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Bromination of 2-methylfuropyridines **1a-d-Me** gave the 3-bromo derivatives **2a-d**, while the 2-cyano compounds **1a-d-CN** resulted in the recovery of the starting compounds. Nitration of **1a-d-Me** and **1a-d-CN** did not yield the corresponding nitro derivative, except for **1c-CN** giving 3-nitro derivative **3c** in 7% yield. *N*-Oxidation of **1a-d-Me** and **1b-d-CN** with *m*-chloroperbenzoic acid yielded the *N*-oxides **4a-d-Me** and **4b-d-CN**, whereas **1a-CN** did not afford the *N*-oxide. Cyanation of *N*-oxides **4a-d-Me** and **4b-d-CN** with trimethylsilyl cyanide gave the corresponding α -cyanopyridine compounds **5a-d-Me** and **5b-d-CN**. Chlorination of **4a-d-Me** and **4b-d-CN** with phosphorus oxychloride also gave the α -chloropyridine compounds **6b-d-Me** and **6b-d-CN**, accompanying formation of γ -chloropyridine **6a-Me**, **6'b-Me** and **6'b-CN**, β -chloropyridine **6''b-CN**, and α' -chloropyridine derivatives **6'c-Me** and **6'c-CN**. Acetoxylation of **4a-d-Me** and **4b-d-CN** with acetic anhydride yielded α -acetoxy pyridine compounds **7a-Me** and **7b-CN**, pyridone compounds **11d-Me**, **11c-CN** and **11d-CN**, 3-acetoxy compounds **8**, **9b**, **9c**, and 2-acetoxymethyl derivatives **10b** and **10c**.

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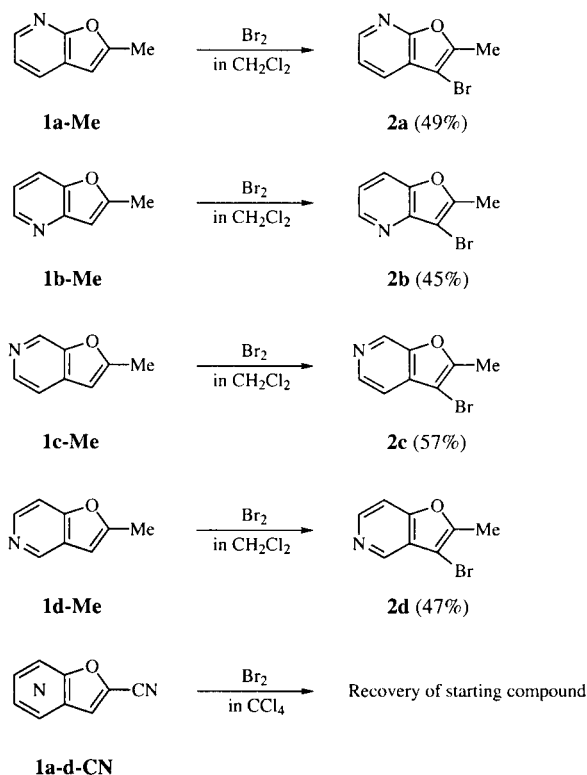
In continuation of our studies on the chemistry of furopyridines, we recently reported the reactions of cyanopyridine derivatives of furo[2,3-*b*]-, -[3,2-*b*]-, -[2,3-*c*]- and -[3,2-*c*]pyridine and their *N*-oxides to see the effects of a functional group at the furan or the pyridine ring upon the reactivity of the monosubstituted furopyridines for the sec-

ond and electrophilic and/or nucleophilic reaction [1]. In this paper we describe the bromination and nitration of 2-methyl- and 2-cyanofuropyridines, and the cyanation, chlorination and acetoxylation of their *N*-oxides.

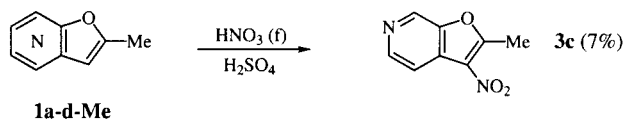
Bromination of 2-methylfuro[2,3-*b*]- (**1a-Me**) [2], -[3,2-*b*]- (**1b-Me**) [3], -[2,3-*c*]- (**1c-Me**) [4] and -[3,2-*c*]pyridine (**1d-Me**) [5] with molecular bromine in dichloromethane afforded the corresponding 3-bromo derivative **2a-d** in yield of 49% for **2a**, 45% for **2b**, 57% for **2c** and 47% for **2d** accompanying recovery of the starting compound. While, bromination of 2-cyanofuropyridines **1a-d-CN** gave no brominated product but resulted in recovery of the starting compound (88% for **1a-CN**, 84% for **1b-CN**, 80% for **1c-CN** and 80% for **1d-CN**). Nitration of **1a-d-Me** with a mixture of fuming nitric acid and sulfuric acid resulted in decomposition of the furopyridines and no compound could be isolated from the reaction mixture, except for **1c-Me** which yielded the 3-nitrated compound **3c** in 7% yield. Nitration of **1a-d-CN** again resulted in decomposition of the furopyridines accompanying recovery of the starting compound (33% for **1a-CN**, 56% for **1b-CN**, 63% for **1c-CN** and 39% for **1d-CN**). Structures of the 3-bromo compounds **2a-d** and the 3-nitro derivative **3c** were confirmed from their ¹H-nmr spectra showing disappearance of the signal of the 3-proton and the presence of three pyridine protons in each compound.

N-Oxidation of 2-methylfuropyridines **1a-d-Me** and 2-cyanofuropyridines **1b-d-CN** with *m*-chloroperbenzoic acid yielded the *N*-oxides **4a-d-Me** and **4b-d-CN** in excellent yield (81% for **4a-Me**, 98% for **4b-Me**, 98% for **4c-Me**, 94% for **4d-Me**, 92% for **4b-CN**, 86% for **4c-CN** and 39% for **4d-CN**). Compound **1a-CN**, however, did not

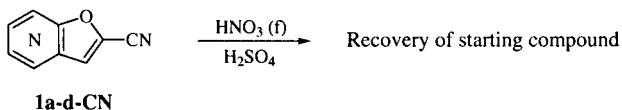
Scheme 1



Scheme 2



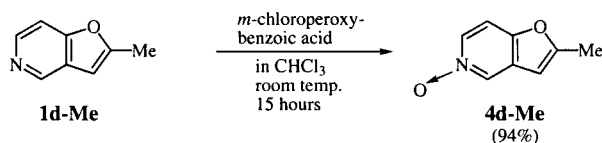
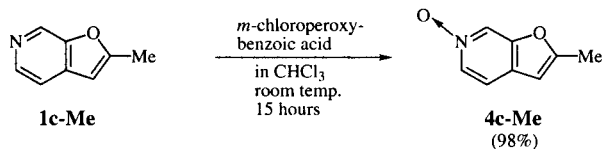
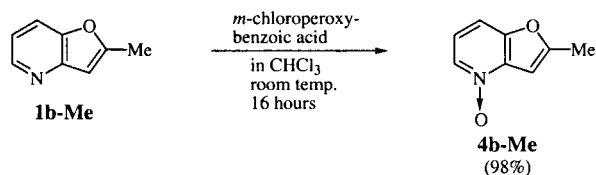
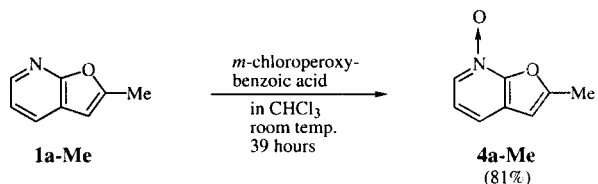
Decomposition for 1a,b,d-Me



give the *N*-oxide but recovered the starting compound (80%). These results suggested that the electronic effects of methyl and cyano groups at the 2-position do not have an affect upon the basicity of the ring nitrogen of furo-pyridines, except for the *N*-oxidation of 1a-CN. In this case, the electron withdrawing inductive effect of the ring oxygen would be enhanced by the cyano group at the 2-position, therefore, the electrons at the ring nitrogen would be strongly attracted by the ring oxygen through the C_{7a}-O bond.

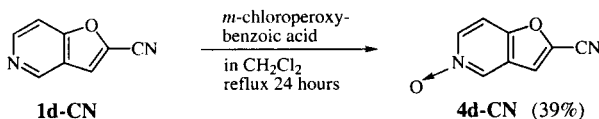
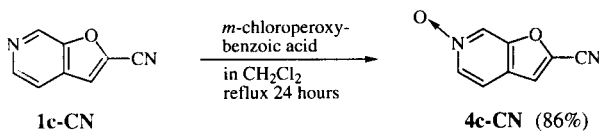
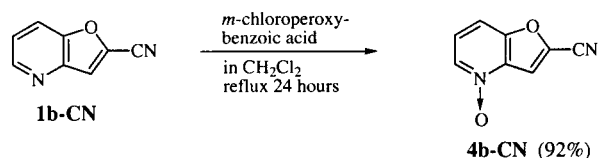
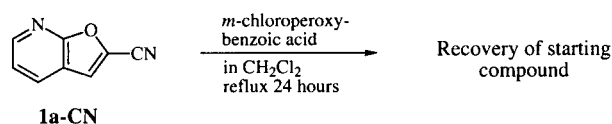
Cyanation of the *N*-oxides 4a-d-Me and 4b-d-CN with trimethylsilyl cyanide in the presence of triethylamine in acetonitrile yielded the compound having a second cyano group at the α -position to the ring nitrogen, 6-cyano-2-methylfuro[2,3-*b*]- (5a-Me, 36%), 5-cyano-2-methylfuro[3,2-*b*]- (5b-Me, 84%), 7-cyano-2-methylfuro[2,3-*c*]- (5c-Me, 87%) and 4-cyano-2-methylfuro[3,2-*c*]- (5d-Me,

Scheme 3



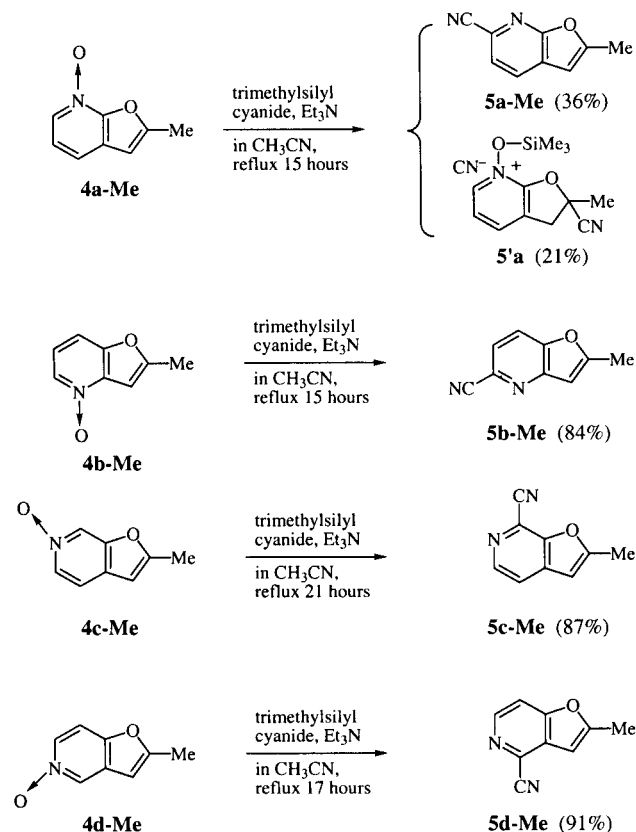
91%), 2,5-dicyanofuro[3,2-*b*]- (5b-CN, 68%), 2,7-dicyanofuro[2,3-*c*]- (5c-CN, 99%) and 2,4-dicyanofuro[3,2-*c*]pyridine (5d-CN, 99%). These compounds showed signals of the pyridine protons as a pair of doublets ($J = 7.9$ Hz for 5a-Me, 8.0 Hz for 5b-Me and 5b-CN, 5.0 Hz for 5c-Me, 5.3 Hz for 5c-CN and 5.6 Hz for 5d-Me and 5d-CN) in their ¹H-nmr spectra. These facts suggested the position of the second cyano group of 5a-Me at C-6, 5b-Me and 5b-CN at C-5, 5c-Me and 5c-CN at C-7, and 5d-Me and 5d-CN at C-4. In the case of 4a-Me, a strange compound 5'a was isolated, which had mp 143-147°, showed signals of three pyridine protons, of methylene protons and of protons of four methyl groups in its ¹H-nmr spectrum, exhibited three aromatic methine, two aromatic quaternary, one methine, one aliphatic methine, two cyano, one C-methyl carbon and three carbons of trimethylsilyl in the ¹³C-nmr spectrum, and exhibited absorption of cyano group at 2239 cm⁻¹ in the ir spectrum. The elemental analysis indicated the molecular formula C₁₃H₁₇N₃O₂Si. Thus, the structure of 5'a was assigned as 2-cyano-2-methyl-2,3-dihydro-7-trimethylsiloxyfuro[2,3-*b*]pyridinium cyanide.

Scheme 4



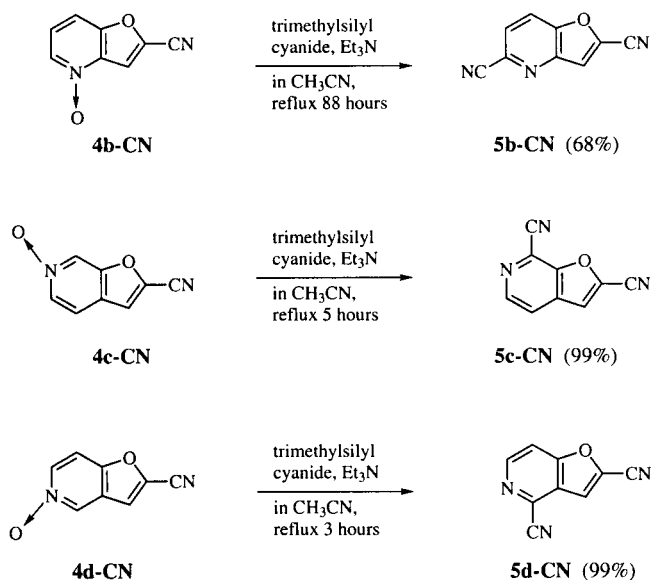
Chlorination of compounds 4a-d-Me and 4b-d-CN with phosphorus oxychloride gave 4-chloro-2-methylfuro[2,3-*b*]- (6a-Me, 71%) from 4a-Me, 5-chloro-2-methylfuro[3,2-*b*]- (6'b-Me, 4%) and 7-chloro-2-methylfuro[3,2-*b*]- (6b-Me, 79%) from 4b-Me, 5-chloro-2-methylfuro[2,3-*c*]- (6'c-Me, 3%) and 7-chloro-2-methylfuro[2,3-*c*]- (6c-Me, 60%) from 4c-Me, 4-chloro-2-methylfuro[3,2-*c*]- (6d-Me, 61%) from 4d-Me, 5-chloro-

Scheme 5



2-cyanofuro[3,2-*b*]- (**6b-CN**, 53%), 6-chloro-2-cyanofuro[3,2-*b*]- (**6''b-CN**, 3%) and 7-chloro-2-cyanofuro[3,2-*b*]- (**6'b-CN**, 14%) from **4b-CN**, 7-chloro-2-cyanofuro[2,3-*c*]- (**6c-CN**, 60%), 5-chloro-2-cyanofuro[2,3-*c*]- (**6'c-CN**, 5%) and 4-chloro-2-

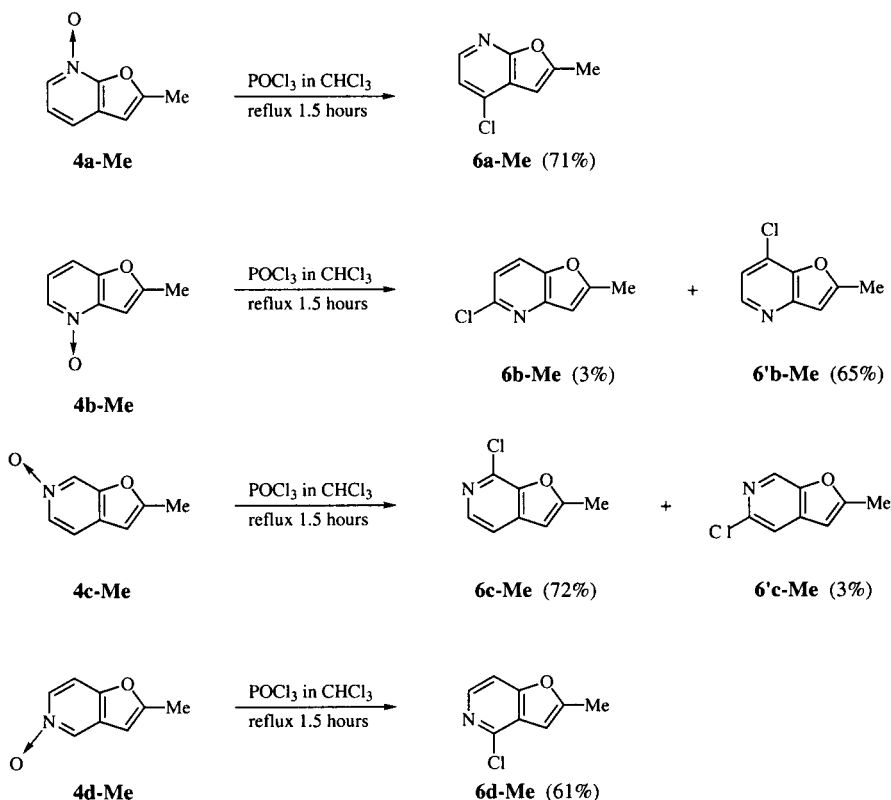
Scheme 6



cyanofuro[2,3-*c*]- (**6''c-CN**, 2%) from **4c-CN**, and 4-chloro-2-cyanofuro[3,2-*c*]pyridine (**6d-CN**, 67%) from **4d-CN**. Compounds **6a-Me**, **6b-Me**, **6'b-Me**, **6c-Me**, **6d-Me**, **6b-CN**, **6'b-CN**, **6c-CN** and **6d-CN** showed, in the ^1H -nmr spectra, signals of a furan proton, methyl protons and pyridine protons as a pair of doublets ($J = 4.6$ Hz for **6d-Me**, 5.2 Hz for **6'b-CN**, 5.3 Hz for **6a-Me**, **6'b-Me**, **6c-Me** and **6c-CN**, 5.9 Hz for **6d-CN**, 8.5 Hz for **6b-Me** and 8.8 Hz for **6b-CN**). From these facts, the position of the chlorine atom in each compound was determined. Compound **6'c-Me**, **6''b-CN**, **6'c-CN** and **6''c-CN** showed signals of the pyridine protons as two singlets, and the position of the chlorine atom in **6'c-Me** and **6'c-CN** was determined as the 5-position, that in **6''b-CN** as the 6-position, and that in **6''c-CN** as the 4-position.

Acetoxylation of the N-oxides **4a-d-Me** and **4b-d-CN** afforded somewhat complex results; **4a-Me** yielded 6-acetoxy-2-methylfuro[2,3-*b*]- (**7a-Me**, 70%) and 2,3-diacetoxy-2-methyl-2,3-dihydrofuro[2,3-*b*]pyridine (**8**, 10%), **4b-Me** gave 3-acetoxy-2-methylfuro[3,2-*b*] (**9b**, 64%) and 2-acetoxymethylfuro[3,2-*b*]pyridine (**10b**, 34%), **4c-Me** gave 3-acetoxy-2-methylfuro[2,3-*c*]- (**9c**, 55%) and 2-acetoxymethylfuro[2,3-*c*]pyridine (**10c**, 28%), **4d-Me** gave 2-methylfuro[3,2-*c*]pyridin-4(5*H*)-one (**11d-Me**, 52%) [5], **4b-CN** gave 5-acetoxy-2-cyanofuro[3,2-*b*]- (**7b-CN**, 25%) and 6-acetoxy-2-cyanofuro[3,2-*b*]pyridine (**7'b**, 4%), **4c-CN** gave 2-cyanofuro[2,3-*c*]pyridin-7(6*H*)-one (**11c-CN**, 72%), and **4d-CN** gave 2-cyanofuro[3,2-*c*]pyridin-4(5*H*)-one (**11d-CN**, 64%). The position of the acetoxy group in **7a-Me** (C-6) and **7b-CN** (C-5) was confirmed by the ^1H -nmr spectra showing signals of a furan proton as a singlet and the pyridine protons as a pair of doublets ($J = 8.0$ Hz for **7a-Me**, 9.1 Hz for **7b-CN**). Compound **7'b** showed in its ^1H -nmr spectrum signals of a furan proton and two pyridine protons with small coupling constants (H-3; d, $J = 0.9$ Hz, H-5; d, $J = 2.1$ Hz, H-7; dd, $J = 0.9, 2.1$ Hz). The structure of **8** was determined from the elemental analysis and the ^1H -nmr spectrum exhibiting signals of three pyridine protons at δ 8.20 (dd), 7.73 (dd) and 6.95 (dd), two acetoxy methyls at δ 2.14 and 2.04, singlet of an aliphatic methylene at δ 6.35, and a singlet of C-methyl protons at δ 1.88. The ^1H -nmr spectra of **9b** and **9c** showed signals of three pyridine protons (δ 8.50 (dd), 7.64 (dd) and 7.17 (dd) for **9b**, and 8.75 (s), 8.31 (d) and 7.29 (d) for **9c**), an acetoxy methyl (δ 2.43 for **9b**, and 2.41 for **9c**) and a singlet of C-methyl (δ 2.43 for **9b**, and 2.39 for **9c**). The structures of compound **10b** and **10c** were determined from the ^1H -nmr spectra, in which signals of an acetoxy methyl (δ 2.15 for **10b** and **10c**), a methylene (δ 5.25 for **10b** and **10c**), three pyridine protons (δ 8.55 (dd), 7.75 (ddd) and 7.24 (dd) for **10b**, and 8.88 (s), 8.43 (d) and 7.52 (d) for **10c**) and a furan proton (δ 6.98 for **10b**, and 6.80 for **10c**) were exhibited. The lactam structure of com-

Scheme 7

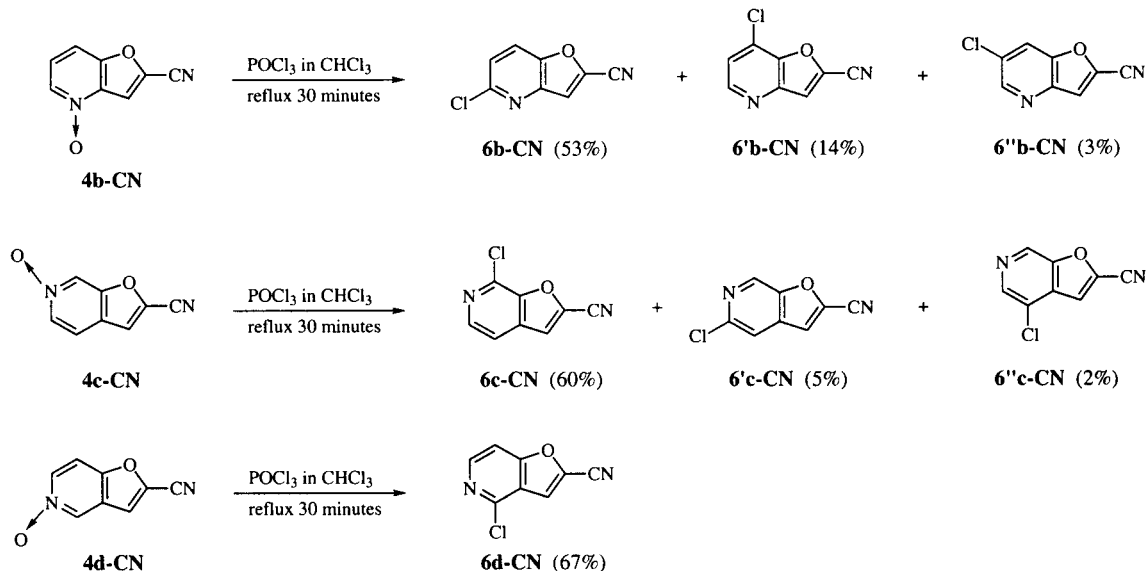


pound **11c-CN** and **11d-CN** was confirmed from the ir spectrum of each compound showing absorption of lactam carbonyl at 1683 cm^{-1} for **11c-CN** and 1696 cm^{-1} for **11d-CN**, and the ^1H -nmr spectrum showing signals of two pyridine protons as a pair of doublet (δ 7.43 and 6.70 for **11c-CN**, and 7.54 and 6.76 for **11d-CN**) and a furan proton

as a singlet (δ 7.68 for **11c-CN**, and 7.80 for **11d-CN**) respectively.

Formation of compounds having a cyano, a chloro or an acetoxy substituent at the pyridine carbon and furopyridones **11d-Me**, **11c-CN** and **11d-CN** is interpreted by the well known mechanism for the cyanation, chlorination and

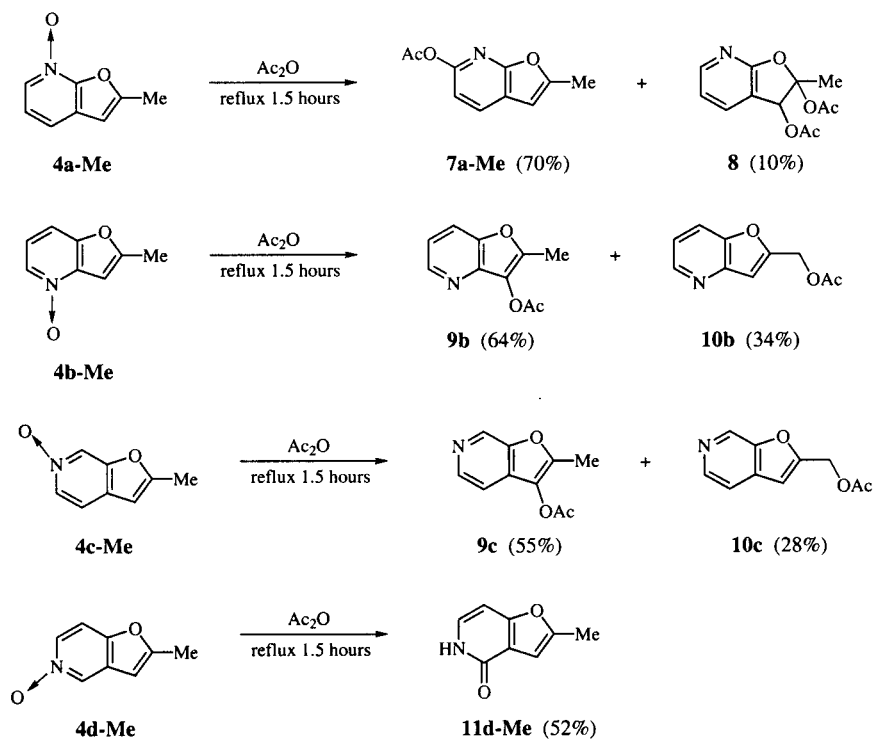
Scheme 8



acetoxylation of the *N*-oxides of pyridine, quinoline and isoquinoline [6]. Formation of the compounds acetoxy-
lated at the furan ring or the C-methyl group at 2-position **9b**, **9c**, **10b** and **10c** can be interpreted by the mechanism
previously postulated by us [7].

the 2-position is much decreased by its electron with-
drawing effect, and the cyanation, chlorination and ace-
toxylation of the *N*-oxides of 2-methylfuropyridines are
virtually not affected by the substituent, while, the
2-cyano group of the *N*-oxides of 2-cyanofuropyridines

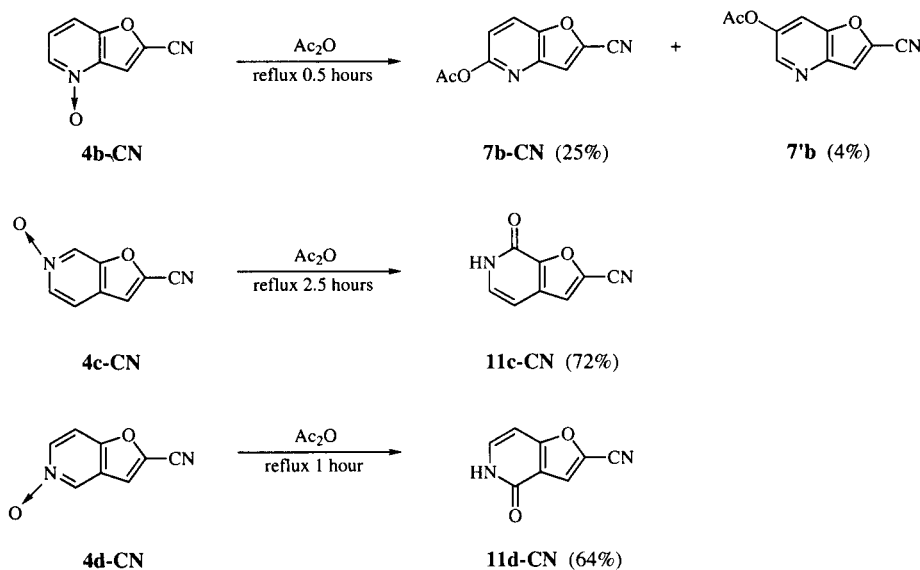
Scheme 9



Thus, this research has demonstrated that the reaction
of an electrophile (bromination and nitration) at the
furan moiety in furopyridines having a cyano group at

inhibits the attack of chloride or acetate anion at the 2-
position, in comparison with those of unsubstituted
furopyridines [8].

Scheme 10



EXPERIMENTAL

Melting points were determined by using a Yanagimoto micro melting point apparatus and are uncorrected. The ir spectra were taken on a JASCO FT/IR 7300 spectrometer. The nmr spectra were recorded on a JEOL A-400 or MAC-FX (90 MHz) instrument with tetramethylsilane as an internal reference in deuteriochloroform. The mass spectra were obtained by using JEOL JMS-OISG-2 spectrometer.

General Procedure for Bromination of 2-Methylfuropyridines **1a-Me** to **1d-Me**.

To a solution of 2-methylfuropyridine **1a-Me**, **1b-Me**, **1c-Me** or **1d-Me** (124 mg, 0.93 mmole) in dichloromethane (3 ml) at -15° was added 520 mg (3.3 mmoles) of bromine in 2 ml of dichloromethane dropwise with stirring. After the addition was complete, the mixture was stirred for 7 hours for **1a-Me** (5 hours for **1b-Me**, 20 hours for **1d-Me**) at room temperature. In the case of **1c-Me** the reaction mixture was refluxed for 20 hours. The solvent was removed under reduced pressure to give an orange mass, which was treated with 10% sodium hydroxide solution (10 ml) and extracted with ether three times. The ether extracts were combined, dried (magnesium sulfate) and evaporated to give a solid mass. The residue was purified by chromatography on a silica gel column eluting with hexane-ethyl acetate (9:1) to give 3-bromo-2-methylfuro[2,3-*b*]-**2a** (97 mg, 49%) from **1a-Me**, -[3,2-*b*]-**2b** (86 mg, 45%) and **1b-Me** (5 mg, 4%) from **1b-Me**, -[2,3-*c*]-**2c** (113 mg, 57%) and **1c-Me** (46 mg, 37%) from **1c-Me**, and -[3,2-*c*]-pyridine **2d** (92 mg, 47%) from **1d-Me**.

Compound **2a**.

This compound had bp $90-110^{\circ}$ (bath temperature)/25 mm Hg, colorless oil; ir (neat): 3069, 2920, 2850, 1643, 1603, 1550, 1463, 1399, 1378, 1233, 1049, 977, 772, 748 cm^{-1} ; ^1H -nmr: δ 8.16 (dd, $J = 5.0, 1.6$ Hz, 1H, H-6), 7.62 (dd, $J = 7.5, 1.6$ Hz, 1H, H-4), 7.12 (dd, $J = 7.5, 5.0$ Hz, 1H, H-5), 2.39 (s, 3H, 2-Me); ms: m/z (relative intensity) 213 ($\text{M}^+ + 2$, 96), 212 (39), 211 (M^+ , 100), 210 (32), 132 (48), 104 (51); hrms: 210.9620; M^+ , Calcd. for $\text{C}_8\text{H}_6\text{NOBr}$: 210.9632.

Anal. Calcd. for $\text{C}_8\text{H}_6\text{NOBr}$: C, 45.31; H, 2.85; N, 6.61. Found: C, 45.75; H, 2.84; N, 6.34.

Compound **2b**.

This compound had mp $42-46^{\circ}$ (from ether, colorless crystals); ir (potassium bromide): 3069, 3056, 3035, 3019, 2982, 2922, 2848, 1610, 1572, 1558, 1415, 1265, 1235, 1226, 1170, 1055, 982, 917, 800, 772 cm^{-1} ; ^1H -nmr: δ 8.54 (dd, $J = 4.7, 1.1$ Hz, 1H, H-5), 7.65 (dd, $J = 8.2, 1.1$ Hz, 1H, H-7), 7.19 (dd, $J = 8.2, 4.7$ Hz, 1H, H-6), 2.53 (s, 3H, 2-Me).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{NOBr}$: C, 45.31; H, 2.85; N, 6.61. Found: C, 45.31; H, 2.90; N, 6.53.

Compound **2c**.

This compound had mp $60-63^{\circ}$ (from ether, colorless crystals); ir (potassium bromide): 2925, 2854, 1637, 1601, 1467, 1426, 1253, 1182, 1159, 1056, 911, 820 cm^{-1} ; ^1H -nmr: δ 8.75 (d, $J = 0.8, 1\text{H}$, H-7), 8.45 (d, $J = 5.2$ Hz, 1H, H-5), 7.38 (dd, $J = 5.2, 0.8$ Hz, 1H, H-4), 2.52 (s, 3H, 2-Me).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{NOBr}$: C, 45.31; H, 2.85; N, 6.61. Found: C, 45.61; H, 2.98; N, 6.35.

Compound **2d**.

This compound had mp $35-38^{\circ}$ (from ether, colorless crystals); ir (neat): 3059, 2963, 2923, 2854, 1634, 1607, 1585, 1457, 1446, 1436, 1285, 1259, 1184, 1157, 1050, 1029, 970, 866, 824, 815 cm^{-1} ; ^1H -nmr: δ 8.75 (d, $J = 0.8$ Hz, 1H, H-4), 8.50 (d, $J = 5.6$ Hz, 1H, H-6), 7.33 (dd, $J = 5.6, 0.8$ Hz, 1H, H-7), 2.49 (s, 3H, 2-Me); ms: m/z (relative intensity) 213 ($\text{M}^+ + 2$, 91), 212 (49), 211 (M^+ , 100), 210 (37), 132 (97); hrms: 210.9637; M^+ , Calcd. for $\text{C}_8\text{H}_6\text{NOBr}$: 210.9632.

Anal. Calcd. for $\text{C}_8\text{H}_6\text{NOBr}$: C, 45.31; H, 2.85; N, 6.61. Found: C, 45.47; H, 3.03; N, 6.25.

General Procedure for Bromination of 2-Cyanofuropyridines **1a-CN** to **1d-CN**.

To a stirred solution of **1a-CN**, **1b-CN**, **1c-CN** or **1d-CN** (50 mg, 0.35 mmole) in carbon tetrachloride (5 ml) at -15° was added a solution of bromine (168 mg, 1.05 mmoles) in carbon tetrachloride (1.7 ml) during 10 minutes. After being stirred for 16 hours at room temperature, the mixture was refluxed for 2.5 hours. The mixture was cooled, evaporated, treated with 10% sodium hydroxide solution and extracted with chloroform. Evaporation of the dried chloroform extract afforded the starting compound (**1a-CN**, 45 mg, 88%; **1b-CN**, 42 mg, 84%; **1c-CN**, 40 mg, 80%; **1d-CN**, 40 mg, 80%), which was identified by the ir and ^1H -nmr spectra.

General Procedure for Nitration of 2-Methylfuropyridines **1a-d-Me** and 2-Cyanofuropyridines **1a-d-CN**.

Sulfuric acid (0.4 ml) was added to the 2-methyl- **1a-d-Me** or 2-cyanofuropyridines **1a-d-CN** (105 mg, 0.79 mmole) at -15° during 5 minutes. To this solution was added a mixture of 0.3 ml of sulfuric acid and 1.0 ml of fuming nitric acid (d, 1.50) at $0-5^{\circ}$. After being stirred for 30 minutes at room temperature, the mixture was treated with ice, basified with sodium bicarbonate, extracted with ethyl acetate (5 times). Evaporation of the dried extract from 2-methylfuropyridines **1a-Me**, **1b-Me** and **1d-Me** afforded almost a negligible amount of residue. The residue from **1c-Me** was recrystallized from ether-acetone to give 10 mg (7%) of 3-nitro-2-methylfuro[2,3-*c*]pyridine **3c**. Evaporation of the dried extract from **1a-CN**, **1b-CN**, **1c-CN** and **1d-CN** afforded the starting compound in 33%, 56%, 63% and 39%, respectively, which were identified by comparison of the ir and ^1H -nmr spectra.

Compound **3c**.

This compound had mp $97-102^{\circ}$ (colorless crystals); ir (potassium bromide): 2925, 2854, 1608, 1596, 1509, 1419, 1389, 1332, 1254, 1178, 1161, 941, 839, 825 cm^{-1} ; ^1H -nmr: δ 8.90 (d, $J = 0.9$ Hz, 1H, H-7), 8.63 (d, $J = 5.3$ Hz, 1H, H-5), 8.05 (dd, $J = 5.3, 0.9$ Hz, 1H, H-4), 3.00 (s, 3H, 2-Me).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_2\text{O}_3$: C, 53.94; H, 3.39; N, 15.72. Found: C, 54.03; H, 3.50; N, 15.68.

General Procedure for the Preparation of the *N*-oxide of 2-Methylfuro[2,3-*b*]- **4a-Me**, -[3,2-*b*]- **4b-Me**, -[2,3-*c*]- **4c-Me** and -[3,2-*c*]pyridines **4d-Me**.

A mixture of **1a-Me**, **1b-Me**, **1c-Me** or **1d-Me** (1.11 g, 8.3 mmoles) and *m*-chloroperbenzoic acid (75% purity, 2.5 g, 10.0 mmoles) in chloroform (20 ml) was stirred at room temperature for 16 hours (40 hours for **1a-Me**). The reaction mixture was filtered slowly with an alumina (basic, 100 g) pad to remove the acidic compounds. The filtrate was evaporated to give a solid mass which was purified by distillation or sublimation under

reduced pressure to afford **4a-Me** (1.01 g, 81%) from **1a-Me**, **4b-Me** (1.21 g, 98%) from **1b-Me**, **4c-Me** (1.21 g, 98%) from **1c-Me** and **4d-Me** (1.16 g, 94%) from **1d-Me**.

Compound **4a-Me**.

This compound had mp 140-145° (colorless crystals, bp 145-150° (bath temperature)/0.1 mm Hg); ir (potassium bromide): 3119, 3098, 3083, 2968, 2925, 2853, 1611, 1469, 1456, 1440, 1251, 1204, 1056, 918, 820, 728 cm⁻¹; ¹H-nmr: δ 8.07 (dd, J = 6.2, 1.2 Hz, 1H, H-6), 7.36 (dd, J = 7.9, 1.2 Hz, 1H, H-4), 7.05 (dd, J = 7.9, 6.2 Hz, 1H, H-6), 6.42 (q, J = 1.2 Hz, 1H, H-3), 2.48 (d, J = 1.2 Hz, 3H, 2-Me).

Anal. Calcd. for C₈H₇NO₂: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.42; H, 4.66; N, 9.45.

Compound **4b-Me**.

This compound had mp 107-111° (colorless crystals, bp 130-140° (bath temperature)/0.1 mm Hg); ir (potassium bromide): 3134, 2961, 2923, 2853, 1619, 1593, 1467, 1439, 1269, 1246, 1209, 1049, 937, 867, 783, 765 cm⁻¹; ¹H-nmr: δ 8.15 (dd, J = 6.5, 0.8 Hz, 1H, H-5), 7.36 (dd, J = 8.2, 0.8 Hz, 1H, H-7), 7.08 (dd, J = 8.2, 6.5 Hz, 1H, H-6), 6.87 (q, J = 0.9 Hz, 1H, H-3), 2.53 (d, J = 0.9 Hz, 3H, 2-Me).

Anal. Calcd. for C₈H₇NO₂: C, 64.42; H, 4.73; N, 9.39. Found: C, 63.97; H, 4.85; N, 9.30.

Compound **4c-Me**.

This compound had mp 143-147° (colorless crystals, sublimed at 130-140° (bath temperature)/0.1 mm Hg); ir (potassium bromide): 3119, 3097, 2924, 2854, 1671, 1599, 1459, 1293, 1159, 1126, 988, 919, 857, 843, 782 cm⁻¹; ¹H-nmr: δ 8.50 (d, J = 1.5 Hz, 1H, H-7), 8.10 (dd, J = 6.7, 1.5 Hz, 1H, H-5), 7.31 (d, J = 6.7 Hz, 1H, H-4), 6.45 (q, J = 1.1 Hz, 1H, H-3), 2.50 (d, J = 1.1 Hz, 3H, 2-Me).

Anal. Calcd. for C₈H₇NO₂: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.64; H, 4.86; N, 9.42.

Compound **4d-Me**.

This compound had mp 166-171° (colorless crystals, sublimed at 140-150° (bath temperature)/0.1 mm Hg); ir (potassium bromide): 3118, 3096, 2925, 2854, 1603, 1453, 1198, 1164, 1129, 927, 848, 786 cm⁻¹; ¹H-nmr: δ 8.45 (d, J = 2.1 Hz, 1H, H-4), 8.12 (dd, J = 7.0, 2.1 Hz, 1H, H-6), 7.29 (d, J = 7.0 Hz, 1H, H-7), 6.38 (q, J = 0.9 Hz, 1H, H-3), 2.49 (d, J = 0.9 Hz, 3H, 2-Me).

Anal. Calcd. for C₈H₇NO₂: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.47; H, 4.82; N, 9.43.

General Procedure for the *N*-Oxidation of 2-Cyanofuro[2,3-*b*]-**1a-CN**, -[3,2-*b*]-**1b-CN**, -[2,3-*c*]-**1c-CN** and -[3,2-*c*]pyridines **1d-CN**.

A mixture of **1a-CN**, **1b-CN**, **1c-CN** or **1d-CN** (410 mg, 2.8 mmoles) and *m*-chloroperbenzoic acid (75% purity, 1.75 g, 7.0 mmoles) in dichloromethane (20 ml) was stirred at room temperature for 18 hours (in the case of **1a-CN**, the reaction mixture was refluxed for 18 hours after being stirred at room temperature for 20 hours). The reaction mixture was filtered slowly with an alumina (basic, 50 g) pad to remove the acidic compounds. The filtrate was evaporated to give a solid mass which was purified by recrystallization from ether-acetone for **4b-CN** (418 mg, 92%) and **4c-CN**·1/2H₂O (412 mg, 86%) and from ether-methanol for **4d-CN** (177 mg, 39%). The residue (330 mg, 80%) from the reaction of **1a-CN** was identified as the starting compound by comparison of the ir spectrum.

Compound **4b-CN**.

This compound had mp 188-191° (colorless crystals); ir (potassium bromide): 3124, 3099, 3030, 2238, 1610, 1576, 1461, 1431, 1361, 1270, 1250, 1216, 1152, 1060, 1047, 947, 892, 782 cm⁻¹; ¹H-nmr: δ 8.29 (dd, J = 6.3, 0.7 Hz, 1H, H-5), 7.85 (d, J = 1.0 Hz, 1H, H-3), 7.50 (ddd, J = 8.8, 1.0, 0.7 Hz, 1H, H-7), 7.40 (dd, J = 8.8, 6.3 Hz, 1H, H-6).

Anal. Calcd. for C₈H₄N₂O: C, 60.01; H, 2.52; N, 17.49. Found: C, 59.61; H, 2.39; N, 17.16.

Compound **4c-CN**.

This compound had mp 185-189° (colorless crystals); ir (potassium bromide): 3142, 3111, 3076, 3041, 2231, 1637, 1567, 1481, 1445, 1308, 1177, 1134, 933, 880, 861, 821 cm⁻¹; ¹H-nmr: δ 8.62 (dd, J = 1.5, 1.2 Hz, 1H, H-7), 8.20 (dd, J = 6.8, 1.5 Hz, 1H, H-5), 7.54 (d, J = 6.8 Hz, 1H, H-4), 7.45 (d, J = 1.2 Hz, 1H, H-3).

Anal. Calcd. for C₈H₄N₂O·1/2H₂O: C, 56.81; H, 2.98; N, 16.56. Found: C, 56.87; H, 2.59; N, 16.31.

Compound **4d-CN**.

This compound had mp 164-167° (colorless crystals); ir (potassium bromide): 3136, 3118, 3106, 3070, 3039, 2242, 1630, 1437, 1209, 1166, 1135, 1119, 948, 896, 851, 828, 785 cm⁻¹; ¹H-nmr: δ 8.65 (dd, J = 1.8, 0.6 Hz, 1H, H-4), 8.32 (dd, J = 7.3, 1.8 Hz, 1H, H-6), 7.51 (ddd, J = 7.3, 0.9, 0.6 Hz, 1H, H-7), 7.43 (d, J = 0.9 Hz, 1H, H-3).

Anal. Calcd. for C₈H₄N₂O: C, 60.01; H, 2.52; N, 17.49. Found: C, 59.71; H, 2.53; N, 17.17.

General Procedure for Cyanation of **4a-Me**, **4b-Me**, **4c-Me** and **4d-Me** with Trimethylsilyl Cyanide.

A mixture of *N*-oxide **4a-d-Me** (120 mg, 0.8 mmoles), trimethylsilyl cyanide (0.17 ml, 1.2 mmoles) and triethylamine (0.26 ml, 2.0 mmoles) in acetonitrile (3 ml) was stirred and refluxed for 15 hours (21 hours for **4c-Me**). After evaporation of the solvent, the reaction mixture was dissolved in chloroform, washed with water and dried over magnesium sulfate. The residue of the chloroform solution from **4b-Me**, **4c-Me** and **4d-Me** was recrystallized from acetone-ether to give 5-cyano-2-methylfuro[3,2-*b*]-**5b-Me** (106 mg, 84%), 7-cyano-2-methylfuro[2,3-*c*]-**5c-Me** (112 mg, 87%) and 4-cyano-2-methylfuro[3,2-*c*]pyridine **5d-Me** (117 mg, 91%) respectively. The residue from **4a-Me** was chromatographed on a silica gel column eluting with hexane-ethyl acetate (9:1) to give 46 mg (36%) of 6-cyano-2-methylfuro[2,3-*b*]pyridine **5a-Me** and 58 mg (21%) of 2-cyano-2-methyl-2,3-dihydro-7-trimethylsilylfuro[2,3-*b*]pyridinium cyanide **5'a**.

Compound **5a-Me**.

This compound had mp 126-130° (from acetone, colorless crystals); ir (potassium bromide): 3107, 2923, 2853, 2231, 1608, 1590, 1581, 1398, 1387, 1358, 1290, 1272, 1220, 1157, 1106, 969, 912, 852, 775 cm⁻¹; ¹H-nmr: δ 7.90 (d, J = 7.9 Hz, 1H, H-4), 7.58 (d, J = 7.9 Hz, 1H, H-5), 7.53 (q, J = 0.9 Hz, 1H, H-3), 2.56 (d, J = 0.9 Hz, 3H, 2-Me).

Anal. Calcd. for C₉H₆N₂O: C, 68.35; H, 3.82; N, 17.71. Found: C, 68.33; H, 3.91; N, 17.76.

Compound **5'a**.

This compound had mp 143-147° (from acetone-ether, colorless crystals); ir (potassium bromide): 3128, 3106, 3061, 3027,

2995, 2962, 2901, 2239, 1639, 1589, 1428, 1290, 1250, 1194, 1178, 1127, 1105, 1035, 991, 854, 761 cm^{-1} ; ^1H -nmr: δ 8.22 (d, $J = 6.3$ Hz, 1H, H-6), 7.42 (dd, $J = 7.8, 6.3$ Hz, 1H, H-5), 7.37 (d, $J = 7.8$ Hz, 1H, H-4), 3.23 and 3.13 (AB-q, $J = 14.0$ Hz, 2H, H-3 and H-3'), 1.74 (s, 3H, 2-Me), 0.150 (s, 9H, SiMe_3); ^{13}C -nmr: δ 139.2 (s, C-7a), 138.8 (d, C-6), 128.2 (s, Si-CN), 127.6 (d, C-5), 126.9 (d, C-4), 120.3 (s, C-3a), 111.2 (s, 2-CN), 69.1 (s, C-2), 45.7 (t, C-3), 29.2 (q, 2-Me), 0.92 (q, 3 $\times$ C, SiMe_3).

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_2\text{Si}$: C, 56.70; H, 6.22; N, 15.26. Found: C, 56.95; H, 6.15; N, 15.13.

Compound 5b-Me.

This compound had mp 130–133° (colorless crystals); ir (potassium bromide): 3115, 3072, 3048, 3000, 2965, 2925, 2853, 2231, 1605, 1419, 1268, 1223, 1162, 1155, 946, 925, 845, 817 cm^{-1} ; ^1H -nmr: δ 7.74 and 7.65 (AB-q, $J = 8.5$ Hz, 2H, H-6 and H-7), 6.67 (s, 1H, H-3), 2.57 (s, 3H, 2-Me).

Anal. Calcd. for $\text{C}_9\text{H}_6\text{N}_2\text{O}$: C, 68.35; H, 3.82; N, 17.71. Found: C, 68.51; H, 3.91; N, 17.69.

Compound 5c-Me.

This compound had mp 124–128° (colorless crystals); ir (potassium bromide): 3137, 3082, 3009, 2961, 2922, 2855, 2234, 1606, 1442, 1423, 1262, 1182, 1144, 1064, 992, 925, 861 cm^{-1} ; ^1H -nmr: δ 8.44 (d, $J = 5.0$ Hz, 1H, H-5), 7.65 (d, $J = 5.0$ Hz, 1H, H-4), 6.57 (q, $J = 1.1$ Hz, 1H, H-3), 2.60 (d, $J = 1.2$ Hz, 3H, 2-Me).

Anal. Calcd. for $\text{C}_9\text{H}_6\text{N}_2\text{O}$: C, 68.35; H, 3.82; N, 17.71. Found: C, 68.57; H, 3.93; N, 17.77.

Compound 5d-Me.

This compound had 115–119° (colorless crystals); ir (potassium bromide): 3185, 3145, 3104, 3086, 3002, 2963, 2927, 2854, 2236, 1600, 1572, 1434, 1385, 1274, 1239, 1187, 1058, 992, 923, 830 cm^{-1} ; ^1H -nmr: δ 8.51 (d, $J = 5.6$ Hz, 1H, H-6), 7.54 (dd, $J = 5.6, 0.9$ Hz, 1H, H-7), 6.66 (qn, $J = 0.9$ Hz, 1H, H-3), 2.57 (d, $J = 0.9$ Hz, 3H, 2-Me).

Anal. Calcd. for $\text{C}_9\text{H}_6\text{N}_2\text{O}$: C, 68.35; H, 3.82; N, 17.71. Found: C, 68.32; H, 4.16; N, 17.63.

General Procedure for Cyanation of 4b-CN, 4c-CN and 4d-CN with Trimethylsilyl Cyanide.

A mixture of *N*-oxide 4b-d-CN (500 mg, 3.1 mmol), trimethylsilyl cyanide (1.12 g, 11.3 mmol) and triethylamine (440 mg, 4.3 mmol) in acetonitrile (50 ml) was stirred and refluxed for 5 hours (88 hours for 4b-CN). After evaporation of the solvent, the reaction mixture was dissolved in chloroform, washed with water and dried over magnesium sulfate. The residue of the chloroform solution was recrystallized from ether to give 2,5-dicyanofuro[3,2-*b*] 5b-CN (361 mg, 68%), 2,7-dicyanofuro[2,3-*c*] 5c-CN (520 mg, 99%) and 2,4-dicyanofuro[3,2-*c*]pyridine 5d-Me (522 mg, 99%) respectively.

Compound 5b-CN.

This compound had mp 165–168° (colorless crystals); ir (potassium bromide): 3147, 3094, 2241, 1600, 1571, 1448, 1407, 1308, 1257, 1215, 1155, 1132, 946, 935, 853 cm^{-1} ; ^1H -nmr: δ 8.06 (dd, 8.5, 0.9 Hz, 1H, H-7), 7.88 (d, $J = 8.5$ Hz, 1H, H-6), 7.74 (d, $J = 0.9$ Hz, 1H, H-3).

Anal. Calcd. for $\text{C}_9\text{H}_3\text{N}_3\text{O}$: C, 63.91; H, 1.78; N, 24.84. Found: C, 64.00; H, 1.91; N, 24.66.

Compound 5c-CN.

This compound had mp 119–123° (colorless crystals); ir (potassium bromide): 3139, 3115, 3084, 2240, 1609, 1448, 1409, 1325, 1266, 1196, 1069, 936, 884 cm^{-1} ; ^1H -nmr: δ 8.71 (d, $J = 5.3$ Hz, 1H, H-5), 7.91 (d, $J = 5.3$ Hz, 1H, H-4), 7.60 (s, 1H, H-3).

Anal. Calcd. for $\text{C}_9\text{H}_3\text{N}_3\text{O}$: C, 63.91; H, 1.78; N, 24.84. Found: C, 63.98; H, 1.97; N, 24.81.

Compound 5d-CN.

This compound had mp 126–128° (colorless crystals); ir (potassium bromide): 3137, 3116, 3085, 2237, 1603, 1581, 1557, 1446, 1426, 1311, 1286, 1270, 1208, 1164, 1055, 1007, 945, 871, 849 cm^{-1} ; ^1H -nmr: δ 8.82 (d, $J = 5.6$ Hz, 1H, H-6), 7.84 (d, $J = 5.6$ Hz, 1H, H-7), 7.75 (s, 1H, H-3).

Anal. Calcd. for $\text{C}_9\text{H}_3\text{N}_3\text{O}$: C, 63.91; H, 1.78; N, 24.84. Found: C, 63.76; H, 1.80; N, 24.66.

General Procedure for Chlorination of 4a-Me, 4b-Me, 4c-Me, 4d-Me, 4b-CN, 4c-CN and 4d-CN with Phosphorus Oxychloride.

A mixture of 4a-d-Me (112 mg, 0.75 mmol) or 4b-d-CN (119.5 mg, 0.75 mmol), phosphorus oxychloride (1 ml, 11.3 mmol) and absolute chloroform (0.5 ml, ethanol in commercial chloroform was removed by treatment with sulfuric acid, phosphorus pentoxide and potassium carbonate and distillation) was refluxed for 1.5 hours for 4a-d-Me (0.5 hours for 4b-d-CN). After being cooled, the mixture was treated with ice-water and chloroform, basified with sodium bicarbonate and separated the layers. The chloroform layer was dried over magnesium sulfate and evaporated. Further processing of the residue is indicated in a subsequent paragraph.

4-Chloro-2-methylfuro[2,3-*b*]pyridine 6a-Me.

The residue (100 mg) from 4a-Me was distilled under reduced pressure to give 90 mg (71%) of 6a-Me as a colorless oil of bp 120–140° (bath temperature)/20 mm Hg; ir (neat): 3184, 3120, 3084, 3019, 2968, 2925, 2853, 1602, 1578, 1468, 1440, 1371, 1358, 1241, 1169, 1148, 1012, 945, 935, 858, 815, 803, 765, 716 cm^{-1} ; ^1H -nmr: δ 8.12 (d, $J = 5.3$ Hz, 1H, H-6), 7.18 (d, $J = 5.3$ Hz, 1H, H-5), 6.48 (q, $J = 1.3$ Hz, 1H, H-3), 2.51 (d, $J = 1.3$ Hz, 3H, 2-Me); ms: m/z (relative intensity) 169 ($M^+ + 2$, 39), 168 ($M^+ + 1$, 36), 167 (M^+ , 100), 166 (84), 131 (21), 104 (31); hrms: 167.0136; M^+ , Calcd. for $\text{C}_8\text{H}_6\text{NOCl}$: 167.0138.

Anal. Calcd. for $\text{C}_8\text{H}_6\text{NOCl}$: C, 57.33; H, 3.61; N, 8.36. Found: C, 57.15; H, 3.54; N, 8.67.

5-Chloro-2-methyl- 6b-Me and 7-Chloro-2-methylfuro[3,2-*b*]pyridine 6'b-Me.

The residue (105 mg) from 4b-Me was chromatographed on a silica gel column eluting with hexane-ethyl acetate (95:5) to afford compound 6b-Me (4 mg, 3%) and 6'b-Me (82 mg, 65%).

Compound 6b-Me.

This compound had mp 90–92° (from ether, colorless crystals); ir (potassium bromide): 3119, 3074, 2964, 2919, 2854, 1598, 1561, 1413, 1290, 1265, 1198, 1186, 1151, 1093, 937, 907, 828, 802, 695 cm^{-1} ; ^1H -nmr: δ 7.60 (dd, $J = 8.5, 0.9$ Hz, 1H, H-7), 7.13 (d, $J = 8.5$ Hz, 1H, H-6), 6.54 (qn, $J = 0.9$ Hz, 1H, H-3), 2.51 (d, $J = 0.9$ Hz, 3H, 2-Me); ms: m/z (relative intensity) 169 ($M^+ + 2$, 30), 168 ($M^+ + 1$, 23), 167 (M^+ , 100), 166 (46), 104 (50); hrms: 167.0141; M^+ , Calcd. for $\text{C}_8\text{H}_6\text{NOCl}$: 167.0138.

Anal. Calcd. for C_8H_6NOCl : C, 57.33; H, 3.61; N, 8.36. Found: C, 56.95; H, 3.58; N, 8.09.

Compound **6'b-Me**.

This compound had bp 105–115° (bath temperature)/18 mm Hg (colorless oil); ir (neat): 3117, 3049, 3009, 2958, 2923, 2854, 1607, 1557, 1439, 1393, 1348, 1241, 1226, 1169, 967, 926, 956, 817, 762, 719 cm^{-1} ; 1H -nmr: δ 8.34 (d, $J = 5.3$ Hz, 1H, H-5), 7.14 (d, $J = 5.3$ Hz, 1H, H-6), 6.64 (q, $J = 0.9$ Hz, 1H, H-3), 2.54 (d, $J = 0.9$ Hz, 3H, 2-Me); ms: m/z (relative intensity) 169 ($M^+ + 2$, 33), 168 ($M^+ + 1$, 23), 167 (M^+ , 100), 166 (47), 138 (16), 132 (15), 104 (62); hrms: 167.0136; M^+ , Calcd. for C_8H_6NOCl : 167.0138.

Anal. Calcd. for C_8H_6NOCl : C, 57.33; H, 3.61; N, 8.36. Found: C, 57.90; H, 3.54; N, 8.49.

7-Chloro-2-methyl- **6c-Me** and 5-chloro-2-methylfuro[2,3-*c*]pyridine **6'c-Me**.

The residue (120 mg) from **4c-Me** was chromatographed on a silica gel column eluting with hexane-ethyl acetate (97:3) to afford compound **6'c-Me** (4 mg, 3%) and **6c-Me** (91 mg, 72%).

Compound **6c-Me**.

This compound had mp 88–90° (from ether, colorless crystals); ir (potassium bromide): 3115, 3068, 2957, 2918, 2853, 1610, 1600, 1560, 1439, 1424, 1280, 1209, 1200, 1170, 1068, 969, 929, 839, 726 cm^{-1} ; 1H -nmr: δ 8.13 (d, $J = 5.3$ Hz, 1H, H-5), 7.35 (d, $J = 5.3$ Hz, 1H, H-7), 6.47 (q, $J = 0.9$ Hz, 1H, H-3), 2.55 (d, $J = 0.9$ Hz, 3H, 2-Me).

Anal. Calcd. for C_8H_6NOCl : C, 57.33; H, 3.61; N, 8.36. Found: C, 57.55; H, 3.89; N, 8.36.

Compound **6'c-Me**.

This compound had bp 100–120° (bath temperature)/30 mm Hg (colorless oil); 1H -nmr: δ 8.49 (s, 1H, H-7), 7.41 (s, 1H, H-4), 6.39 (q, $J = 0.9$ Hz, 1H, H-3), 2.52 (d, $J = 0.9$ Hz, 1H, 2-Me); ms: m/z (relative intensity) 169 ($M^+ + 2$, 37), 168 ($M^+ + 1$, 25), 167 (M^+ , 100), 166 (39), 149 (34), 138 (16), 132 (15), 104 (11); hrms: 167.0145; M^+ , Calcd. for C_8H_6NOCl : 167.0138.

Anal. Calcd. for C_8H_6NOCl : C, 57.33; H, 3.61; N, 8.36. Found: C, 56.98; H, 3.47; N, 8.56.

4-Chloro-2-methylfuro[3,2-*c*]pyridine **6d-Me**.

The residue (120 mg) from **4d-Me** was distilled under reduced pressure to give compound **6d-Me** (78 mg, 61%), colorless oil of bp 115–125° (bath temperature)/20 mm Hg; ir (neat): 3121, 3059, 2963, 2923, 2854, 1603, 1569, 1431, 1282, 1271, 1179, 1003, 952, 932, 816, 800, 757, 721 cm^{-1} ; 1H -nmr: δ 8.18 (d, $J = 4.6$ Hz, 1H, H-6), 7.29 (dd, $J = 4.6, 0.9$ Hz, 1H, H-7), 6.48 (qn, $J = 0.9$ Hz, 1H, H-3), 2.50 (d, $J = 0.9$ Hz, 1H, 2-Me); ms: m/z (relative intensity) 169 ($M^+ + 2$, 32), 168 ($M^+ + 1$, 32), 167 (M^+ , 100), 166 (68), 132 (33); hrms: 167.0140; M^+ , Calcd. for C_8H_6NOCl : 167.0138.

Anal. Calcd. for C_8H_6NOCl : C, 57.33; H, 3.61; N, 8.36. Found: C, 57.34; H, 3.56; N, 7.98.

5-Chloro-2-cyano- **6b-CN**, 7-Chloro-2-cyano- **6'b-CN** and 6-Chloro-2-cyanofuro[3,2-*b*]pyridine **6''b-CN**.

The residue (105 mg) was chromatographed on a silica gel column eluting with chloroform to give 70 mg (53%) of **6b-CN**, 19 mg (14%) of **6'b-CN** and 4 mg (3%) of **6''b-CN**.

Compound **6b-CN**.

This compound had mp 175–177° (from acetone-ether, colorless crystals); ir (potassium bromide): 3135, 3074, 2235, 1579,

1548, 1407, 1265, 1195, 1139, 1104, 944, 851, 833, 705 cm^{-1} ; 1H -nmr: δ 7.89 (dd, $J = 8.8, 0.9$ Hz, 1H, H-7), 7.60 (d, $J = 0.9$ Hz, 1H, H-3), 7.47 (d, $J = 8.8$ Hz, 1H, H-6).

Anal. Calcd. for $C_8H_3N_2OCl$: C, 53.81; H, 1.69; N, 15.69. Found: C, 53.85; H, 1.83; N, 15.74.

Compound **6'b-CN**.

This compound had mp 105–108° (from ether-hexane, colorless crystals); ir (potassium bromide): 3138, 3087, 2238, 1600, 1564, 1544, 1479, 1380, 1243, 1234, 1130, 971, 937, 860, 844, 824, 693 cm^{-1} ; 1H -nmr: δ 8.62 (d, $J = 5.2$ Hz, 1H, H-5), 7.71 (s, 1H, H-3), 7.49 (d, $J = 5.2$ Hz, 1H, H-6).

Anal. Calcd. for $C_8H_3N_2OCl$: C, 53.81; H, 1.69; N, 15.69. Found: C, 53.81; H, 1.77; N, 15.58.

Compound **6''b-CN**.

This compound had mp 98–102° (from hexane, colorless crystals); ir (potassium bromide): 3139, 3032, 2235, 1599, 1568, 1461, 1409, 1382, 1254, 1179, 1082, 1052, 954, 847, 802, 771 cm^{-1} ; 1H -nmr: δ 8.70 (d, $J = 2.0$ Hz, 1H, H-5), 7.91 (dd, $J = 2.0, 0.9$ Hz, 1H, H-7), 7.87 (d, $J = 0.9$ Hz, 1H, H-3); ms: m/z (relative intensity) 180 ($M^+ + 2$, 34), 179 ($M^+ + 1$, 12), 178 (M^+ , 100), 150 (20), 135 (12), 132 (10); hrms: 177.9928; M^+ , Calcd. for $C_8H_3N_2OCl$: 177.9934.

Anal. Calcd. for $C_8H_3N_2OCl$: C, 53.81; H, 1.69; N, 15.69. Found: C, 53.91; H, 1.85; N, 15.48.

7-Chloro-2-cyano- **6c-CN**, 5-Chloro-2-cyano- **6'c-CN** and 4-Chloro-2-cyanofuro[2,3-*c*]pyridine **6''c-CN**.

The residue (100 mg) from **4c-CN** was chromatographed on a silica gel column eluting with chloroform to give **6c-CN** (80 mg, 60%), **6'c-CN** (7 mg, 5%) and **6''c-CN** (3 mg, 2%).

Compound **6c-CN**.

This compound had mp 131–134° (from hexane-ether, colorless needles); ir (potassium bromide): 3122, 3104, 3071, 2239, 1603, 1575, 1448, 1404, 1184, 1069, 974, 939, 865, 823 cm^{-1} ; 1H -nmr: δ 8.35 (d, $J = 5.3$ Hz, 1H, H-5), 7.61 (d, $J = 5.3$ Hz, 1H, H-4), 7.55 (s, 1H, H-3).

Anal. Calcd. for $C_8H_3N_2OCl$: C, 53.81; H, 1.69; N, 15.69. Found: C, 53.68; H, 1.70; N, 15.59.

Compound **6'c-CN**.

This compound had mp 144–147° (from acetone-ether, colorless needles); ir (potassium bromide): 3126, 3102, 3079, 3024, 2241, 1603, 1578, 1551, 1445, 1388, 1273, 1251, 1184, 1171, 1069, 943, 921, 883, 723 cm^{-1} ; 1H -nmr: δ 8.78 (dd, $J = 0.8, 0.6$ Hz, 1H, H-7), 7.67 (d, $J = 0.8$ Hz, 1H, H-3), 7.44 (d, $J = 0.6$ Hz, 1H, H-4).

Anal. Calcd. for $C_8H_3N_2OCl$: C, 53.81; H, 1.69; N, 15.69. Found: C, 53.70; H, 1.80; N, 15.51.

Compound **6''c-CN**.

This compound had mp 112–117° (from ether, colorless crystals); ir (potassium bromide): 3114, 3089, 2243, 1579, 1556, 1456, 1403, 1259, 1176, 1109, 957, 947, 882, 835 cm^{-1} ; 1H -nmr: δ 8.91 (d, $J = 0.6$ Hz, 1H, H-7), 8.56 (s, 1H, H-5), 7.58 (d, $J = 0.6$ Hz, 1H, H-3); ms: m/z (relative intensity) 180 ($M^+ + 2$, 33), 179 ($M^+ + 1$, 12), 178 (M^+ , 100), 143 (35), 123 (15), 115 (16), 88 (47); hrms: 177.9925; M^+ , Calcd. for $C_8H_3N_2OCl$: 177.9934.

4-Chloro-2-cyanofuro[3,2-*c*]pyridine **6d-CN**.

The residue (103 mg) from **4d-CN** was recrystallized from ether to afford 89 mg (67%) of compound **6d-CN**, colorless

needles of mp 115-116°; ir (potassium bromide): 3140, 3105, 3086, 3071, 2236, 1601, 1576, 1437, 1419, 1301, 1263, 1188, 961, 939, 836, 817 cm^{-1} ; ^1H -nmr: δ 8.47 (d, J = 5.9 Hz, 1H, H-6), 7.58 (d, J = 1.2 Hz, 1H, H-3), 7.49 (dd, J = 5.9, 1.2 Hz, 1H, H-7).

Anal. Calcd. for $\text{C}_8\text{H}_3\text{N}_2\text{OCl}$: C, 53.81; H, 1.69; N, 15.69. Found: C, 53.57; H, 1.73; N, 15.50.

General Procedure for Acetoxylation of **4a-Me**, **4b-Me**, **4c-Me**, **4d-Me**, **4b-CN**, **4c-CN** and **4d-CN** with Acetic Anhydride.

A mixture of **4a-d-Me** (112 mg, 0.75 mmole) or **4b-d-CN** (119.5 mg, 0.75 mmole) in acetic anhydride (2 ml) was refluxed for 1.5 hours (2.5 hours for **4b-CN**, 1 hour for **4c-CN** and **4d-CN**). After removal of the excess of acetic anhydride under reduced pressure, the reaction mixture was treated with water, basified with sodium bicarbonate and extracted with chloroform. The chloroform extract was dried over magnesium sulfate and evaporated. Further processing of the residue is indicated in a subsequent paragraph.

6-Acetoxy-2-methyl- **7a-Me** and *trans*-2,3-Diacetyl-2-methyl-2,3-dihydrofuro[2,3-*b*]pyridine **8**.

The residue (145 mg) from **4a-Me** was chromatographed on a silica gel column eluting with hexane-ethyl acetate (97:3) to give 102 mg (70%) of **7a-Me** and 25 mg (10%) of **8**.

Compound **7a-Me**.

This compound had bp 105-125° (bath temperature)/0.1 mm Hg (colorless oil); ir (neat): 3115, 2924, 2855, 1770, 1593, 1459, 1401, 1371, 1294, 1272, 1194, 1162, 1110, 1021, 984, 899, 830, 765 cm^{-1} ; ^1H -nmr: δ 7.84 (d, J = 8.0 Hz, 1H, H-4), 6.94 (d, J = 8.0 Hz, 1H, H-5), 6.38 (q, J = 0.9 Hz, 1H, H-3), 2.48 (d, J = 0.9 Hz, 3H, 2Me), 2.35 (s, 3H, -Ac).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.78; H, 4.77; N, 7.21.

Compound **8**.

This compound had mp 137-142° (sublimated at 110-120°(bath temperature)/0.1 mm Hg, colorless crystals); ir (potassium bromide): 3068, 3035, 3010, 2923, 2858, 1742, 1605, 1426, 1386, 1302, 1248, 1234, 1197, 1111, 1090, 1036, 947, 896, 802 cm^{-1} ; ^1H -nmr: δ 8.20 (dd, J = 5.3, 1.8 Hz, 1H, H-6), 7.73 (dd, J = 7.3, 1.8 Hz, 1H, H-4), 6.95 (dd, J = 7.3, 5.3 Hz, 1H, H-5), 6.35 (s, 1H, H-3), 2.14 (s, 3H, -Ac), 2.04 (s, 3H, -Ac), 1.88 (s, 3H, 2-Me).

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_5$: C, 57.37; H, 5.10; N, 5.58. Found: C, 57.60; H, 5.10; N, 5.45.

3-Acetoxy-2-methyl- **9b** and 2-Acetoxyethylfuro[3,2-*b*]pyridine **10b**.

The residue (165 mg) from **4b-Me** was chromatographed on a silica gel column eluting with hexane-ethyl acetate (95:5) to yield **9b** (92 mg, 64%) and **10b** (48 mg, 34%).

Compound **9b**.

This compound had bp 130-140° (bath temperature)/0.01 mm Hg (colorless oil); ir (neat): 3122, 3072, 2926, 2851, 1741, 1587, 1482, 1431, 1372, 1272, 1201, 1154, 935, 805 cm^{-1} ; ^1H -nmr: δ 8.50 (dd, J = 5.0, 1.2 Hz, 1H, H-5), 7.64 (dd, J = 8.5, 1.2 Hz, 1H, H-7), 7.17 (dd, J = 8.5, 5.0 Hz, 1H, H-6), 2.43 (s, 6H, -Ac and 2-Me); ms: m/z (relative intensity) 191 (M^+ , 1), 165 (64), 149 (61), 147 (35), 122 (71), 95 (85), 94 (100), 79 (29), 77 (29); hrms: 191.0583. M^+ , Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: 191.0582.

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.48; H, 4.71; N, 7.01.

Compound **10b**.

This compound had bp 135-140° (bath temperature)/0.1 mm Hg (colorless oil); ir (neat): 3120, 3024, 2926, 2851, 1747, 1604, 1414, 1378, 1365, 1236, 1172, 1143, 1030, 938, 818, 794 cm^{-1} ; ^1H -nmr: δ 8.55 (dd, J = 4.7, 1.5 Hz, 1H, H-5), 7.75 (ddd, 8.5, 1.5, 0.5 Hz, 1H, H-7), 7.24 (dd, J = 8.5, 4.7 Hz, 1H, H-6), 6.98 (d, J = 0.5 Hz, 1H, H-3), 5.25 (s, 2H, 2- CH_2OAc), 2.15 (s, 3H, -Ac); ms: m/z (relative intensity) 191 (M^+ , 18), 149 (46), 132 (35), 120 (19), 103 (19); hrms: 191.0578; M^+ , Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: 191.0582.

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.49; H, 4.68; N, 6.98.

3-Acetoxy-2-methyl- **9c** and 2-Acetoxyethylfuro[2,3-*c*]pyridine **10c**.

The residue (150 mg) from **4c-Me** was chromatographed on a silica gel column eluting with hexane-ethyl acetate (95:5) to give **9c** (80 mg, 55%) and **10c** (40 mg, 28%).

Compound **9c**.

This compound had bp 145-155° (bath temperature)/0.1 mm Hg (colorless oil); ir (neat): 3036, 2996, 2925, 2854, 1756, 1606, 1584, 1434, 1374, 1224, 1200, 1155, 1040, 959, 946, 888, 801 cm^{-1} ; ^1H -nmr: δ 8.75 (s, 1H, H-7), 8.31 (d, 5.0 Hz, 1H, H-5), 7.29 (d, J = 5.0 Hz, 1H, H-4), 2.42 (s, 3H, -Ac), 2.39 (s, 3H, 2-Me); ms: m/z (relative intensity) 191 (M^+ , 13), 149 (52), 148 (17), 132 (11), 120 (9), 103 (6); hrms: 191.0587; M^+ , Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: 191.0582.

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.50; H, 4.61; N, 7.52.

Compound **10c**.

This compound had bp 140-150°(bath temperature)/0.1 mm Hg (colorless oil); ir (neat): 3054, 2926, 1749, 1608, 1472, 1428, 1367, 1189, 1143, 1032, 830 cm^{-1} ; ^1H -nmr: δ 8.88 (s, 1H, H-7), 8.43 (d, J = 5.3 Hz, 1H, H-5), 7.52 (d, J = 5.3 Hz, 1H, H-4), 6.80 (s, 1H, H-3), 5.25 (s, 2H, 2- CH_2OAc), 2.15 (s, 3H, -Ac).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.87; H, 4.68; N, 7.22.

2-Methylfuro[3,2-*c*]pyridin-4(5H)-one **11d-Me**.

The residue (100 mg) from **4d-Me** was recrystallized from acetone to give 58 mg (52%) of compound **11d-Me** which was identified by comparison of the ir and ^1H -nmr spectra with those of authentic sample [5].

5-Acetoxy-2-cyano- **7b-CN** and 6-Acetoxy-2-cyanofuro[3,2-*b*]pyridine **7'b**.

The residue (90 mg) from **4b-CN** was chromatographed on a silica gel column eluting with chloroform to give 37 mg (25%) of **7b-CN** and 6 mg (4%) of **7'b**.

Compound **7b-CN**.

This compound had mp 147-151° (from ether-hexane, colorless crystals); 3113, 3105, 3083, 2923, 2853, 2234, 1762, 1553, 1415, 1369, 1210, 1114, 941, 906, 863, 839 cm^{-1} ; ^1H -nmr: δ 7.96 (dd, J = 9.1, 0.9 Hz, 1H, H-7), 7.59 (d, J = 0.9 Hz, 1H, H-3), 7.21 (d, J = 9.1 Hz, 1H, H-6), 2.39 (s, 3H, Ac).

Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_3$: C, 59.41; H, 2.99; N, 13.86. Found: C, 59.30; H, 3.15; N, 13.64.

Compound 7'b.

This compound had mp 88-92° (from hexane, colorless crystals); ir (potassium bromide): 3066, 2924, 2854, 2238, 1774, 1606, 1579, 1485, 1373, 1274, 1202, 1137, 1015, 935, 905, 877 cm^{-1} ; ^1H -nmr: δ 8.54 (d, $J = 2.1$ Hz, 1H, H-5), 7.76 (dd, $J = 2.1$, 0.9 Hz, 1H, H-7), 7.66 (d, $J = 0.9$ Hz, 1H, H-3), 2.40 (s, 3H, -Ac); ms: m/z (relative intensity) 202 (M^+ , 20), 161 (15), 160 (100), 120 (17), 118 (18), 117 (8), 87 (45), 85 (100), 83 (100); hrms: 202.0368; M^+ , Calcd. for $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_3$: 202.0378.

2-Cyanofuro[2,3-*c*]pyridin-7(6*H*)-one 11c-CN.

The residue (100 mg) from 4c-CN was recrystallized from acetone to give compound 11c-CN (86 mg, 72%), mp 295-298° (colorless crystals); ir (potassium bromide): 3114, 3055, 3009, 2965, 2898, 2237, 1683, 1616, 1519, 1483, 1369, 1293, 1264, 1200, 1132, 955, 856, 779 cm^{-1} ; ^1H -nmr (deuteriomethanol): δ 7.68 (s, 1H, H-3), 7.30 (d, $J = 6.7$ Hz, 1H, H-4), 6.70 (d, $J = 6.7$ Hz, 1H, H-5).

Anal. Calcd. for $\text{C}_8\text{H}_4\text{N}_2\text{O}_2$: C, 60.01; H, 2.52; N, 17.49. Found: C, 59.89; H, 2.82; N, 17.12.

2-Cyanofuro[3,2-*c*]pyridin-4(5*H*)-one 11d-CN.

The residue (95 mg) from 4d-CN was recrystallized from acetone to give 76 mg (64%) of 11d-CN, colorless crystals of mp 251-255°; ir (potassium bromide): 3300-2755 (broad), 2236, 1696, 1581, 1428, 1220, 1163, 1066, 952, 859, 785 cm^{-1} ; ^1H -nmr

(deuteriomethanol): δ 7.80 (d, $J = 0.9$ Hz, 1H, H-3), 7.54 (d, $J = 7.3$ Hz, 1H, H-6), 6.76 (dd, $J = 7.3$, 0.9 Hz, 1H, H-7).

Anal. Calcd. for $\text{C}_8\text{H}_4\text{N}_2\text{O}_2$: C, 60.01; H, 2.52; N, 17.49. Found: C, 59.60; H, 2.70; N, 17.09.

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