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Condensed Heteroaromatic Ring Systems. VII.[1] Synthesis of Thienopyridines, Thienopyrimidines, and Furopyridines from *o*-Substituted N-Heteroarylacetylenes

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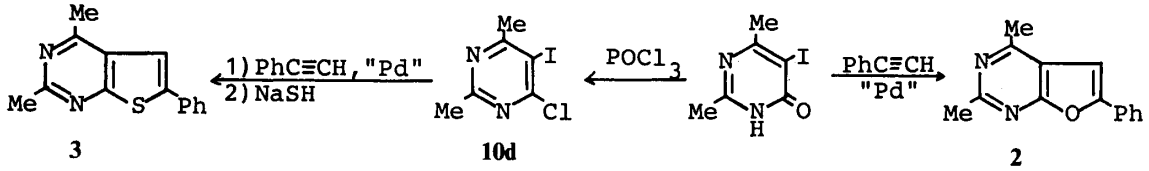
The cross-coupling reaction of 2-chloro-3-iodo- and 4-chloro-3-iodopyridines with phenylacetylene in the presence of dichlorobis(triphenylphosphine)palladium occurred at the 3-position. The 3-ethynylpyridines containing an adjacent chloro group were convertible to thienopyridines by treatment with sodium hydrosulfide. Similarly, various thieno[2,3-*d*]pyrimidines were synthesized from 4-chloro-5-iodopyrimidines. One-step synthesis of furopyridines by the palladium-catalyzed reaction of iodohydroxypyridines with terminal acetylenes is also described.

Keywords——chloroiodopyridine; chloroiodopyrimidine; hydroxyiodopyridine; acetylene; palladium-catalyzed reaction; thienopyridine; thienopyrimidine; furopyridine

We have previously reported that heating of 5-iodo-2,6-dimethyl-4(3*H*)-pyrimidinone (**1**) with phenylacetylene in the presence of dichlorobis(triphenylphosphine)palladium, followed by spontaneous cyclization of the intermediate, 2,6-dimethyl-5-phenylethynyl-4(3*H*)-pyrimidinone, gave 2,4-dimethyl-6-phenylfuro[2,3-*d*]pyrimidine (**2**).[2] Reaction of 4-chloro-5-iodo-2,6-dimethylpyrimidine (**10d**) derived from **1** by treatment with phenylacetylene, followed by treatment of the product with sodium hydrosulfide, was also reported to give 2,4-dimethyl-6-phenylthieno[2,3-*d*]pyrimidine (**3**).[2] As an extension of the findings mentioned above, the title compounds were synthesized in satisfactory yields.

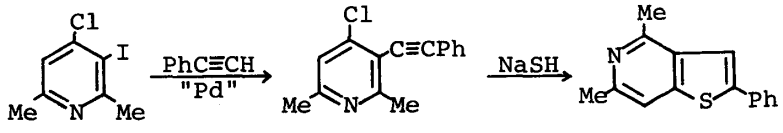


3 10d 2

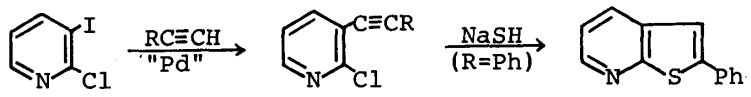
Chart 1

Synthesis of Thienopyridines

Firstly, the synthesis of two kinds of thienopyridines, which were expected to be obtainable by the above-mentioned method, was examined. When 4-chloro-3-iodo-2,6-dimethylpyridine (**4**) and 2-chloro-3-iodopyridine (**7**) were allowed to react with phenylacetylene in the presence of the palladium catalyst, the iodo substituents on **4** and **7** were replaced selectively to afford 4-chloro-2,6-dimethyl-3-phenylethynylpyridine (**5**) and 2-chloro-3-phenylethynylpyridine (**8a**) in good yields, respectively. On treatment with sodium hydrosulfide, these phenylethynylpyridines (**5** and **8a**) were transformed into 4,6-dimethyl-2-phenylthieno[3,2-*c*]pyridine (**6**) and 2-phenylthieno[2,3-*b*]pyridine (**9**). Based on these results, 3-iodopyridines containing a chloro substituent at the adjacent positions should be suitable substrates for the synthesis of such thienopyridines.



4 5 6



7 8a,b 9

a: R=Ph

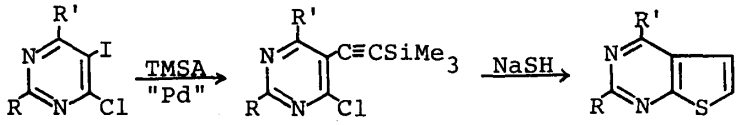
b: $R=SiMe_3$

Chart 2

Synthesis of Thieno[2,3-*d*]pyrimidines

Secondly, in order to synthesize thienopyridines containing no substituent on the five-membered ring, the synthetic utility of trimethylsilylacetylene (TMSA) was examined. The reaction of **7** with TMSA proceeded smoothly to give 2-chloro-3-(trimethylsilylethynyl)-pyridine (**8b**), but on treatment with sodium hydrosulfide in ethanol under conditions similar to the above, **8b** did not undergo thiophene-cyclization, though the reason for this is not clear.[3)]

In contrast to the above reaction, the thiophene-cyclization of 4-chloro-5-(trimethylsilylethynyl)pyrimidines (**11a—h**) gave satisfactory results. Namely, 4-chloro-5-iodopyrimidine (**10a**) and its alkyl homologs (**10b—e**) reacted with TMSA to give the 5-trimethylsilylethynyl compounds (**11a—e**) which, unlike **8b**, were converted smoothly to thieno[2,3-*d*]pyrimidines (**12a—e**) under the conventional conditions. 2-Methylthiothieno-[2,3-*d*]pyrimidines (**12f, g**) and 4-methoxy-2-methylthieno[2,3-*d*]pyrimidine (**12h**) were also prepared in this manner. Accordingly, this method appears to be of wide applicability to 4-chloro-5-iodopyrimidines.



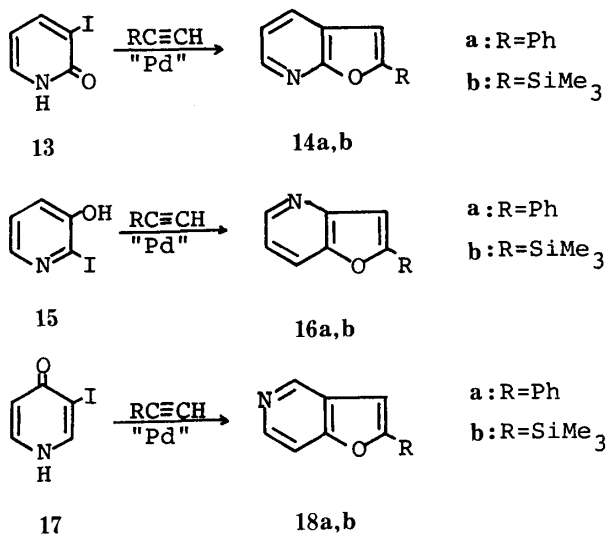
10a—h 11a—h 12a—h

a: R=H, R′=H
b: R=H, R′=Me
c: R=Me, R′=H
d: R=Me, R′=Me
e: R=iso-Pr, R′=Me
f: R=SMe, R′=Me
g: R=SMe, R′=H
h: R=Me, R′=OMe

Chart 3

Synthesis of Furopyridines

Finally, one-step preparation of furopyridines was carried out. When a triethylamine solution of 3-iodo-2-pyridone (**13**) and phenylacetylene was heated in a sealed tube in the presence of the palladium catalyst, 2-phenylfuro[2,3-*b*]pyridine (**14a**) was directly obtained in good yield. Similarly, 2-phenylfuro[3,2-*b*]pyridine (**16a**) and 2-phenylfuro[3,2-*c*]pyridine (**18a**) were prepared from 2-iodo-3-hydroxypyridine (**15**) and 3-iodo-4-pyridone (**17**), respectively. These halohydroxypyridines (**13**, **15**, and **17**) also reacted with TMSA to give the corresponding 2-trimethylsilylfuropyridines (**14b**, **16b**, and **18b**), although the yields of the products were low.



13 14a,b

15 16a,b

17 18a,b

Chart 4

Experimental

All melting points and boiling points are uncorrected. Infrared (IR) spectra were measured with a JASCO IRA-1 spectrometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were taken at 60 MHz with a JEOL JMN-PMX 60 spectrometer. Chemical shifts are expressed in δ (ppm) values. The following abbreviations are used: s = singlet, d = doublet, and m = multiplet.

2,6-Dimethyl-3-iodo-4(1*H*)-pyridone——A mixture of 2,6-dimethyl-4(1*H*)-pyridone (1.3 g, 10 mmol), NaOH (400 mg, 10 mmol), I_2 (2.60 g, 10 mmol), and H_2O (10 ml) was stirred at room temperature for 12 h. The resulting precipitate was collected, washed with H_2O, and recrystallized from MeOH to give colorless needles, mp 235—236 °C. Yield 1.6 g (64%). ^{1}H-NMR (CF_3COOH): 2.66 (3H, s), 2.93 (3H, s), 7.10 (1H, s). *Anal.* Calcd for C_7H_8INO: C, 33.76; H, 3.24; N, 5.63. Found: C, 33.58; H, 3.24; N, 5.39.

4-Chloro-2,6-dimethyl-3-iodopyridine——A mixture of 2,6-dimethyl-3-iodo-4(1*H*)-pyridone (2.5 g, 10 mmol) and $POCl_3$ (20 ml) was refluxed for 3 h. After removal of the excess $POCl_3$ under reduced pressure, the residue was poured onto ice. The mixture was made alkaline with K_2CO_3 and extracted with $CHCl_3$. The $CHCl_3$ extract was purified by SiO_2 column chromatography using C_6H_6 as an eluent. The crude product obtained from the C_6H_6 eluate was recrystallized from hexane to give colorless needles, mp 87—88 °C. Yield 2.2 g (83%). ^{1}H-NMR (CCl_4): 2.36 (3H, s), 2.70 (3H, s), 6.96 (1H, s). *Anal.* Calcd for C_7H_7ClIN: C, 31.43; H, 2.64; N, 5.24. Found: C, 31.52; H, 2.59; N, 5.31.

4-Chloro-2,6-dimethyl-3-phenylethynylpyridine (5)——A mixture of 4-chloro-3-iodo-2,6-dimethylpyridine (**4**) (2.67 g, 10 mmol), phenylacetylene (1.2 g, 12 mmol), $Pd(PPh_3)_2Cl_2$ (160 mg), CuI (80 mg), and Et_3N (10 ml) was heated at 60 °C for 24 h. After evaporation of the Et_3N, the residue was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was purified by SiO_2 column chromatography using C_6H_6 as an eluent. The product obtained from the C_6H_6 eluate was recrystallized from hexane to give colorless needles, mp 85—87 °C. Yield 1.7 g (70%). IR ($CHCl_3$) cm^{-1}: 2240. ^{1}H-NMR ($CDCl_3$): 2.50 (3H, s), 2.74 (3H, s), 7.70 (1H, s), 7.2—7.6 (5H, m). *Anal.* Calcd for $C_{15}H_{12}ClN$: C, 74.73; H, 5.02; N, 5.81. Found: C, 74.85; H, 5.13; N, 5.78.

4,6-Dimethyl-2-phenylthieno[3,2-*c*]pyridine (6)——An EtONa–EtOH solution [prepared from Na (100 mg, 4.4 mmol) and dry EtOH (5 ml)] was saturated with H_2S gas, and then **5** (600 mg, 2.5 mmol) was added to this solution. The mixture was heated in a sealed tube at 90 °C for 3 h. After removal of the EtOH, the residue was diluted with H_2O and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was recrystallized from hexane to give colorless needles, mp 114—115 °C. Yield 500 mg (80%). ^{1}H-NMR ($CDCl_3$): 2.60 (3H, s), 2.77 (3H, s), 7.3—7.9 (7H, m). *Anal.* Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.50; H, 5.36; N, 5.87.

2-Chloro-3-phenylethynylpyridine (8a)——A mixture of 2-chloro-3-iodopyridine[4] (**7**) (4.8 g, 20 mmol), phenylacetylene (2.5 g, 25 mmol), $Pd(PPh_3)_2Cl_2$ (300 mg), CuI (150 mg), and Et_3N (40 ml) was stirred at room temperature for 24 h. After removal of the Et_3N, the residue was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was purified by SiO_2 column chromatography using C_6H_6 as an eluent. The crude product obtained from the C_6H_6 eluate was recrystallized from hexane to give colorless prisms, mp 60—62 °C. Yield 3.0 g (70%). IR ($CHCl_3$) cm^{-1}: 2240. ^{1}H-NMR ($CDCl_3$): 7.1—7.7 (7H, m), 7.9—8.1 (1H, m). *Anal.* Calcd for $C_{13}H_8ClN$: C, 73.08; H, 3.77; N, 6.56. Found: C, 72.84; H, 3.74; N, 6.22.

2-Phenylthieno[2,3-*b*]pyridine (9)——An EtONa–EtOH solution [prepared from Na (230 mg, 10 mmol) and dry EtOH (10 ml)] was saturated with H_2S gas, and then **8a** (500 mg, 2.34 mmol) was added to this solution. The mixture was refluxed for 3 h. After removal of the EtOH, the residue was diluted with H_2O and extracted with $CHCl_3$. The

crude product obtained from the $CHCl_3$ extract was recrystallized from hexane to give pale yellow needles, mp 96—97 °C. Yield 340 mg (69%). ^{1}H-NMR ($CDCl_3$): 7.1—7.9 (7H, m), 7.9—8.1 (1H, m), 8.4—8.6 (1H, m). *Anal.* Calcd for $C_{13}H_9NS$: C, 73.90; H, 4.29; N, 6.63. Found: C, 73.85; H, 4.16; N, 6.39.

5-Iodo-4(3*H*)-pyrimidinone——A mixture of 4(3*H*)-pyrimidinone (1.44 g, 15 mmol), I_2 (3.81 g, 15 mmol), NaOH (800 mg, 20 mmol), and H_2O (15 ml) was stirred at 80 °C for 19 h. After neutralization of the mixture with AcOH, the resulting precipitate was recrystallized from acetone to give colorless scales, mp 240 °C (dec.) (lit.[5] mp 254—265 °C). Yield 1.87 g (56%). IR (KBr) cm^{-1}: 1630. ^{1}H-NMR (CF_3CO_2H): 8.21 (1H, s), 8.98 (1H, s). *Anal.* Calcd for $C_4H_3IN_2O$: C, 21.64; H, 1.36; N, 12.62. Found: C, 21.88; H, 1.20; N, 12.63.

5-Iodo-2-methyl-4(3*H*)-pyrimidinone——Iodine (7.61 g, 30 mmol) was added to a solution of 2-methyl-4(3*H*)-pyrimidinone (5.51 g, 50 mmol) in conc. HNO_3 (75 ml), and the mixture was heated at 80 °C for 6 h. After neutralization of the mixture with Na_2CO_3, the resulting precipitate was recrystallized from MeOH to give colorless prisms, mp 200—202 °C (dec.). Yield 4.94 g (46%). IR (KBr) cm^{-1}: 1650. ^{1}H-NMR (CF_3CO_2H): 2.43 (3H, s), 8.01 (1H, s). *Anal.* Calcd for $C_5H_5IN_2O$: C, 25.45; H, 2.14; N, 11.87. Found: C, 25.29; H, 2.08; N, 11.61.

5-Iodo-6-methyl-2-methylthio-4(3*H*)-pyrimidinone——A mixture of 6-methyl-2-methylthio-4(3*H*)-pyrimidinone (3.12 g, 20 mmol), I_2 (6.10 g, 24 mmol), NaOH (1.0 g, 25 mmol), and H_2O (15 ml) was heated at 80 °C for 13 h. After neutralization of the mixture with AcOH, the resulting precipitate was recrystallized from EtOH to give colorless scales, mp 198—199 °C (dec.). Yield 4.27 g (81%). IR (KBr) cm^{-1}: 1630. ^{1}H-NMR (CF_3CO_2H): 2.29 (3H, s), 2.45 (3H, s). *Anal.* Calcd for $C_6H_7IN_2OS$: C, 25.55; H, 2.50; N, 9.93; S, 11.36. Found: C, 25.62; H, 2.34; N, 9.89; S, 11.52.

5-Iodo-2-methylthio-4(3*H*)-pyrimidinone——A mixture of 2-methylthio-4(3*H*)-pyrimidinone (2.84 g, 20 mmol), I_2 (6.1 g, 24 mmol), NaOH (1.0 g, 25 mmol), and H_2O (15 ml) was heated at 80 °C for 7 h. After neutralization of the mixture with AcOH, the resulting precipitate was recrystallized from EtOH to give colorless prisms, mp 212—213 °C (dec.). Yield 4.54 g (84%). IR (KBr) cm^{-1}: 1650. ^{1}H-NMR (CF_3CO_2H): 2.49 (3H, s), 7.89 (1H, s). *Anal.* Calcd for $C_5H_5IN_2OS$: C, 22.40; H, 1.88; N, 10.45; S, 11.96. Found: C, 22.54; H, 1.71; N, 10.40; S, 11.98.

6-Chloro-5-iodo-2-methyl-4(3*H*)-pyrimidinone——A mixture of 6-chloro-2-methyl-4(3*H*)-pyrimidinone (7.23 g, 50 mmol), I_2 (14.98 g, 59 mmol), NaOH (2.4 g, 60 mmol), and H_2O (40 ml) was heated at 50 °C for 16 h. After neutralization of the mixture with AcOH, the resulting precipitate was recrystallized from EtOH to give colorless prisms, mp 251—252 °C (dec.). Yield 8.22 g (61%). IR (KBr) cm^{-1}: 1650. ^{1}H-NMR (CF_3CO_2H): 2.36 (3H, s). *Anal.* Calcd for $C_5H_4ClIN_2O$: C, 22.21; H, 1.49; N, 10.36. Found: C, 22.50; H, 1.40; N, 10.37.

4-Chloro-5-iodopyrimidines (10a, c, f, g, i) (General Procedure)——A mixture of a 5-iodo-4(3*H*)-pyrimidinone (10 mmol) and $POCl_3$ (5 ml) was refluxed for 0.5—3 h. After removal of excess $POCl_3$, the residue was poured into ice-water. The mixture was made alkaline with K_2CO_3 and extracted with $CHCl_3$. The $CHCl_3$ extract was purified by Al_2O_3 column chromatography using C_6H_6 as an eluent. The crude product obtained from the C_6H_6 eluate was recrystallized from hexane to give colorless prisms.

4-Methyl-[6] (**10b**), 2,4-dimethyl-[6] (**10d**), and 2-isopropyl-4-methyl-6-chloro-5-iodopyrimidine[7] (**10e**) were prepared according to the reported method.

4-Chloro-5-iodo-6-methoxy-2-methylpyrimidine (10h)——4,6-Dichloro-5-iodo-2-methylpyrimidine (**10i**) (1.44 g, 5 mmol) was added to an MeONa–MeOH solution [prepared from Na (120 mg, 5 mmol) and dry MeOH (25 ml)], and the mixture was stirred at room temperature for 24 h. After removal of the MeOH, the residue was diluted with H_2O and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was recrystallized from hexane to

TABLE I. 4-Chloro-5-iodopyrimidines (**10**)

No.	R	R′	Yield (%)	mp (°C)	^{1}H-NMR δ (ppm) (CCl_4)	Formula	Analysis (%) Calcd (Found)		
							C	H	N
10a	H	H	74	63—65	8.82 (1H, s) 8.92 (1H, s)	$C_4H_2ClIN_2$	19.98 (20.07	0.84 0.77	11.65 11.73)
10c	Me	H	82	77—77.5	2.62 (3H, s) 8.78 (1H, s)	$C_5H_4ClIN_2$	23.60 (23.73	1.58 1.47	11.01 10.76)
10f	MeS	Me	91	93—94	2.48 (3H, s) 2.67 (3H, s)	$C_6H_6ClIN_2S$	23.98 (24.05	2.01 1.84	9.32 9.35)
10g	MeS	H	91	63.5—64.5	2.52 (3H, s) 8.64 (1H, s)	$C_5H_4ClIN_2S$	20.96 (20.84	1.41 1.18	9.78 9.75)
10h	Me	MeO	84	82.5—83	2.53 (3H, s) 4.02 (3H, s)	$C_6H_6ClIN_2O$	25.33 (25.38	2.13 1.93	9.85 9.70)
10i	Me	Cl	87	90—91	2.63 (3H, s)	$C_5H_3Cl_2IN_2$	20.79 (20.97	1.05 0.91	9.70 9.73)

give colorless prisms. Yield 1.19 g.

4-Chloro-5-(trimethylsilylethynyl)pyrimidines (11) (General Procedure)——A mixture of a 4-chloro-5-iodopyrimidine (**10**) (10 mmol), TMSA (12 mmol), $Pd(PPh_3)_2Cl_2$ (0.2 mmol), CuI (0.4 mmol), and Et_3N (3 ml) was heated in a sealed tube at 80 °C for 12 h. The mixture was diluted with H_2O and extracted with ether. The ethereal extract was purified by SiO_2 column chromatography using ether–hexane (1 : 9) as an eluent. The crude product obtained from the ether–hexane (1 : 9) eluate was distilled under reduced pressure to give a colorless or pale yellow liquid, which was used in the next step without analysis.

Thieno[2,3-*d*]pyrimidines (12) (General Procedure)——An EtONa–EtOH solution [prepared from Na (350 mg, 15 mmol) and dry EtOH (20 ml)] was saturated with H_2S, and then **11** (5 mmol) was added to this solution. The mixture was refluxed for 1.5 h. After removal of the EtOH, the residue was diluted with H_2O and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by recrystallization from hexane or distillation under reduced pressure.

2-Phenylfuropyridines (14a, 16a, and 18a) (General Procedure)——A mixture of an iodohydroxypyridine (**13**,[9] **15**,[10] or **17**[9]) (2.21 g, 10 mmol), phenylacetylene (1.2 g, 12 mmol), $Pd(PPh_3)_2Cl_2$ (160 mg), CuI (80 mg), and Et_3N (5 ml)[11] was heated at 120 °C for 24 h. The mixture was diluted with H_2O and extracted with $CHCl_3$. The product obtained from the $CHCl_3$ extract was purified by SiO_2 column chromatography using $CHCl_3$ as an eluent. The crude product was recrystallized from hexane.

2-Phenylfuro[2,3-*b*]pyridine: Colorless needles, mp 90—91 °C (lit.[12] mp 91—91.5 °C). Yield 1.27 g (65%). ^{1}H-

Table II. 4-Chloro-5-(trimethylsilyl)ethynylpyrimidines (**11**)

No.	R	R′	Yield (%)	bp (mmHg)[a] [mp] (°C)	IR (neat) cm^{-1}	^{1}H-NMR δ (ppm) (CCl_4)
11a	H	H	70	90 (5)	2160	0.29 (9H, s), 8.66 (1H, s), 8.83 (1H, s)
11b	H	Me	70	95 (4)	2150	0.29 (9H, s), 2.63 (3H, s), 8.67 (1H, s)
11c	Me	H	77	90 (5)	2160	0.28 (9H, s), 2.67 (3H, s), 8.54 (1H, s)
11d	Me	Me	75	95 (5)	2140	0.28 (9H, s), 2.58 (3H, s), 2.61 (3H, s)
11e	iso-Pr	Me	83	100 (5)	2150	0.27 (9H, s), 1.28 (6H, d, J=7.0 Hz), 2.58 (3H, s), 2.7—3.3 (1H, m)
11f	MeS	Me	68	135 (4) [56—59]	2150	0.28 (9H, s), 2.51 (3H, s), 2.54 (3H, s)
11g	MeS	H	81	130 (4)	2150	0.27 (9H, s), 2.54 (3H, s), 8.40 (1H, s)
11h	Me	MeO	75	120 (5) [81—84]	2150	0.27 (9H, s), 2.54 (3H, s), 4.02 (3H, s)

a) Bath temperature.

Table III. Thieno[2,3-*d*]pyrimidines (**12**)

No.	R′	R	Yield (%)	mp (°C) [bp (mmHg)[a]]	Appearance	^{1}H-NMR δ (ppm) (CCl_4)
12a	H	H	95	51—52[b]	Scales	7.28 (1H, d, J=6.0 Hz), 7.49 (1H, d, J=6.0 Hz), 8.97 (1H, s), 9.05 (1H, s)
12b	Me	H	86	79.5—80.5	Scales	2.78 (3H, s), 7.36 (1H, d, J=6.0 Hz), 7.47 (1H, d, J=6.0 Hz), 8.88 (1H, s)
12c	H	Me	73	78—78.5[c]	Prisms	2.69 (3H, s), 7.15 (1H, d, J=6.0 Hz), 7.30 (1H, d, J=6.0 Hz), 8.88 (1H, s)
12d	Me	Me	79	79.5—80	Scales	2.71 (6H, s), 7.27 (2H, s)
12e	Me	iso-Pr	79	44—46 [130 (5)]	Prisms	1.35 (6H, d, J=7.0 Hz), 2.73 (3H, s), 2.8—3.5 (1H, m), 7.29 (2H, s)
12f	Me	MeS	66	81—82	Needles	2.56 (3H, s), 2.68 (3H, s), 7.18 (2H, s)
12g	H	MeS	69	75—76	Prisms	2.58 (3H, s), 7.16 (1H, d, J=6.0 Hz), 7.24 (1H, d, J=6.0 Hz), 8.82 (1H, s)
12h	MeO	Me	53	51—52.5 [90 (4)]	Prisms	2.63 (3H, s), 4.07 (3H, s), 7.21 (2H, s)

a) Bath temperature. *b*) Lit.[8] mp 50 °C. *c*) Lit.[8] mp 78 °C.

TABLE IV. Analytical Data for Thieno[2,3-*d*]pyrimidines (**12**)

No.	Formula	Calcd (%)				Found (%)			
		C	H	N	S	C	H	N	S
12a	$C_6H_4N_2S$	52.92	2.96	20.57	23.54	53.22	2.68	20.90	23.66
12b	$C_7H_6N_2S$	55.98	4.03	18.65	21.35	55.99	3.85	18.53	21.52
12c	$C_7H_6N_2S$	55.98	4.03	18.65	21.35	56.09	3.96	18.37	21.08
12d	$C_8H_8N_2S$	58.51	4.91	17.06	19.52	58.77	4.97	17.11	19.27
12e	$C_{10}H_{12}N_2S$	62.46	6.29	14.57	16.68	62.23	6.26	14.63	16.67
12f	$C_8H_8N_2S_2$	48.95	4.11	14.27	32.67	49.42	4.01	14.32	32.24
12g	$C_7H_6N_2S_2$	46.13	3.32	15.37	35.18	46.15	3.29	15.51	34.97
12h	$C_8H_8N_2OS$	53.32	4.47	15.54	17.79	53.57	4.28	15.76	17.92

NMR ($CDCl_3$): 7.1—7.6 (6H, m), 7.7—8.0 (2H, m), 8.2—8.4 (1H, m).

2-Phenylfuro[3,2-*b*]pyridine: Colorless prisms, mp 88—89 °C (lit.[13] mp 88—89 °C). Yield 1.48 g (76%). ^{1}H-NMR ($CDCl_3$): 7.0—8.1 (8H, m), 8.4—8.6 (1H, m).

2-Phenylfuro[3,2-*c*]pyridine: Colorless needles, mp 120—121 °C. Yield 1.37 g (70%). ^{1}H-NMR ($CDCl_3$): 7.05 (1H, s), 7.3—7.7 (4H, m), 7.8—8.0 (2H, m), 8.50 (1H, d, J=6.0 Hz), 8.95 (1H, m). *Anal.* Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 80.27; H, 4.55; N, 7.25.

2-Trimethylsilylfuropyridines (14b, 16b, and 18b) (General Procedure)——A mixture of a hydroxyiodopyridine (**13**,[9] **15**,[10] or **17**[9]) (1.1 g, 5 mmol), TMSA (750 mg, 7.5 mmol), $Pd(PPh_3)_2Cl_2$ (100 mg), CuI (50 mg), and Et_3N (3 ml)[11] was heated in a sealed tube at 120 °C for 24 h. The mixture was diluted with H_2O and extracted with ether. The ethereal extract was purified by SiO_2 column chromatography using $CHCl_3$ as an eluent. The crude product obtained from the $CHCl_3$ eluate was distilled under reduced pressure.

2-Trimethylsilylfuro[2,3-*b*]pyridine: Colorless liquid, bp 105—110 °C (16 mmHg). Yield 300 mg (32%). ^{1}H-NMR (CCl_4): 0.36 (9H, s), 6.87 (1H, s), 7.0—7.3 (1H, m), 7.7—7.9 (1H, m), 8.2—8.4 (1H, m). *Anal.* Calcd for $C_{10}H_{13}NOSi$: C, 62.78; H, 6.85; N, 7.32. Found: C, 62.55; H, 6.56; N, 7.33.

2-Trimethylsilylfuro[3,2-*b*]pyridine: Colorless liquid, bp 110—115 °C (16 mmHg). Yield 240 mg (25%). ^{1}H-NMR (CCl_4): 0.36 (9H, s), 6.9—7.3 (2H, m), 7.5—7.8 (2H, m), 8.4—8.6 (1H, m). *Anal.* Calcd for $C_{10}H_{13}NOSi$: C, 62.78; H, 6.85; N, 7.32. Found: C, 62.49; H, 6.62; N, 7.26.

2-Trimethylsilylfuro[3,2-*c*]pyridine: Colorless liquid, bp 90—95 °C (5 mmHg). Yield 160 mg (17%). ^{1}H-NMR (CCl_4): 0.36 (9H, s), 6.93 (1H, s), 7.33 (1H, d, J=5.0 Hz), 8.36 (1H, d, J=5.0 Hz), 8.80 (1H, s). *Anal.* Calcd for $C_{10}H_{13}NOSi$: C, 62.78; H, 6.85; N, 7.32. Found: C, 62.63; H, 6.58; N, 7.37.

References and Notes

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