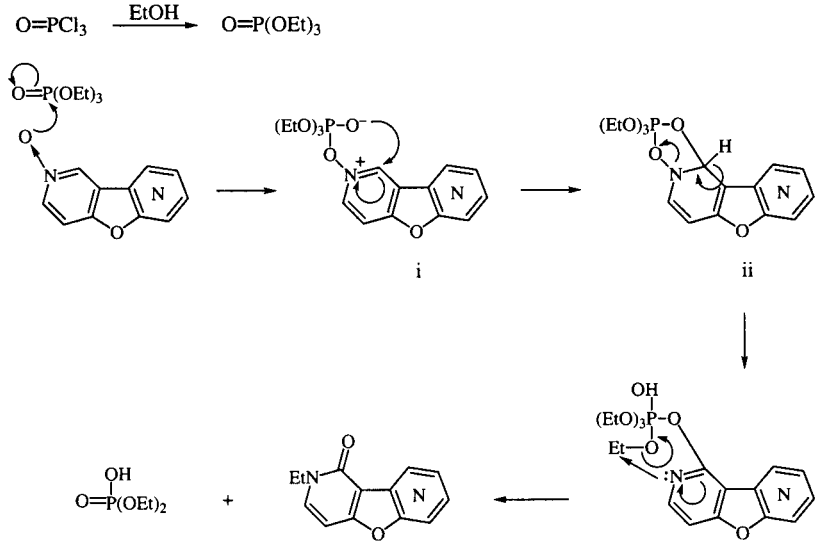


Chart 1



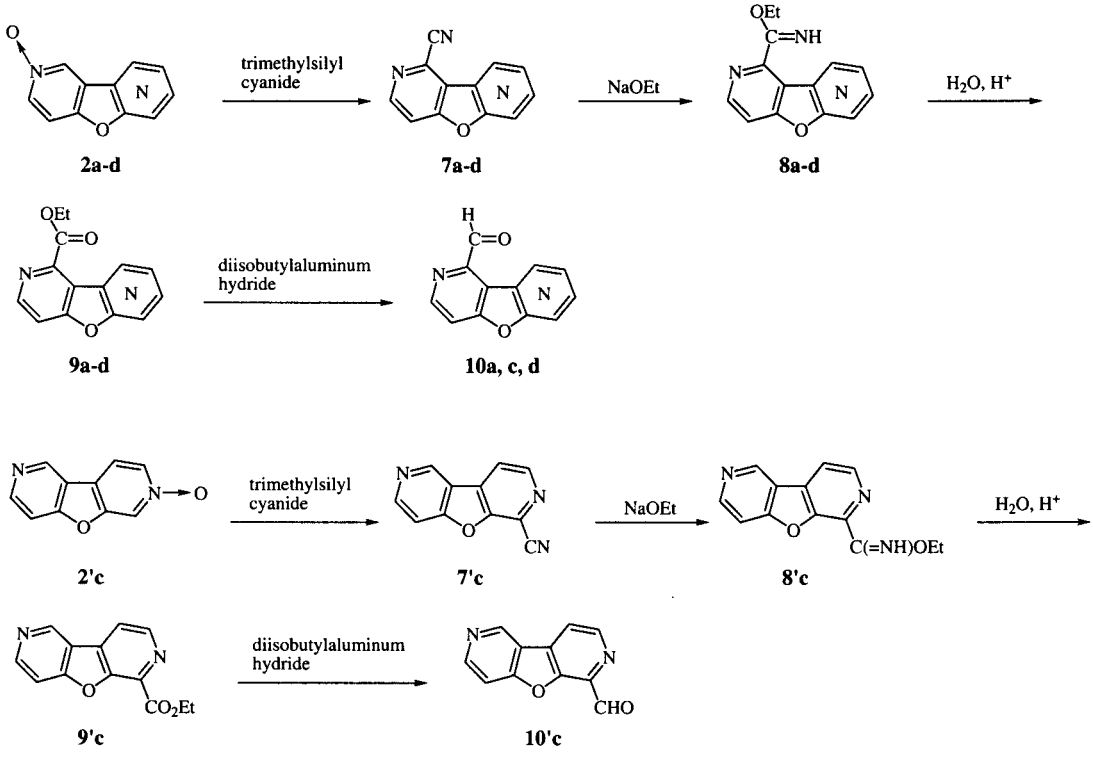
(34%). The α-chloro compounds **4a** and **4b** were converted to the corresponding α-ethoxy derivatives **5'a** and **5'b**. The reaction course for the formation of the *N*-ethylpyridone compound can be interpreted as follows: Ethanol in commercial chloroform reacts with phosphorus oxychloride to give triethyl phosphate (or its equivalent). The phosphate attacks the *N*-oxide oxygen to form an intermediate **i**, attack of the negatively charged oxygen on the phosphate part at the α-position would give the cyclic intermediate **ii**, from which the *N*-ethylpyridone would be formed through electron transfer as shown in Chart 1.

Refluxing of the *N*-oxides **2a-d** and **2'c** with acetic anhydride yielded the pyridone compound **6a** (54%), **6b** (47%), **6c** (98%), **6'c** (81%) and **6d** (56%) respectively, while the same treatment of *N,N'*-dioxides **3b**, **3c** and **3d** did not give any compound isolable by column chromatography on silica gel. Compounds **6a-d** were identified with the corresponding pyridones prepared previously in our laboratory by mixed melting point test. The structure of **6'c** was confirmed from its pmr spectrum showing two pairs of doublets at δ 8.72 and 7.83 (J = 6.1 Hz) and at δ 7.48 and 7.17 (J = 7.0 Hz) and a singlet at δ 9.34.

Cyanation of the *N*-oxides **2a-d** and **2'c** with trimethylsilyl cyanide afforded α-cyanopyridine derivative **7a** (96%), **7b** (96%), **7c** (99%), **7'c** (91%) and **7d** (99%). The positions of the cyano group in **7a-d** and **7'c** were confirmed from their pmr spectra in which the signal (doublet or double doublet split by a small coupling constant) of the proton at the α-position to the *N*-oxidized ring nitrogen shown in the spectrum of each *N*-oxide **2a-d** and **2'c** disappeared. The cyano compounds were converted to the corresponding imino esters **8a** (85%), **8b** (87%), **8c** (93%), **8'c** (99%) and **8d** (85%) with sodium ethoxide, from which ethyl esters **9a** (98%), **9b** (83%), **9c** (93%), **9'c** (99%) and **10d** (99%) were obtained by treatment with hydrohloric acid in ethanol. Reduction of the esters with diisobutylaluminium hydride yielded the corresponding aldehyde **10a** (88%), **10c** (77%), **10'c** (58%) and **10d** (64%), except for ester **9b** from which the corresponding aldehyde could not be obtained. The cyano compounds **7a** and **7b** were converted to the acetyl derivatives **11a** and **11b** by the Grignard reaction with methylmagnesium bromide in yields of 90% and 95% respectively. Condensation of the aldehyde **10a** with nitromethane afforded the nitroethanol compounds **12** (98%). The aldehydes was also converted to the methyl acrylate compound **13** (88%) by the Wittig-Horner reaction with methyl diethylphosphonoacetate.

The *N,N'*-dioxide **3b** afforded the α,α'-dichlorofurodipyridine compound **14b** (46%) and α,γ-dichloro derivative **14'b** (32%), and **3c** and **3d** gave the α,α'-dichloro compound **14c** (82%) and **14d** (56%) by refluxing with phosphorus oxychloride. These dichloro derivatives exhibited, in the pmr spectra, two pairs of doublet respectively at δ 8.54 and 7.54 (J = 5.9 Hz) and δ 7.91 and 7.51 (J = 8.8 Hz) for **14b**, at δ 8.74 and 7.54 (J = 5.3 Hz) and δ 8.58 and 7.62 (J = 5.9 Hz) for **14'b**, and at δ 8.61 and 7.65 (J = 5.6 Hz) and δ 8.52 and 8.15 (J = 5.0 Hz) for **14c**, and a pair of doublets at δ 8.54 and 7.55 (J = 5.6 Hz) for **14d**. Cyanation of the *N,N'*-dioxides **3b**, **3c** and **3d** afforded 9-cyanofuro[3,2-*b*:4,5-*c*']dipyridine 1-oxide **15b** (97%), 1-cyanofuro[2,3-*c*:4,5-*c*']dipyridine 7-oxide **15c** (31%) and 1,6-dicyanofuro[2,3-*c*:4,5-*c*']dipyridine **15'c** (55%), and 1-cyanofuro[3,2-*c*:4,5-*c*']dipyridine 8-oxide **15d** (20%)

Scheme 3

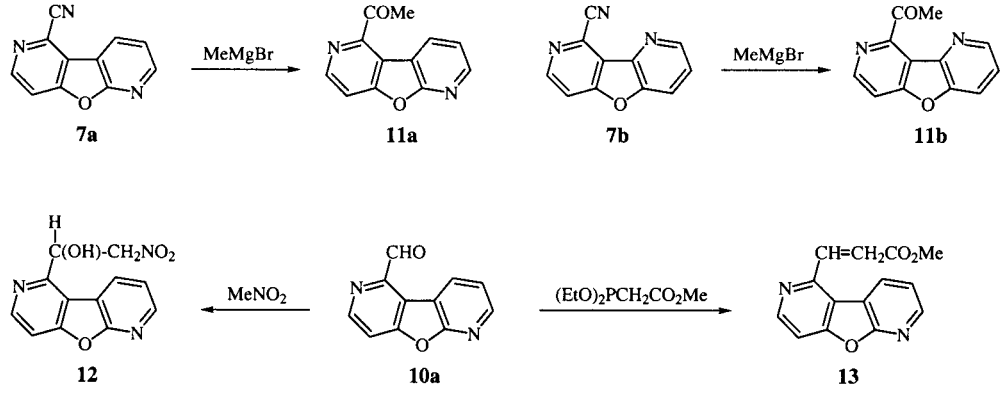


and 1,9-dicyanofuro[3,2-*c*:4,5-*c*']dipyridine **15'd** (47%) respectively. The monocyano *N*-oxide **15b** was allowed to react with methylmagnesium bromide to give 9-acetylfuro[3,2-*b*:4,5-*c*']dipyridine1-oxide **16** (47%) and 9-acetyl-2-methylfuro[3,2-*b*;4,5-*c*']dipyridine **16'** (16%). The pmr spectrum of **16** showed signals of five pyridine protons at δ 8.78 (J = 5.6 Hz), 8.26 (J = 1.5, 5.9 Hz), 7.61 (J = 5.6 Hz), 7.52 (J = 1.5, 8.2 Hz) and 7.43 (J = 5.9, 8.2 Hz) and methyl protons at δ 2.86 (s), and that of **16'** four pyridine protons at δ 8.74 (J = 5.6 Hz), 7.81 (J = 8.5 Hz), 7.68 (J = 5.6 Hz) and 7.35 (J = 8.5 Hz) and methyl protons at δ 2.96 (s) and 2.80 (s). The dicyano compound **15'c** was converted to the diethyl ester **18** by treatment with sodium ethoxide and subsequent hydrolysis with hydrochloric acid in aqueous ethanol.

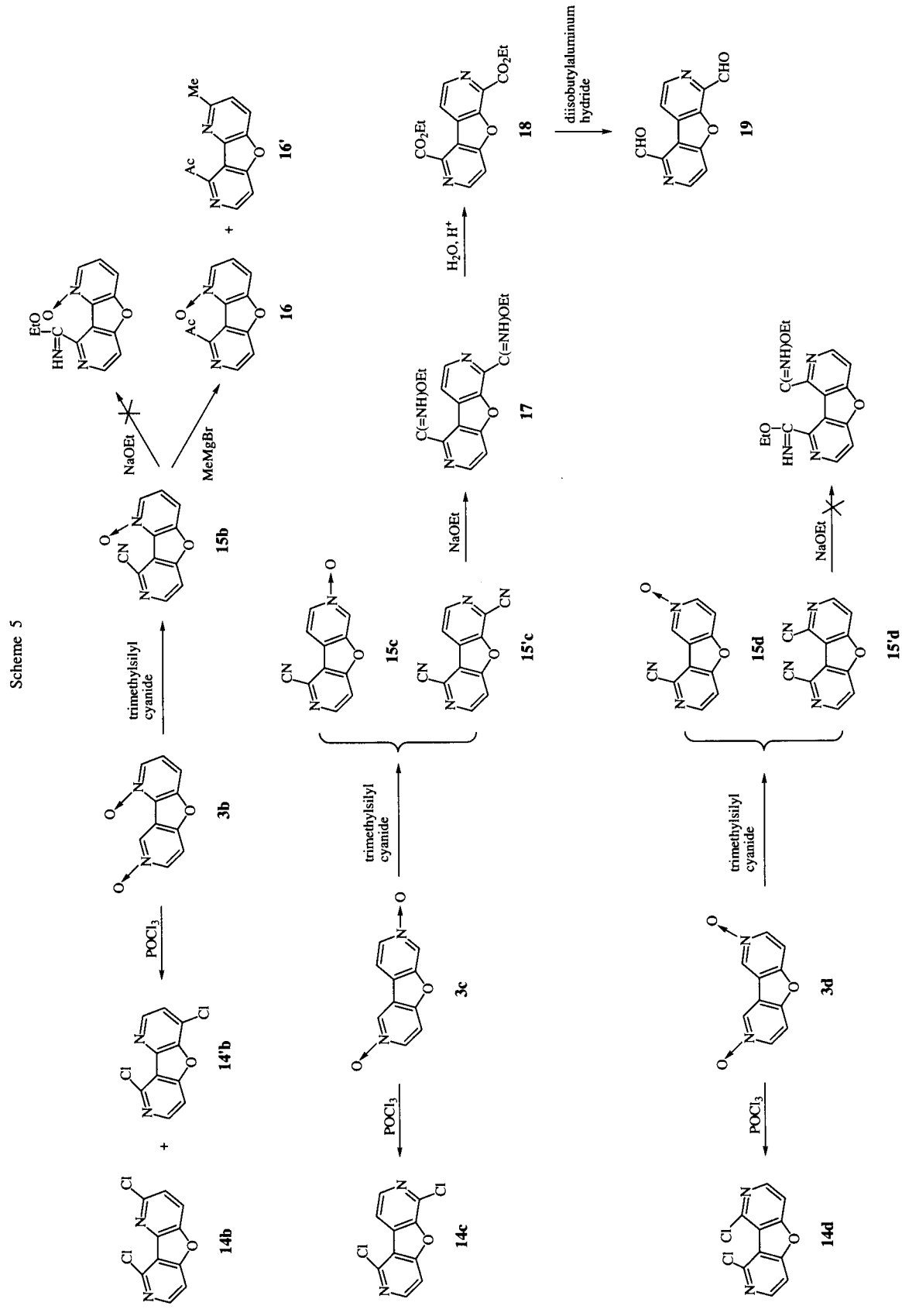
Reduction **18** with diisobutylaluminium hydride afforded dialdehyde **19**. The same reaction of compound **15b** and **15'd** with sodium ethoxide did not give the imino ester but a complex mixture of products from which no compound could be isolated from the mixture.

From the results described above, it can be concluded that the reactivities of the *N*-oxides of furodipyridines and their derivatives resemble those of the *N*-oxides of pyridine and furopyridines.

Scheme 4



Scheme 5


trimethylsilyl cyanide
POCl3
NaOEt
MeMgBr
H2O, H+
diisobutylaluminum hydride
3b
14'b
14b
15b
16
16'
3c
14c
15c
15'c
17
18
19
3d
14d
15d
15'd

EXPERIMENTAL

Melting points were determined by using a Yanagimoto micro melting point apparatus and are uncorrected. The ir spectra were recorded on a JASCO FT/IR 7300 spectrometer. The pmr spectra were recorded on a JEOL MAC-FX (90 MHz) and/or JEOL FX-A400 (400 MHz) spectrometer. The mass spectra were taken by using JEOL JMS-OISG-2 instrument. Column chromatography was performed with silica gel (Chromatography Silica Gel, BW-820MH, Fuji Silysia Chemical Ltd) or alumina (MercK, Aluminium Oxide 90 active, neutral).

General Procedure for the *N*-Oxidation of Furodipyridine **1a**, **1b**, **1c** and **1d** with 1.1 Molar Equivalents of *m*-Chloroperbenzoic Acid.

A mixture of furodipyridine **1a**, **1b**, **1c** or **1d** (1.0 g, 5.9 mmoles) and *m*-chloroperbenzoic acid (1.59 g, 70% purity, 6.45 mmoles) in chloroform (160 ml) was stirred at room temperature for 24 hours for **1a**, 3 hours for **1b**, 2.5 hours for **1c** and 3.5 hours for **1d**. The mixture was filtered slowly through a sintered glass filter with an alumina (Merck, Aluminium Oxide G II, basic, 50 g) pad, and the filtrate was evaporated. Further processing of the residual mass is indicated in a subsequent paragraph.

Furo[2,3-*b*:4.5-*c*']dipyridine 6-Oxide **2a**.

The residual crystalline mass from **1a** was recrystallized from acetone-methanol to give 1.07 g (98%) of **2a**, mp 253-257° (colorless crystals); ir (potassium bromide): 3048, 3012, 2925, 7589, 1470, 1446, 1400, 1314, 1204, 1166, 1112, 1025, 867, 830, 774 cm^{-1}.

Anal. Calcd. for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.78; H, 3.35; N, 15.07.

The crystalline mass from **1b** was chromatographed on an alumina (150 g) column eluting with chloroform-methanol (99:1) to give furo[3,2-*b*:4,5-*c*']dipyridine 8-oxide **2b** (840 mg, 73%), furo[3,2-*b*: 4,5-*c*']dipyridine 1-oxide **2'b** (66 mg, 6%) and furo[3,2-*b*:4,5-*c*']dipyridine 1,8-dioxide **3b** (95 mg, 8%).

Furo[3,2-*b*:4,5-*c*']dipyridine 8-Oxide **2b**.

This compound had mp 245-248° (from acetone-ether, colorless crystals); ir (potassium bromide): 3103, 3057, 3036, 2961, 1602, 1581, 1446, 1403, 1296, 1263, 1224, 1208, 1165, 1102, 1050, 871, 854, 827, 809, 779, 741 cm^{-1}.

Anal. Calcd. for $C_{10}H_6N_2O_2 \cdot 1/2H_2O$: C, 61.54; H, 3.61; N, 14.35. Found: C, 61.34; H, 3.70; N, 14.25.

Furo[3,2-*b*:4,5-*c*']dipyridine 1-Oxide **2'b**.

This compound had mp 231-232° (from acetone-ether, colorless crystals); ir (potassium bromide): 3120, 3083, 2924, 1592, 1562, 1462, 1428, 1416, 1337, 1278, 1264, 1239, 1222, 1212, 1160, 1046, 1000, 861, 815, 785, 766, 720 cm^{-1}.

Anal. Calcd. for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.39; H, 3.43; N, 14.87.

Furo[3,2-*b*:4,5-*c*']dipyridine 1,8-Dioxide **3b**.

This compound had mp 298-302° (from acetone-methanol, colorless crystals); ir (potassium bromide): 3142, 3112, 3044, 3014, 1584, 1497, 1465, 1444, 1429, 1293, 1278, 1256, 1172, 1055, 1020, 976, 853, 837, 804, 745, 722 cm^{-1}; pmr (deuteriochloroform): δ 9.43 (dd, J = 0.6, 1.8 Hz, 1H, H-9), 8.43 (dd, J = 1.8, 7.0 Hz, 1H, H-7), 8.31 (dd, J = 2.1, 5.3 Hz, 1H, H-2), 7.60-7.46 (m, 3H, H-3, H-4 and H-6).

Anal. Calcd. for $C_{10}H_6N_2O_3$: C, 59.41; H, 2.99; N, 13.86. Found: C, 59.62; H, 3.09; N, 13.89.

The crystalline mass from **1c** was chromatographed on an alumina (150 g) column eluting with chloroform-methanol (97:3) to afford the starting **1c** (140 mg, 14%), furo[2,3-*c*:4,5-*c*']dipyridine 2-oxide **2c** (380 mg, 35%), furo[2,3-*c*:4,5-*c*']dipyridine 7-oxide **2'c** (240 mg, 23%) and furo[2,3-*c*:4,5-*c*']dipyridine 2,7-dioxide **3c** (270 mg, 23%).

Furo[2,3-*c*:4,5-*c*']-dipyridine 2-Oxide **2c**.

This compound had mp 263-265° (from acetone-methanol, colorless crystals); ir (potassium bromide): 3104, 3045, 1634, 1501, 1579, 1452, 1426, 1294, 1237, 1222, 1209, 1182, 1153, 1024, 922, 843, 833, 747 cm^{-1}.

Anal. Calcd. for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.56; H, 3.28; N, 14.85.

Furo[2,3-*c*:4,5-*c*']dipyridine 7-Oxide **2'c**.

This compound had mp 204-206.5° (from acetone-ether, colorless crystals); ir (potassium bromide): 3103, 3030, 1600, 1488, 1565, 1479, 1454, 1426, 1328, 1291, 1261, 1201, 1151, 1134, 1043, 976, 865, 838, 767 cm^{-1}.

Anal. Calcd. for $C_{10}H_6N_2O_2 \cdot H_2O$: C, 58.82; H, 4.33; N, 13.72. Found: C, 58.62; H, 4.03; N, 13.33.

Furo[2,3-*c*:4,5-*c*']dipyridine 2,7-Dioxide **3c**.

This compound had mp >300° (from acetone-methanol, pale yellow crystals); ir (potassium bromide): 3116, 3037, 1639, 1489, 1468, 1447, 1297, 1290, 1250, 1231, 1212, 1149, 1108, 1032, 977, 919, 875, 835, 754 cm^{-1}; pmr (deuteriomethanol): δ 9.27 (d, J = 2.0 Hz, 1H, H-1), 9.01 (d, J = 1.5 Hz, 1H, H-6), 8.53 (dd, J = 2.0, 7.3 Hz, 1H, H-3), 8.43 (dd, J = 1.5, 6.8 Hz, 1H, H-8), 8.27 (d, J = 6.8 Hz, 1H, H-9), 7.95 (d, J = 7.3 Hz, 1H, H-4).

Anal. Calcd. for $C_{10}H_6N_2O_3 \cdot 1/5H_2O$: C, 58.37; H, 3.13; N 13.61. Found: C, 58.75; H, 3.04; N, 13.49.

Furo[3,2-*c*:4,5-*c*']dipyridine 2-Oxide **2d**.

The solid mass from **1d** was recrystallized from acetone-methanol to give compound **2d** (720 mg, 66%) as colorless crystals of mp 245-247°; ir (potassium bromide): 3061, 1581, 1469, 1444, 1425, 1295, 1275, 1244, 1231, 1203, 1188, 1154, 1043, 1019, 913, 856, 841, 818, 752 cm^{-1}.

Anal. Calcd. for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.24; H, 3.34; N, 14.98.

General Procedure for the *N*-Oxidation of Furodipyridines **1a**, **1b**, **1c** and **1d** with 4.4 Molar Equivalents of *m*-Chloroperbenzoic Acid.

A mixture of furodipyridine **1a**, **1b**, **1c** or **1d** (430 mg, 2.5 mmoles) and *m*-chloroperbenzoic acid (2.75 g, 70% purity, 11.1 mmoles) in chloroform (90 ml) was stirred at room temperature for 24 hours for **1a**, 48 hours for **1b** and **1c** and 55 hours for **1d**. The mixture was filtered slowly through a sintered glass filter with an alumina (Merck, Aluminium Oxide G II, basic, 50 g) pad, and the filtrate was evaporated. The residue from the filtrate was recrystallized from acetone-methanol to yield the mono *N*-oxide **2a** (460 mg, 98%) from **1a** and *N,N'*-dioxide **3b** (470 mg, 92%), **3c** (505 mg, 99%) and **3d** (340 mg, 65%).

Furo[3,2-*c*:4,5-*c*']pyridine 2.8-Dioxide **3d**.

This compound had mp >300° (colorless crystals); ir (potassium bromide): 3076, 3048, 1684, 1468, 1448, 1293, 1231, 1182, 1138, 1125, 1037, 962, 925, 850, 820, 741 cm^{-1}; pmr

(deuteriomethanol): δ 9.31 (d, J = 1.8 Hz, 2H, H-1 and H-9), 8.50 (dd, J = 1.8, 7.3 Hz, 2H, H-3 and H-7), 7.96 (d, J = 7.3 Hz, 2H, H-4 and H-6).

Anal. Calcd. for $C_{10}H_6N_2O_3$: C, 59.42; H, 2.99; N, 13.86. Found: C, 59.19; H, 3.05; N, 13.60.

General Procedure for the Chlorination of Mono *N*-Oxides **2a**, **2b**, **2c**, **2'c** and **2d** with Phosphorus Oxychloride.

a) A solution of **2a**, **2b**, **2c**, **2'c** or **2d** (30 mg, 0.16 mmole) and phosphorus oxychloride (1.5 g, 9.8 mmoles) in absolute chloroform (1 ml) was refluxed for 5 hours. After being cooled, the mixture was treated with ice-water, basified with aqueous ammonia and extracted with chloroform. The chloroform layer was dried over magnesium sulfate and evaporated to leave a solid mass. Recrystallization of the residue from ether gave pure samples of chloro compounds **4a** (25 mg, 76%), **4b** (28 mg, 85%), **4c** (28 mg, 85%), **4'c** (30 mg, 86%) and **4d** (27 mg, 82%). Compounds **4a**, **4b**, **4c** and **4d** were identified by comparison of the ir and pmr spectra with those of an authentic sample prepared previously in our laboratory [2].

6-Chlorofuro[2,3-*c*:4,5-*c*']dipyridine **4'c**.

This compound had mp 178-180° (colorless needles); ir (potassium bromide): 3075, 1629, 1564, 1460, 1429, 1404, 1326, 1261, 1219, 1204, 1182, 1170, 1077, 1018, 881, 837, 826, 707 cm^{-1}; pmr (deuteriochloroform): δ 9.35 (d, J = 0.9 Hz, 1H, H-1), 8.84 (d, J = 5.9 Hz, 1H, H-3), 8.46 (d, J = 5.0 Hz, 1H, H-8), 7.91 (d, J = 5.0 Hz, 1H, H-9), 7.68 (dd, J = 0.9, 5.9 Hz, 1H, H-4).

Anal. Calcd. for $C_{10}H_5N_2OCl$: C, 58.70; H, 2.46; N, 13.69. Found: C, 58.62; H, 2.55; N, 13.59.

b) A solution of **2a** or **2b** (30 mg, 0.16 mmole) and phosphorus oxychloride (1.5 g, 9.8 mmoles) in chloroform (commercial grade, 1 ml) was refluxed for 5 hours. After being cooled, the mixture was treated with ice-water, basified with sodium bicarbonate and extracted with chloroform. The chloroform extract was dried over magnesium sulfate and evaorated to leave a solid mass. The residue from **2a** was chromatographed on a silica gel (10 g) column eluting with chloroform-methanol (99:1) to give chloro compound **4a** (24 mg, 73%) and *N*-ethylpyridone compound **5a** (8.6 mg, 25%). The residue from **2b** was chromatographed on a silica gel (7 g) column eluting with chloroform to give chloro compound **4b** (11 mg, 34%) and *N*-ethylpyridone compound **5b** (10.7 mg, 31%).

6-Ethylfuro[2,3-*b*:4,5-*c*']dipyridine-5(6*H*)-one **5a**.

This compound had mp 164-166° (from acetone-ether, colorless crystals); ir (potassium bromide): 3081, 2926, 2856, 1668, 1589, 1554, 1387, 1361, 1188, 1138, 1112, 808, 765 cm^{-1}; pmr (deuteriochloroform): δ 8.51 (d, J = 7.6 Hz, 1H, H-2), 8.39 (d, J = 4.4 Hz, 1H, H-4), 7.49 (d, J = 7.3 Hz, 1H, H-7), 7.35 (dd, J = 4.4, 7.6 Hz, 1H, H-3), 6.70 (d, J = 7.3 Hz, 1H, H-8), 4.18 (q, J = 7.1 Hz, 2H, -CH_2-CH_3), 1.44 (t, J = 7.1 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.37; H, 4.88; N, 12.98.

8-Ethylfuro[3,2-*b*:4,5-*c*']dipyridine-9(8*H*)-one **5b**.

This compound had mp 151-154° (from acetone-ether, colorless crystals); ir (potassium bromide): 3066, 2925, 2854, 1652, 1616, 1585, 1557, 1458, 1424, 1395, 1361, 1242, 1199, 1136, 797 cm^{-1}; pmr (deuteriochloroform): δ 8.72 (dd, J = 1.2, 4.7 Hz, 1H, H-2), 7.49 (dd, J = 1.2, 8.2 Hz, 1H, H-4), 7.50 (d, J = 7.3 Hz, 1H, H-7), 7.29 (dd, J = 4.7, 8.2 Hz, 1H, H-3), 6.60 (d, J = 7.3 Hz, 1H, H-6), 4.18 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.43 (t, J = 7.0 Hz, 3H, -CH_2-CH_3)

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.42; H, 4.87; N, 13.01.

Preparation of 5-Ethoxyfuro[2,3-*b*:4,5-*c*']dipyridine **5'a** and 9-Ethoxyfuro[3,2-*b*:4,5-*c*']dipyridine **5'b**.

A mixture of **4a** or **4b** (20 mg, 0.1 mmole) and sodium ethoxide (70 mg, 1.0 mmole) in ethanol (2 ml) was refluxed for 2 hours under nitrogen atmosphere. After evaporation of the solvent, the solid residue was treated with water and chloroform. The chloroform layer was dried over magnesium sulfate and evaporated. Recrystallization of the crystalline residue from hexane gave compound **5'a** or **5'b**.

5-Ethoxyfuro[2,3-*b*:4,5-*c*']dipyridine **5'a**.

This compound had mp 123-125° (colorless crystals); ir (potassium bromide): 3077, 3025, 2984, 2971, 2928, 2866, 1602, 1584, 1460, 1440, 1396, 1336, 1227, 1117, 1089, 1079, 1047, 856, 837, 802, 779, 764 cm^{-1}; pmr (deuteriochloroform): δ 8.43 (dd, J = 1.5, 5.0 Hz, 1H, H-2), 8.34 (dd, J = 1.5, 7.6 Hz, 1H, H-4), 8.22 (d, J = 5.9 Hz, 1H, H-7), 7.38 (dd, J = 5.0, 7.6 Hz, 1H, H-3), 7.20 (d, J = 5.9 Hz, 1H, H-8), 4.64 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.54 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.47; H, 4.73; N, 12.96.

9-Ethoxyfuro[3,2-*b*:4,5-*c*']dipyridine **5'b**.

This compound had mp 85-88° (colorless crystals); ir (potassium bromide): 3052, 3015, 2976, 2929, 2902, 2869, 1625, 1599, 1465, 1453, 1405, 1386, 1339, 1259, 1235, 1178, 1083, 787, 741 cm^{-1}; pmr (deuteriochloroform): δ 8.76 (dd, J = 1.2, 5.0 Hz, 1H, H-2), 8.25 (d, J = 5.9 Hz, 1H, H-7), 7.84 (dd, J = 1.2, 8.2 Hz, 1H, H-4), 7.36 (dd, J = 5.0, 8.2 Hz, 1H, H-3), 7.17 (d, J = 5.9 Hz, 1H, H-6), 4.78 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.50 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.52; H, 4.76; N, 13.02.

General Procedure for the Acetoxylation of Compound **2a**, **2b**, **2c**, **2'c** and **2d** with Acetic Anhydride.

A mixture of compound **2a**, **2b**, **2c**, **2'c** or **2d** (40 mg, 0.22 mmole) in acetic anhydride (3 ml) was refluxed for 17 hours. After evaporation of the excess acetic anhydride, the residual syrup was treated with water, basified with sodium bicarbonate and extracted with chloroform. The chloroform extract was dried over magnesium sulfate and evaporated to leave a solid mass, which was recrystallized from methanol to give pyridone compound **6a** (22 mg, 55%, mp 302-307°, literature: mp 307-308° [2]), **6b** (19 mg, 47%, mp >320°, literature: mp >320° [2]), **6c** (39 mg, 98%, mp >320°; literature: mp >320° [2]), **6'c** (33 mg, 81%), **6d** (22 mg, 56%, mp >320°, literature: mp >320° [2]).

Furo[2,3-*c*:4,5-*c*']dipyridine-6(7*H*)-one **6'c**.

This compound had mp >320° (colorless crystals); ir (potassium bromide): 3200-2500 (broad), 3104, 3045, 2996, 1675, 1620, 1580, 1490, 1429, 1318, 1289, 1251, 1220, 1178, 1164, 956, 863, 831, 821, 784, 755 cm^{-1}; pmr (deuteriomethanol): δ 9.34 (s, 1H, H-1), 8.72 (d, J = 6.0 Hz, 1H, H-3), 7.83 (d, J = 6.0 Hz, 1H, H-4), 7.48 (d, J = 7.0 Hz, 1H, H-8), 7.17 (d, J = 7.0 Hz, 1H, H-9).

Anal. Calcd. for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.47; H, 3.29; N, 14.91.

General Procedure for the Cyanation of **2a**, **2b**, **2c**, **2'c** and **2d** with Trimethylsilyl Cyanide.

A mixture of **2a**, **2b**, **2c**, **2'c** or **2d** (103 mg, 0.55 mmole), triethylamine (84 mg, 0.83 mmole) and trimethylsilyl cyanide (192 mg, 1.94 mmole) in acetonitrile (6 ml) was stirred and refluxed under nitrogen atmosphere for 5.5 hours for **2a** and **2b**, 3.5 hours for **2c** and **2d**, and 24 hours for **2'c**. After evaporation of the solvent, the residue was treated with water and chloroform. The chloroform layer was dried over magnesium sulfate and evaporated to yield a solid mass, which was recrystallized from appropriate solvent to give a pure sample of **7a** (104 mg, 96%), **7b** (105 mg, 96%), **7c** (107 mg, 99%), **7'c** (98 mg, 91%), **7d** (107 mg, 99%).

5-Cyanofuro[2,3-*b*:1,5-*c*']dipyridine **7a**.

This compound had mp 167-169° (from hexane-ether, colorless crystals); ir (potassium bromide): 3055, 3023, 2361 (CN), 1588, 1397, 1253, 1217, 1178, 1005, 887, 810, 780 cm^{-1}; pmr (deuteriochloroform): δ 8.83 (d, J = 5.9 Hz, 1H, H-7), 8.75 (dd, J = 1.8, 7.6 Hz, 1H, H-2), 8.67 (dd, J = 1.8, 5.0 Hz, 1H, H-4), 7.83 (d, J = 5.9 Hz, 1H, H-8), 7.59 (dd, J = 5.0, 7.6 Hz, 1H, H-3).

Anal. Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.58; N, 21.53. Found: C, 68.05; H, 2.82; N, 21.39.

9-Cyanofuro[3,2-*b*:4,5-*c*']dipyridine **7b**.

This compound had mp 228-230° (from acetone-ether, colorless crystals); ir (potassium bromide): 3067, 3052, 2230, 1625, 1586, 1569, 1427, 1399, 1266, 1243, 1178, 1111, 1019, 997, 854, 807, 798 cm^{-1}; pmr (deuteriochloroform): δ 8.91 (dd, J = 1.5, 4.7 Hz, 1H, H-2), 8.85 (d, J = 5.9 Hz, 1H, H-7), 8.00 (dd, J = 1.5, 8.8 Hz, 1H, H-4), 7.80 (d, J = 5.9 Hz, 1H, H-6), 7.59 (dd, J = 4.7, 8.8 Hz, 1H, H-3).

Anal. Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.58; N, 21.53. Found: C, 68.81; H, 2.92; N, 21.15.

1-Cyanofuro[2,3-*c*:4,5-*c*']dipyridine **7c**.

This compound had mp 179-180° (from acetone-ether, colorless crystals); ir (potassium bromide): 3084, 3069, 2992, 2233, 1626, 1569, 1418, 1325, 1268, 1257, 1239, 1184, 1165, 1037, 998, 851, 841, 810 cm^{-1}; pmr (deuteriochloroform): δ 9.18 (d, J = 1.0 Hz, 1H, H-6), 8.90 (d, J = 5.6 Hz, 1H, H-3), 8.84 (d, J = 5.1 Hz, 1H, H-8), 8.33 (dd, J = 1.0, 5.1 Hz, 1H, H-9), 7.85 (d, J = 5.6 Hz, 1H, H-4).

Anal. Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.58; N, 21.53. Found: C, 67.42; H, 2.72; N, 21.29.

6-Cyanofuro[2,3-*c*:4,5-*c*']dipyridine **7'c**.

This compound had mp 191-193° (from acetone-ether, colorless crystals); ir (potassium bromide): 3064, 3044, 2237 (CN), 1630, 1571, 1458, 1440, 1407, 1266, 1209, 1159, 1101, 1072, 1028, 905, 858, 849, 837, 722 cm^{-1}; pmr (deuteriochloroform): δ 9.43 (d, J = 0.6 Hz, 1H, H-1), 8.91 (d, J =5.9 Hz, 1H, H-3), 8.80 (d, J = 5.0 Hz, 1H, H-8), 8.21 (d, J = 5.0 Hz, 1H, H-9), 7.74 (dd, J = 0.6, 5.9 Hz, 1H, H-4).

Anal. Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.58; N, 21.53. Found: C, 67.43; H, 2.58; N, 21.22.

1-Cyanofuro[3,2-*c*:4,5-*c*']dipyridine **7d**.

This compound had mp 189-193° (from acetone, colorless crystals); ir (potassium bromide): 3104, 3055, 3016, 2988, 2230 (CN), 1631, 1585, 1566, 1467, 1436, 1407, 1328, 1291, 1255, 1242, 1203, 1161, 1036, 1003, 859, 832, 807, 751 cm^{-1}; pmr (deuteriochloroform): δ 9.68 (s, H, H-9), 8.89 (d, J = 5.6, 1H, H-7), 8.84 (d, J = 5.6 Hz, 1H, H-3), 7.82 (d, J = 5.6 Hz, 1H, H-4), 7.68 (d, J = 5.6 Hz, 1H, H-6).

Anal. Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.58; N, 21.53. Found: C, 67.78; H, 2.62; N, 21.53.

Preparation of Ethyl Furo[2,3-*b*:4,5-*c*']dipyridine-5-imidate **8a**, -[3,2-*b*:4,5-*c*']dipyridine-9-imidate **8b**, -[2,3-*c*:4,5-*c*']dipyridine-1-imidate **8c**, -[2,3-*c*:4,5-*c*']dipyridine-6-imidate **8'c** and -[3,2-*c*:4,5-*c*']dipyridine-1-imidate **8d**.

To a solution of sodium ethoxide prepared from sodium (180 mg, 7.8 mmoles) in absolute ethanol (10 ml) was added a solution of **7a**, **7b**, **7c**, **7'c** or **7d** (760 mg, 3.9 mmoles) in absolute ethanol (30 ml) with stirring at room temperature. After being stirred at room temperature for 18 hours for **7a**, 40 hours for **7b**, 2 hours for **7c** and **7'c**, and 12 hours for **7d**, the mixture was evaporated and the residue was treated with chloroform and water. The chloroform extract was dried over magnesium sulfate and evaporated to give a yellow crystalline mass. Further processing of the crude product is described in the following paragraph.

Ethyl Furo[2,3-*b*:4,5-*c*']dipyridine-5-imidate **8a**.

The residue from **7a** was recrystallized from ether-hexane to give 800 mg (85%) of **8a**, mp 125-129° (colorless crystals); ir (potassium bromide): 3269, 3075, 2984, 2923, 2858, 1640, 1584, 1556, 1408, 1392, 1338, 1294, 1280, 1238, 1131, 1095, 1029, 997, 898, 870, 844, 787, 772 cm^{-1}; pmr (deuteriochloroform): δ 9.46 (broad s, 1H, NH), 8.92 (dd, J = 1.8, 7.9 Hz, 1H, H-2), 8.75 (d, J = 5.6 Hz, 1H, H-7), 8.55 (dd, J = 1.8, 5.0 Hz, 1H, H-4), 7.69 (d, J = 5.6 Hz, 1H, H-8), 7.46 (dd, J = 5.0, 7.9 Hz, 1H, H-3), 4.74 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.63 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.51; H, 4.52; N, 17.59.

Ethyl Furo[3,2-*b*:4,5-*c*']dipyridine-9-imidate **8b**.

The residue from **7b** was chromatographed on a silica gel (85 g) eluting with hexane-ethyl acetate (1:2) to give 820 mg (87%) of **8b**, mp 125.5-129° (from ether-hexane, colorless crystals); ir (potassium bromide): 3227, 3086, 3055, 3031, 2978, 2929, 2899, 2867, 1642, 1626, 1588, 1561, 1424, 1391, 1322, 1264, 1239, 1112, 1081, 1044, 974, 871, 840, 794, 762 cm^{-1}; pmr (deuteriochloroform): δ 11.65 (broad s, 1H, NH), 8.89 (d, J = 5.6 Hz, 1H, H-7), 8.80 (dd, J = 1.5, 5.0 Hz, 1H, H-2), 8.00 (dd, J = 1.5, 8.5 Hz, 1H, H-4), 7.68 (d, J = 5.6 Hz, 1H, H-6), 7.56 (dd, J = 5.0, 8.5 Hz, 1H, H-3), 4.63 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.57 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 65.00; H, 4.69; N, 17.40.

Ethyl Furo[2,3-*c*:4,5-*c*']dipyridine-1-imidate **8c**.

The residue from **7c** was recrystallized from acetone to give 870 mg (93%) of **8c**, mp 133-137° (colorless crystals); ir (potassium bromide): 3252, 3056, 2984, 1644, 1619, 1556, 1421, 1404, 1375, 1337, 1314, 1265, 1191, 1160, 1121, 1100, 1042, 1030, 980, 827, 864 cm^{-1}; pmr (deuteriochloroform): δ 9.42 (broad s, 1H, NH), 9.08 (s, 1H, H-6), 8.80 (d, J = 5.6 Hz, 1H, H-3), 8.70 (d, J = 5.3 Hz, 1H, H-8), 8.45 (d, J = 5.3 Hz, 1H, H-9), 7.70 (d, J = 5.6 Hz, 1H, H-3), 4.74 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.65 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.58; H, 4.72; N, 17.02.

Ethyl Furo[2,3-*c*:4,5-*c*']dipyridine-6-imidate **8'c**.

The residue from **7'c** was recrystallized from acetone-ether to give 930 mg (99%) of **8'c**, mp 135-137° (colorless crystals); ir (potassium bromide): 3283, 3050, 2991, 2924, 2853, 1652, 1623, 1579, 1480, 1407, 1398, 1372, 1339, 1229, 1187, 1166, 1130, 1087, 1017, 912, 887, 857, 825 cm^{-1}; pmr (deuteriochloroform): δ 9.36 (d, J = 0.9 Hz, 1H, H-1), 9.20 (broad s, 1H, NH), 8.83 (d, J = 5.9 Hz, 1H, H-3), 8.71 (d, J = 5.0 Hz, 1H, H-8), 8.05 (d, J = 5.0 Hz, 1H, H-9), 7.67 (dd, J = 0.9, 5.9 Hz, 1H, H-4), 4.61 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.57 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.72; H, 4.51; N, 16.98.

Ethyl Furo[3,2-*c*:4,5-*c*']dipyridine-1-imidate **8d**.

The residue from **7d** was recrystallized from acetone-ether to give 800 mg (85%) of **8d**, mp 152-153° (colorless crystals); ir (potassium bromide): 3274, 3080, 2990, 1639, 1589, 1558, 1470, 1413, 1380, 1345, 1319, 1295, 1266, 1198, 1161, 1129, 1107, 1022, 867, 829, 721 cm^{-1}; pmr (deuteriochloroform): δ 9.83 (s, 1H, H-9), 9.47 (broad s, 1H, NH), 8.76 (d, J = 5.6 Hz, 1H, H-3), 8.75 (d, J = 5.4 Hz, 1H, H-7), 7.67 (d, J = 5.6 Hz, 1H, H-4), 7.60 (d, J = 5.4 Hz, 1H, H-6), 4.76 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.66 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.66; H, 4.59; N, 17.22.

Preparation of Ethyl Furo[2,3-*b*:4,5-*c*']dipyridine-5-carboxylate **9a**, -[3,2-*b*:4,5-*c*']dipyridine-9-carboxylate **9b**, -[2,3-*c*:4,5-*c*']dipyridine-1-carboxylate **9c**, -[2,3-*c*:4,5-*c*']dipyridine-6-carboxylate **9'c** and -[3,2-*c*:4,5-*c*']dipyridine-1-carboxylate **9d**.

A solution of imidate **8** (480 mg, 2.0 mmoles) in 90% ethanol (20 ml) containing 0.1 ml of 10% hydrochloric acid was stirred at room temperature for 15 hours for **8a**, 20 hours for **8b**, 4.5 hours for **8c**, 1.5 hours for **8'c** and 16 hours for **8d**. After evaporation of the solvent, the mixture was basified with sodium bicarbonate and extracted with chloroform. The residue of the dried (magnesium sulfate) extract was recrystallized from ether-acetone to give 475 mg (98%) of **9a**, 400 mg (83%) of **9b**, 450 mg (93%) of **9c**, 480 mg (99%) of **9'c** and 480 mg (99%) of **9d**.

Ethyl Furo[2,3-*b*:4,5-*c*']dipyridine-5-carboxylate **9a**.

This compound had mp 133-135° (colorless crystals); ir (potassium bromide): 3079, 3049, 2986, 2940, 2873, 1722, 1588, 1479, 1424, 1388, 1330, 1315, 1291, 1275, 1260, 1239, 1197, 1176, 1115, 1081, 1036, 997, 980, 870, 845, 797, 775, 744 cm^{-1}; pmr (deuteriochloroform): δ 9.27 (dd, J = 1.8, 7.9 Hz, 1H, H-2), 8.86 (d, J = 5.6 Hz, 1H, H-7), 8.58 (dd, J = 1.8, 4.7 Hz, 1H, H-4), 7.79 (d, J = 5.6 Hz, 1H, H-8), 7.50 (dd, J = 4.7, 7.9 Hz, 1H, H-3), 4.64 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.55 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.45; H, 4.20; N, 11.82.

Ethyl Furo[3,2-*b*:4,5-*c*']dipyridine-9-carboxylate **9b**.

This compound had mp 107.5-111.5° (colorless crystals); ir (potassium bromide): 3078, 2998, 2981, 2932, 1743, 1627, 1589, 1458, 1446, 1426, 1403, 1372, 1343, 1304, 1254, 1241, 1175, 1114, 850, 783, 753 cm^{-1}; pmr (deuteriochloroform): δ 8.81 (dd, J = 1.2, 4.7 Hz, 1H, H-2), 8.76 (d, J = 5.6 Hz, 1H, H-7), 7.87 (dd, J = 1.2, 8.5 Hz, 1H, H-4), 7.65 (d, J = 5.6 Hz, 1H, H-6), 7.43 (dd, J = 4.7, 8.5 Hz, 1H, H-3), 4.61 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.47 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.76; H, 4.44; N, 11.29.

Ethyl Furo[2,3-*c*:4,5-*c*']dipyridine-1-carboxylate **9c**.

This compound had mp 135-137° (colorless crystals); ir (potassium bromide): 3114, 3059, 2979, 2927, 2954, 1722, 1624, 1562, 1475, 1421, 1329, 1305, 1252, 1198, 1187, 1167, 1041, 983, 838, 808, 767 cm^{-1}; pmr (deuteriochloroform): δ 9.12 (d, J = 0.7 Hz, 1H, H-6), 8.92 (d, J = 5.6 Hz, 1H, H-3), 8.78 (dd, J = 0.7, 5.1 Hz, 1H, H-8), 8.74 (d, J = 5.1 Hz, 1H, H-9), 7.82 (d, J = 5.6 Hz, 1H, H-4), 4.66 (q, J = 7.1 Hz, 2H, -CH_2-CH_3), 1.56 (t, J = 7.1 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.59; H, 4.12; N, 11.49.

Ethyl Furo[2,3-*c*:4,5-*c*']dipyridine-6-carboxylate **9'c** .

This compound had mp 172-174° (colorless crystals); ir (potassium bromide): 3084, 3061, 2991, 2908, 1718, 1632, 1579, 1467, 1399, 1364, 1300, 1255, 1216, 1199, 1182, 1156, 1082, 1019, 926, 862, 843, 801 cm^{-1}; pmr (deuteriochloroform): δ 9.40 (s, 1H, H-1), 8.86 (d, J = 5.9 Hz, 1H, H-3), 8.83 (d, J = 4.9 Hz, 1H, H-8), 8.18 (d, J = 4.9 Hz, 1H, H-9), 7.75 (d, J = 5.9 Hz, 1H, H-4), 4.64 (q, J = 7.1 Hz, 2H, -CH_2-CH_3), 1.54 (t, 7.1 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.53; H, 4.09; N, 11.26.

Ethyl Furo[3,2-*c*:4,5-*c*']dipyridine-1-carboxylate **9d**.

This compound had mp 107-110° (colorless crystals); ir (potassium bromide): 3044, 3019, 2987, 1728, 1587, 1556, 1467, 1438, 1406, 1374, 1321, 1298, 1263, 1201, 1177, 1155, 1034, 1017, 992, 972, 881, 865, 845, 834, 807, 742 cm^{-1}; pmr (deuteriochloroform): δ 10.09 (d, J = 0.9 Hz, 1H, H-9), 8.86 (d, J = 5.3 Hz, 1H, H-3), 8.80 (d, J = 5.6 Hz, 1H, H-7), 7.76 (d, J = 5.3 Hz, 1H, H-4), 7.60 (dd, J = 0.9, 5.6 Hz, 1H, H-6), 4.67 (q, J = 7.0 Hz, 2H, -CH_2-CH_3), 1.57 (t, J = 7.0 Hz, 3H, -CH_2-CH_3).

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.35; H, 4.16; N, 11.56.

General Procedure for the Preparation of 5-Formylfuro[2,3-*b*:-4,5-*c*']- **10a,** 1-Formylfuro[2,3-*c*:4,5-*c*']- **10c**, 6-Formylfuro[2,3-*c*:-4,5-*c*']- **10'c** and 1-Formylfuro[3,2-*c*:4,5-*c*']dipyridine **10d**.

To a solution of carboxylic ester **9a**, **9b**, **9c**, **9'c** or **9d** (38 mg, 0.16 mmole) in dichloromethane (5 ml) was added diisobutylaluminium hydride in dichloromethane (0.32 ml of 1.0*M* solution, 0.32 mmole) at -15° under nitrogen atmosphere with stirring.

After being stirred for 30 minutes at this temperature, the mixture was treated with saturated aqueous sodium potassium tartrate solution (5 ml), and separated the layers. The aqueous layer was extracted with chloroform. The organic layers were combined, dried over magnesium sulfate and evaporated to give solid residue, which was chromatographed on a silica gel (3 g) column eluting with chloroform to afford pure sample of **10a** (27 mg, 88%), **10c** (24 mg, 77%), **10'c** (18 mg, 58%) and **10d** (20 mg, 64%). In the case of **9b**, evaporation of the dried organic layer yielded only a brown resinous syrup from which any compound could not be isolated by the chromatography on silica gel.

5-Formylfuro[2,3-*b*:4,5-*c*']dipyridine **10a**.

This compound had mp 172-174° (from hexane-ether, colorless crystals); ir (potassium bromide): 3073, 3035, 2924, 2855, 1709, 1588, 1562, 1431, 1396, 1375, 1326, 1263, 1231, 1180, 1127, 1092, 1030, 994, 859, 826, 778, 709 cm^{-1}; pmr (deuteriochloroform): δ 10.38 (s, 1H, -CHO), 9.35 (dd, J = 1.8, 7.9 Hz, 1H, H-2), 8.92 (d, J = 5.6 Hz, 1H, H-6), 8.61 (dd, J = 1.8, 5.0 Hz, 1H, H-4), 7.82 (d, J = 5.6 Hz, 1H, H-8), 7.52 (dd, J = 5.0, 7.9 Hz, 1H, H-3).

Anal. Calcd. for $C_{11}H_6N_2O_2$: C, 66.67; H, 3.05; N, 14.14. Found: C, 66.95; H, 3.41; N, 14.12.

1-Formylfuro[2,3-*c*:4,5-*c*']dipyridine **10c**.

This compound had mp 198-200° (gradually sublimed, from methanol-ether, colorless crystals); ir (potassium bromide): 3118, 3053, 3018, 2924, 2862, 1707, 1624, 1568, 1420, 1376, 1320, 1291, 1263, 1232, 1183, 1163, 1048, 1026, 1004, 850, 840, 825, 718 cm^{-1}; pmr (deuteriochloroform): δ 1040 (s, 1H, -CHO), 9.14 (s, 1H, H-6), 8.98 (d, J = 5.6 Hz, 1H, H-3), 8.90 (d, J = 5.1 Hz, 1H, H-8), 8.78 (d, J = 5.1 Hz, 1, H-9), 7.85 (d, J = 5.6 Hz, 1H, H-4).

Anal. Calcd. for $C_{11}H_6N_2O_2 \cdot 1/4CH_3OH$: C, 65.53; H, 3.42; N, 13.59. Found: C, 65.74; H, 3.22; N, 13.54.

6-Formylfuro[2,3-*c*:4,5-*c*']dipyridine **10'c**.

This compound had mp 225-228° (gradually sublimed, from methanol-ether, colorless crystals); ir (potassium bromide): 3101, 3082, 2924, 2852, 1708, 1629, 1576, 1463, 1402, 1370, 1269, 1188, 1157, 1120, 1029, 862, 840, 739 cm^{-1}; pmr (deuteriochloroform): δ 10.32 (s, 1H, -CHO), 9.35 (s, 1H, H-1), 8.81 (d, J = 4.9 Hz, 1H, H-8), 8.80 (d, J = 5.6 Hz, 1H, H-8), 8.15 (d, J = 4.9 Hz, 1H, H-9), 7.71 (d, J = 5.6 Hz, 1H, H-4).

Anal. Calcd. for $C_{11}H_6N_2O_2 \cdot CH_3OH$: C, 62.61; H, 4.38; N, 12.19. Found: C, 63.00; H, 4.00; N, 12.27.

1-Formylfuro[3,2-*c*:4,5-*c*']dipyridine **10d**.

This compound had mp 170-171° (gradually sublimed, from methanol-ether, colorless crystals); ir (potassium bromide): 3066, 2927, 2850, 1705, 1588, 1579, 1562, 1470, 1441, 1412, 1257, 1239, 1209, 1159, 1119, 1071, 1027, 962, 865, 839, 823, 726 cm^{-1}; pmr (deuteriochloroform): δ 10.41 (s, 1H, -CHO), 10.24 (s, 1H, H-9), 8.93 (d, J = 5.6 Hz, 1H, H-3), 8.84 (d, J = 5.9 Hz, 1H, H-7), 7.81 (d, J = 5.6 Hz, 1H, H-4), 7.62 (d, J = 5.9 Hz, 1H, H-6).

Anal. Calcd. for $C_{11}H_6N_2O_2 \cdot CH_3OH$: C, 62.61; H, 4.38; N, 12.19. Found: C, 62.27; H, 4.10; N, 12.28.

Reaction of Cyano Compounds **7a** and **7b** with Methylmagnesium Bromide.

A solution of cyano compound **7a** or **7b** (50 mg, 0.26 mmole) in dry tetrahydrofuran (3.5 ml) was added to a stirred solution of methylmagnesium bromide (0.13 ml, 3*M*, 0.39 mmole) in ether by syringe at -10° under nitrogen atmosphere. After being stirred at room temperature for 2 hours, the reaction mixture was treated with 0.5*M* sulfuric acid and stirred at room temperature for 5 minutes. After evaporation of the solvent under reduced pressure, the residual mixture was basified with ammonium hydroxide solution and extracted with chloroform. The chloroform extract was dried over magnesium sulfate and evaporated. The solid residue was recrystallized from hexane-ether for **11a** and acetone-ether for **11b** to give 49 mg (89%) of **11a** and 52 mg (95%) of **11b.**

5-Acetylfuro[2,3-*b*:4,5-*c*']dipyridine **11a**.

This compound had mp 187-190° (colorless crystals); ir (potassium bromide): 3071, 3030, 2923, 1697, 1586, 1555, 1426, 1393, 1354, 1330, 1292, 1267, 1256, 1233, 1183, 1148, 999, 913, 856, 815, 788 cm^{-1}; pmr (deuteriochloroform): δ 9.29 (dd, J = 2.0, 7.9 Hz, 1H, H-2), 8.76 (d, J = 5.6 Hz, 1H, H-7), 8.55 (dd, J = 2.0, 5.0 Hz, 1H, H-4), 7.75 (d, J = 5.6 Hz, 1H, H-8), 7.46 (dd, J = 5.0, 7.9 Hz, 1H, H-3), 2.89 (s, 3H, -COMe).

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 68.14; H, 3.88; N, 13.18.

9-Acetylfuro[3,2-*b*:4,5-*c*']dipyridine **11b**.

This compound had mp 150-153° (colorless crystals); ir (potassium bromide): 3063, 3009, 2924, 2854, 1705, 1625, 1566, 1423, 1402, 1354, 1276, 1239, 1181, 1149, 1020, 911, 855, 812, 801, 756 cm^{-1}; pmr (deuteriochloroform): δ 8.87 (dd, J = 1.2, 4.7 Hz, 1H, H-2), 8.77 (d, J = 5.6 Hz, 1H, H-7), 7.94 (dd, J = 1.2, 8.2 Hz, 1H, H-4), 7.72 (d, J = 5.6 Hz, 1H, H-6), 7.50 (dd, J = 4.7, 8.2 Hz, 1H, H-3), 2.94 (s, 3H, -COMe).

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 68.00; H, 3.99; N, 13.04.

Condensation of **10a** with Nitromethane.

To a solution of aldehyde **10a** (30 mg, 0.15 mmole) and nitromethane (20 mg, 0.26 mmole) in absolute methanol was added a solution of sodium methoxide (13 mg, 0.24 mmole) in methanol (0.5 ml) by syringe under a nitrogen atmosphere and stirring at -15°. The mixture was stirred at -15° for 2.5 hours and at room temperature for 0.5 hour, treated with water, acidified with acetic acid, basified with sodium bicarbonate and evaporated under reduced pressure to remove the methanol. The residue was diluted with water, extracted with ethyl acetate and dried over magnesium sulfate. The solvent was evaporated to give a solid residue, which was recrystallized from hexane-ether to give 5-(1-hydroxy-2-nitroethyl)furo[2,3-*b*:4,5-*c*']dipyridine **12** (38 mg, 98%) as colorless crystals of mp 162-166°; ir (potassium bromide): 3200-2600 (broad), 1589, 1574, 1549, 1432, 1396, 1380, 1325, 1285, 1227, 1177, 1127, 1080, 1053, 1021, 1002, 982, 905, 861, 833, 782 cm^{-1}; pmr (deuteriochloroform): δ 8.67 (d, J = 5.6 Hz, 1H, H-7), 8.58 (d, J = 6.2 Hz, 1H, H-2), 8.57 (d, J = 6.7 Hz, 1H, H-4), 7.57 (d, J = 5.6 Hz, 1H, H-8), 7.53 (dd, J = 6.2, 6.7 Hz, 1H, H-3), 6.20-5.95 (complex m, 1H, H-α), 4.86 (dd, J = 3.8, 14.2 Hz, 1H, H-β1), 4.82 (dd, J = 7.9, 14.2 Hz, 1H, H-β_2).

Anal. Calcd. for $C_{12}H_9N_3O_4$: C, 55.60; H, 3.50; N, 16.21. Found: C, 55.98; H, 3.59; N, 16.10.

Wittig-Horner Reaction of **10a** with Methyl Diethyl Phosphonoacetate.

To a stirred suspension of sodium hydride (6.8 mg of 60% dispersion in mineral oil, 0.17 mmole, washed with hexane) in dry tetrahydrofuran (1 ml) was added a solution of methyl diethyl phosphonoacetate (37 mg, 0.17 mmole) in tetrahydrofuran (5 ml) by syringe under a nitrogen atmosphere with stirring at room temperature. After stirring an additional 20 minutes, the mixture was cooled at 0° and a solution of **10a** (30 mg, 0.15 mmole) in tetrahydrofuran (5 ml) was added to the mixture by syringe. The cooling bath was removed and stirring was con-

tinued at room temperature for 22 hours. After evaporation of the solvent, the residue was treated with chloroform and water. The chloroform layer was dried over magnesium sulfate and evaporated to give a crystalline mass, which was chromatographed on a silica gel (3 g) column eluting with chloroform to give 34 mg (88%) of methyl β-(5-furo[2,3-*b*:4,5-*c*']dipyridyl)acrylate **13** as colorless crystals of mp 192-194° (from acetone); ir (potassium bromide): 3063, 2996, 2951, 2852, 1717, 1646, 1587, 1564, 1455, 1438, 1388, 1333, 1319, 1300, 1257, 1224, 1178, 1162, 1123, 1022, 992, 973, 858, 829, 820, 790 cm^{-1}; pmr (deuteriochloroform): δ 8.72 (d, J = 5.6 Hz, 1H, H-7), 8.54 (dd, J = 1.8, 5.0 Hz, 1H, H-2), 8.52 (dd, J = 1.8, 7.6 Hz, 1H, H-4), 8.28 (d, J = 15.2 Hz, 1H, H-α), 7.57 (d, J = 5.6 Hz, 1H, H-8), 7.48 (dd, J = 5.0, 7.6 Hz, 1H, H-3), 7.31 (d, J = 15.2 Hz, 1H, H-β), 4.00 (s, 3H, $-CO_2Me$).

Anal. Calcd. for $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.96; N, 11.02. Found: C, 66.05; H, 4.07; N, 11.02.

General Procedure for the Chlorination of *N,N'*-Dioxides **3b**, **3c** and **3d** with Phosphorus Oxychloride.

A mixture of **3b**, **3c** or **3d** (30 mg, 0.15 mmole) and phosphorus oxychloride (1 ml, 11 mmoles) in chloroform (1 ml) was refluxed for 5.5 hours. After being cooled, the mixture was poured into ice-water (5 ml), basified with sodium bicarbonate and extracted with chloroform. Further processing of the residue of the dried (magnesium sulfate) chloroform solution is indicated in a subsequent paragraph.

2,9-Dichloro- **14b** and 4,9-Dichloro[3,2-*b*:4,5-*c*']dipyridine **14'b.**

The residue from **3b** was chromatographed on a silica gel (10 g) column. The first fraction eluted with hexane-chloroform (1:4) yielded 16.5 mg (46%) of **14b**, and the second fraction 10.5 mg (32%) of **14'b**.

Compound **14b**.

This compound had mp 200-203° (from acetone-ether, colorless crystals); ir (potassium bromide): 3056, 1628, 1568, 1417, 1384, 1372, 1268, 1247, 1212, 1104, 1024, 954, 915, 853, 833, 803, 718 cm^{-1}; pmr (deuteriochloroform): δ 8.54 (d, J = 5.9 Hz, 1H, H-7), 7.91 (d, J = 8.8 Hz, 1H, H-4), 7.54 (d, J = 5.9 Hz, 1H, H-6), 7.51 (d, J = 8.8 Hz, 1H, H-3).

Anal. Calcd. for $C_{10}H_4N_2OCl_2$: C, 50.24; H, 1.69; N, 11.72. Found: C, 50.47; H, 1.98; N, 11.75.

Compound **14'b**.

This compound had mp 219-223° (from acetone-methanol, colorless crystals); ir (potassium bromide): 3072, 3055, 3009, 1625, 1585, 1567, 1553, 1442, 1425, 1370, 1359, 1318, 1263, 1225, 1191, 1176, 1094, 952, 864, 852, 840, 725 cm^{-1}; pmr (deuteriochloroform): δ 8.74 (d, J = 5.3 Hz, 1H, H-2), 8.58 (d, J = 5.9 Hz, 1H, H-7), 7.62 (d, J = 5.9 Hz, 1H, H-6), 7.54 (d, J = 5.3 Hz, 1H, H-3).

Anal. Calcd. for $C_{10}H_4N_2OCl_2$: C, 50.24; H, 1.69; N, 11.72. Found: C, 50.16; H, 2.02; N, 11.58.

1,6-Dichlorofuro[2,3-*c*:4,5-*c*']dipyridine **14c**.

The crude residue from **10c** was recrystallized from acetone to give pure sample of **14c** (19 mg, 82%) as colorless crystals of mp 232-233°; ir (potassium bromide): 3064, 1626, 1558, 1451, 1421, 1399, 1252, 1192, 1179, 1085, 950, 867, 844, 725 cm^{-1}; pmr (deuteriochloroform): δ 8.61 (d, J = 5.6 Hz, 1H, H-3), 8.52 (d, J = 5.0 Hz, 1H, H-8), 8.15 (d, J = 5.0 Hz, 1H, H-9), 7.65 (d, J = 5.6 Hz, 1H, H-4).

Anal. Calcd. for $C_{10}H_4N_2OCl_2$: C, 50.24; H, 1.69; N, 11.72. Found: C, 50.29; H, 1.69; N, 11.83.

1,9-Dichlorofuro[3,2-*c*:4,5-*c*']dipyridine **14d.**

The residue from **10d** was recrystallized from acetone-ether to yield 20 mg (56%) of pure sample of **14d** as colorless crystals of mp 224-227°; ir (potassium bromide): 3098, 3053, 1580, 1543, 1436, 1416, 1231, 1286, 1269, 1193, 1179, 1080, 951, 905, 830 cm^{-1}; pmr (deuteriochloroform): δ 8.54 (d, J = 5.6 Hz, 2H, H-3 and H-7), 7.55 (d, J = 5.6 Hz, 2H, H-4 and H-6).

Anal. Calcd. for $C_{10}H_4N_2OCl_2$: C, 50.24; H, 1.69; N, 11.72. Found: C, 50.36; H, 1.85; N, 11.68.

General Procedure for the Cyanation of **3b**, **3c** and **3d** with Trimethylsilyl Cyanide.

A mixture of **3b**, **3c** or **3d** (93 mg, 0.45 mmole), triethylamine (140 mg, 1.38 mmoles) and trimethylsilyl cyanide (183 mg, 1.84 mmoles) in acetonitrile (4 ml) was refluxed with stirring under a nitrogen atmosphere. After being refluxed for 5 hours, the reaction mixture was evaporated, and the residue was treated with water and chloroform. The aqueous layer was extracted with chloroform. The combined chloroform layers were dried (magnesium sulfate) and evaporated to leave a light browm solid mass. Further processing of the residue is indicated in a subsequent paragraph.

9-Cyanofuro[3,2-*b*:4,5-*c*']dipyridine 1-Oxide **15b**.

The crude solid mass from **3b** was recrystallized from acetone-ether to give 94 mg (97%) of pure sample of **15b** as slightly yellow crystals of mp 248-251°; ir (potassium bromide): 3086, 3072, 3039, 3012, 2225, 1593, 1583, 1561, 1456, 1423, 1336, 1308, 1270, 1243, 1069, 1055, 1009, 992, 854, 800, 777 cm^{-1}; pmr (deuteriochloroform): δ 8.89 (d, J = 5.6 Hz, 1H, H-7), 8.36 (dd, J = 2.4, 4.7 Hz, 1H, H-2), 7.77 (d, J = 5.6 Hz, 1H, H-6), 7.54 (dd, J = 2.4, 8.1 Hz, 1H, H-4), 7.54 (dd, J = 4.7, 8.1 Hz, 1H, H-3).

Anal. Calcd. for $C_{11}H_5N_3O_2$: C, 62.56; H, 2.39; N, 19.90. Found: C, 62.53; H, 2.60; N, 19.94.

1-Cyanofuro[2,3-*c*:4,5-*c*']dipyridine 7-Oxide **15c** and 1,6-Dicyanofuro[2,3-*c*:4,5-*c*']dipyridine **15'c**.

The residue from **3c** was chromatographed on a silica gel (15 g) column. The first fraction eluted with chloroform-methanol (98:2) yielded 56 mg (55%) of **15'c**, and the second fraction 30 mg (31%) of **15c**.

Compound **15c**.

This compound had mp 263-265° (from acetone-methanol, colorless crystals); ir (potassium bromide): 3110, 3033, 3017, 2233, 1594, 1468, 1433, 1420, 1307, 1269, 1238, 1207, 1162, 1126, 1081, 993, 818 cm^{-1}; pmr (deuteriochloroform): δ 8.84 (d, J = 5.6 Hz, 1H, H-3), 8.72 (d, J = 1.4 Hz, 1H, H-6), 8.38 (dd, J = 1.4, 6.7 Hz, 1H, H-8), 8.19 (d, J = 6.7 Hz, 1H, H-9), 7.79 (d, J = 5.6 Hz, 1H, H-4).

Anal. Calcd. for $C_{11}H_5N_3O_2$: C, 62.56; H, 2.39; N, 19.90. Found: C, 62.25; H, 2.50; N, 19.50.

Compound **15'c**.

This compound had mp 191-193° (from acetone, colorless crystals); ir (potassium bromide): 3105, 3069, 2243, 1630, 1571, 1446, 1427, 1400, 1310, 1245, 1203, 1106, 1067, 1052, 994, 901, 853, 759 cm^{-1}; pmr (deuteriochloroform): δ 9.01 (d, J = 5.9

Hz, 1H, H-3), 8.94 (d, J = 5.0 Hz, 1H, H-8), 8.54 (d, J = 5.0 Hz, 1H, H-9), 7.97 (d, J = 5.9 Hz, 1H, H-4).

Anal. Calcd. for $C_{12}H_4N_4O$: C, 65.46; H, 1.83; N, 25.44. Found: C, 65.68; H, 1.89; N, 25.39.

1-Cyanofuro[3,2-*c*:4,5-*c*'] dipyridine 8-Oxide **15d** and 1,9-Dicyanofuro[3,2-*c*:4,5-*c*']dipyridine **15'd.**

The residue from **3d** was chromatographed on a silica gel (18 g) column. The first fraction eluted with chloroform yielded 48 mg (47%) of **15'd**, and the second fraction 19 mg (20%) of **15d**.

Compound **15d**.

This compound had mp 250-254° (from acetone-methanol, slightly yellow needles); ir (potassium bromide): 3075, 3013, 2234, 1601, 1571, 1459, 1432, 1418, 1305, 1262, 1201, 1183, 995, 857, 838, 790, 705 cm^{-1}; pmr (deuteriochloroform): δ 9.27 (d, J = 1.8 Hz, 1H, H-9), 8.88 (d, J = 5.9 Hz, 1H, H-3), 8.47 (dd, J = 1.8, 7.0 Hz, 1H, H-7), 7.81 (d, J = 5.9 Hz, 1H, H-4), 7.63 (d, J = 7.0 Hz, 1H, H-6).

Anal. Calcd. for $C_{11}H_5N_3O_2$: C, 62.56; H, 2.39; N, 19.90. Found: C, 62.39; H, 2.43; N, 19.79.

Compound **15'd**.

This compound had mp >300° (from methanol, colorless crystals); ir (potassium bromide): 3089, 2247, 1580, 1554, 1417, 1386, 1264, 1242, 1197, 1076, 1051, 1010, 992, 868, 855, 825, 770 cm^{-1}; pmr (deuteriochloroform): δ 8.95 (d, J = 5.9 Hz, 2H, H-3 and H-7), 7.88 (d, J = 5.9 Hz, 2H, H-4 and H-6).

Anal. Calcd. for $C_{12}H_4N_4O$: C, 65.46; H, 1.83; N, 25.44. Found: C 65.21; H, 1.99; N, 25.28.

Reaction of Compound **15b** with Methylmagnesium Bromide.

A solution of cyano compound **15b** (30 mg, 0.14 mmole) in dry tetrahydrofuran (8 ml) was added to a stirred solution of methylmagnesium bromide (0.07 ml, 3*M*, 0.21 mmole) in ether by syringe at -10° under nitrogen atmosphere. After being stirred at room temperature for 2 hours, the reaction mixture was treated with 0.5*M* sulfuric acid and stirred at room temperature for 5 minutes. After evaporation of the solvent under reduced pressure, the residual mixture was basified with ammonium hydroxide solution and extracted with chloroform. The chloroform extract was dried over magnesium sulfate and evaporated. The solid residue was chromatographed on a silica gel (3 g) column eluting with chloroform to give 15 mg (47%) of 9-acetylfuro[3,2-*b*:4,5-*c*']dipyridine 1-oxide **16** and 5 mg (16%) of 9-acetyl-2-methylfuro[3,2-*b*:4,5-*c*']dipyridine **16'**.

Compound **16**.

This compound had mp 195-198° (from acetone-ether, slightly yellow crystals); ir (potassium bromide): 3114, 3061, 3029, 1710, 1595, 1562, 1459, 1427, 1362, 1294, 1280, 1252, 1148, 1054, 1019, 1001, 924, 848, 793, 782, 768, 724, 666 cm^{-1}; pmr (deuteriochloroform): δ 8.78 (d, J = 5.6 Hz, 1H, H-7), 8.26 (dd, J = 1.5, 5.9 Hz, 1H, H-2), 7.61 (d, J = 5.6 Hz, 1H, H-6), 7.52 (dd, J = 1.5, 8.2 Hz, 1H, H-4), 7.43 (dd, J = 5.9, 8.2 Hz, 1H, H-3), 2.86 (s, 3H, -COMe).

Anal. Calcd. for $C_{12}H_8N_2O_3$: C, 63.16; H, 3.53; N, 12.28. Found: C, 63.30; H, 3.74; N, 12.28.

Compound **16'**.

This compound had mp 116.5-119.5° (from hexane-ether, colorless crystals); ir (potassium bromide): 3076, 3046, 2925, 2858, 1698, 1624, 1580, 1557, 1426, 1390, 1354, 1292, 1245, 1179, 1144, 1093, 1039, 882, 913, 849, 824 cm^{-1}; pmr (deuteriochloroform): δ 8.74 (d, J = 5.6 Hz, 1H, H-7), 7.81 (d, J = 8.5 Hz, 1H, H-4), 7.68 (d, J = 5.6 Hz, 1H, H-6), 7.35 (d, J = 8.5 Hz, 1H, H-3), 2.96 (s, 3H, -COMe), 2.80 (s, 3H, -Me).

Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.13; H, 4.53; N, 12.40.

Diethyl Furo[2,3-*c*:4,5-*c*']dipyridine-1,6-diimidate **17**.

To a solution of sodium ethoxide prepared from sodium (13 mg, 0.56 mmole) in absolute ethanol (1 ml) was added a solution of **15'c** (30 mg, 0.14 mmole) in absolute ethanol (8 ml) with stirring at room temperature. After being stirred at room temperature for 15 minutes, the mixture was evaporated and the residue was treated with chloroform and water. The chloroform extract was dried over magnesium sulfate and evaporated to give a yellow crystalline mass. Recrystallization of the crude mass from acetone gave 31 mg (73%) of compound **17** as colorless crystals of mp 137-139°; ir (potassium bromide): 3299, 3278, 3071, 2975, 2927, 1651, 1616, 1558, 1412, 1377, 1342, 1301, 1246, 1198, 1126, 1100, 1023, 983, 897, 866, 841 cm^{-1}; pmr (deuteriochloroform): δ 9.30 (broad s, 2H, NHx2), 8.82 (d, J = 5.6 Hz, 1H, H-3), 8.72 (d, J = 5.2 Hz, 1H, H-8), 8.55 (d, J = 5.2 Hz, 1H, H-9), 7.74 (d, J = 5.6 Hz, 1H, H-4), 4.73 (q, J = 7.0 Hz, 1H, OCH_2CH_3), 4.61 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 1.65 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.57 (t, J = 7.0 Hz, OCH_2CH_3)

Anal. Calcd. for $C_{16}H_{16}N_4O_3$: C, 61.53; H, 5.16; N, 17.94. Found: C, 61.67; H, 5.11; N, 17.82.

Diethyl Furo[2,3-*c*:4,5-*c*']dipyridine-1,6-dicarboxylate **18**.

A solution of imidate **17** (21 mg, 0.067 mmole) in 90% ethanol (3 ml) containing 0.01 ml of 10% hydrochloric acid was stirred at room temperature for 2.5 hours. After evaporation of the solvent, the mixture was basified with sodium bicarbonate and extracted with chloroform. The residue of the dried (magnesium sulfate) extract was recrystallized from acetone to give 21 mg (99%) **18** as colorless crystals of mp 145-148°; ir (potassium bromide): 3090, 2985, 2926, 2853, 1722, 1625, 1571, 1463, 1423, 1391, 1371, 1326, 1295, 1183, 1087, 1025, 863, 854, 810, 757 cm^{-1}; pmr (deuteriochloroform): δ 9.06 (d, J = 5.1 Hz, 1H, H-8), 8.97 (d, J = 5.6 Hz, 1H, H-3), 8.87 (d, J = 5.1 Hz, 1H, H-9), 7.94 (d, J = 5.6 Hz, 1H, H-4), 4.66 (q, J = 7.0 Hz, 1H, OCH_2CH_3), 4.64 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 1.56 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.55 (t, J = 7.0 Hz, OCH_2CH_3)

Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.91. Found: C, 60.82; H, 4.41; N, 9.24.

1,6-Diformylfuro[2,3-*c*:4,5-*c*']dipyridine **19**.

To a solution of **18** (40 mg, 0.13 mmole) in dichloromethane (6 ml) was added diisobutylaluminium hydride in dichloromethane (0.33 ml of 1.0*M* solution, 0.33 mmole) at -15° under nitrogen atmosphere with stirring. After being stirred for 30 minutes at this temperature, the mixture was treated with saturated aqueous sodium potassium tartrate solution (5 ml), and separated the layers. The aqueous layer was extracted with chloroform. The organic layers were combined, dried over magnesium sulfate and evaporated to give a solid residue, which was chromatographed on a silica gel (3 g) column eluting with chloroform to afford 19 mg (65%) of **19**.

Compound **19**.

This compound had mp 143-145° (from ether, slightly yellow crystals); 3125, 3030, 2924, 2853, 1706, 1623, 1567, 1458, 1429, 1401, 1364, 1249, 1196, 1068, 1020, 855, 787 cm^{-1}; pmr (deuteriochloroform): δ 9.06 (d, J = 5.1 Hz, 1H, H-8), 8.97 (d, J = 5.6 Hz, 1H, H-3), 8.87 (d, J = 5.1 Hz, 1H, H-9), 7.94 (d, J = 5.6 Hz, 1H, H-4), 4.66 (q, J = 7.0 Hz, 1H, OCH_2CH_3), 4.64 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 1.56 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.55 (t, J = 7.0 Hz, OCH_2CH_3).

Anal. Calcd. for $C_{12}H_6N_2O_3 \cdot 3/4H_2O$: C, 60.00; H, 3.14; N, 11.66. Found: C, 60.37; H, 2.96; N, 11.53.

REFERNCES AND NOTES

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