Synthesis of Pyrido[1′,2′:1,2]imidazo[4,5-*b*]quinoxalines

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Synthesis of pyrido[1′,2′:1,2]imidazo[4,5-*b*]quinoxalines by the facile cyclizations of 2,3-dichloroquinoxalines with 2-aminopyridines and of 2-amino-3-chloroquinoxalines with various substituted pyridines is described.

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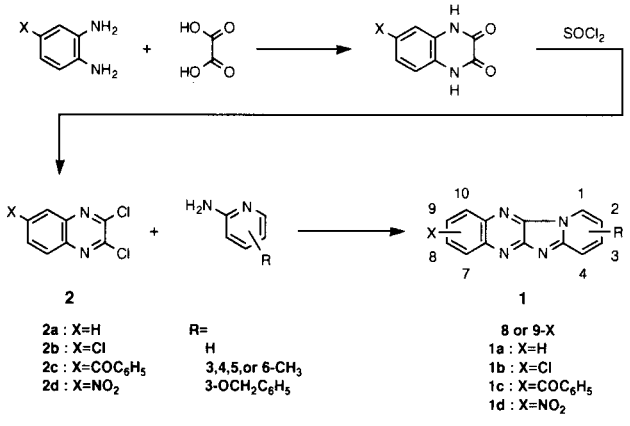
Previously we reported the novel synthesis of 2,3-dicyanopyrido[1′,2′:1,2]imidazo[4,5-*b*]pyrazines by the two different routes *via* the facile cyclizations of 2,3-dichloro-5,6-dicyanopyrazine with 2-aminopyridines and of 2-amino-3-chloro-5,6-dicyanopyrazines with various substituted pyridines [1,2]. Most of products revealed the interesting fluorescent properties. Interest in pyridoimidazopyrazine-chemistry and its photo-function prompted us to extend our method into the synthesis of pyrido[1′,2′:1,2]imidazo-[4,5-*b*]quinoxalines. Such a synthesis has been little explored except a few examples from aminochloroquinoxaline itself with pyridines [3-5]. In this paper, we wish to demonstrate the synthesis of these novel pyridoimidazoquinoxalines by cyclizations of substituted 2,3-dichloro- and 2-amino-3-chloroquinoxalines with 2-aminopyridines and pyridines, respectively, and also report the regioselective feature in these cyclizations.

6-Substituted-2,3-dichloroquinoxalines **2a-d** were prepared in high yields by oxalylation of the corresponding *o*-phenylenediamines with oxalic acid followed by chlorination with thionyl chloride [6]. Dichloroquinoxalines **2a-d** reacted with 3 equivalent of various 2-aminopyridines in dimethylformamide (DMF) to give pyrido[1′,2′:1,2]imidazo[4,5-*b*]quinoxalines **1a-d** (Scheme 1). Reaction conditions, melting points, and yields of **1a-d** are summarized in Table 1. The structures of **1a-d** were assigned by their elemental analyses, ^{1}H-nmr, and ir spectra. These data are listed in Table 2.

Scheme 1

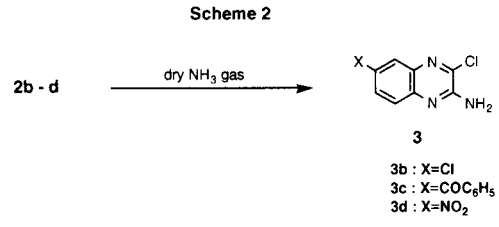


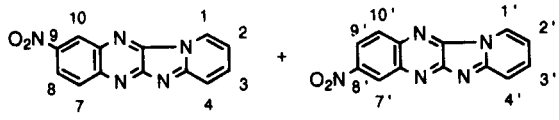
As to substituent X the analysis of the ^{1}H-nmr spectra indicates that cyclizations produce a mixture of 8- and 9-substituted isomers. The regioisomeric ratios of the products are shown together in Table 1. Unfortunately although each isomer could not be separated, the main products are presumed to be 9-substituted pyridoimidazoquinoxalines by their ^{1}H-nmr spectra. For example, ^{1}H-nmr spectra of 9(8)-nitropyridoimidazoquinoxaline **1d** (R = H), as illustrated in Figure 1, indicate the presence of two isomers, though their chemical shifts and patterns are hardly distinguished. Particularly, it is obvious that two types of triplets in upper field are ascribed to 2-H and 2′-H, respectively. As discussed later the reaction of 2-amino-3-chloro-6-nitroquinoxaline and pyridine affords a sole product, 9-nitropyridoimidazoquinoxaline **1d** (R = H), its ^{1}H-nmr spectrum being shown in Figure 2. From the comparison between Figures 1 and 2, the main product of the former reaction corresponds with the 9-nitropyridoimidazoquinoxaline.

6-Substituted 2-amino-3-chloroquinoxalines **3b-d** were prepared by monoamination of **2b-d** as the sole products [6]. The 2-position is presumed to be preferentially substituted from the consideration of the stability of intermediate σ-complex and the calculation of molecular orbitals. For instance the estimated LUMO coefficients for 6-nitro-2,3-dichloroquinoxaline **2d** support the easy access of the nucleophile to the 2-position (Figure 3) [7]. From the similar considerations of **2b,c** carrying electron withdrawing groups, the formation of 2-aminoquinoxalines **3b,c** is presumed.

Cyclization of **3d** with pyridine did not occur at room temperature but proceeded readily at 100°, giving 9-nitropyridoimidazoquinoxaline **1d** (R = H) in 51% yield. Various 4-substituted pyridines reacted with **3b-d** to afford the

Scheme 2





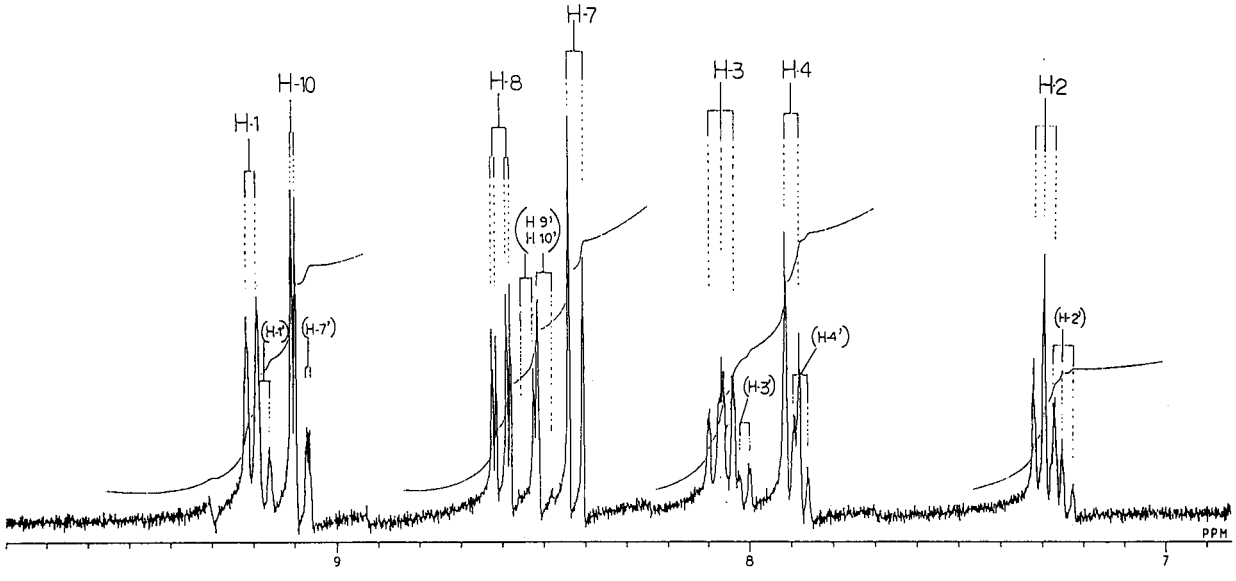
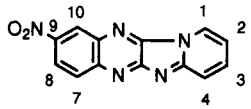


Figure 1. ^{1}H-nmr Spectra of **1d** (R=H) from **2d** with 2-Aminopyridine



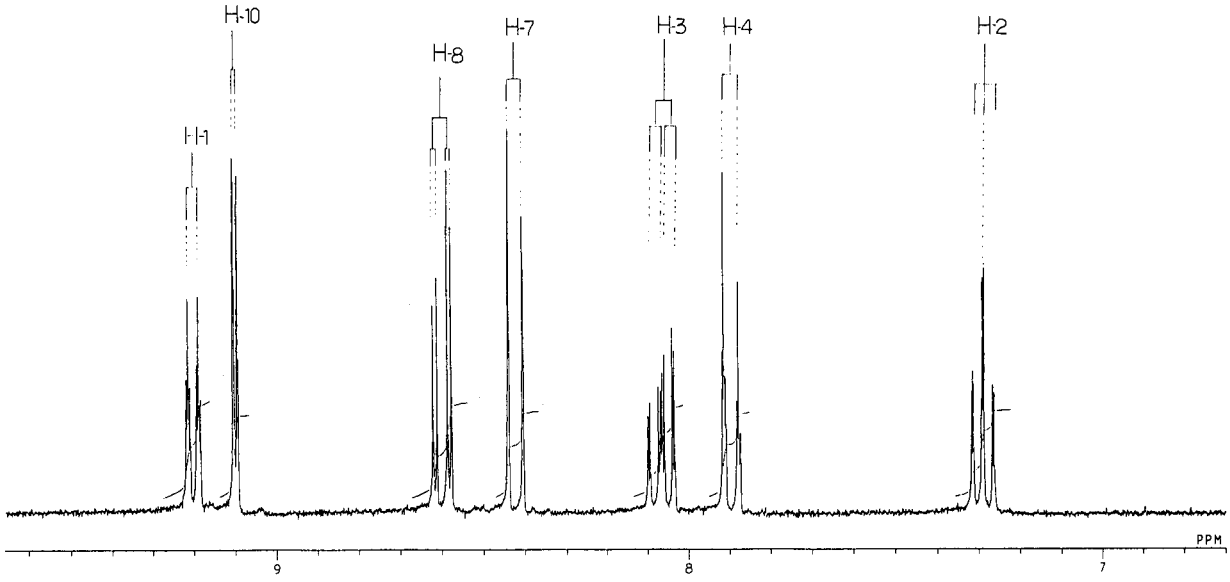


Figure 2. ^{1}H-nmr Spectra of **1d** (R=H) from **3d** with Pyridine

Table 1

Reaction Conditions, Yields, and Physical Properties of Pyridoimidazoquinoxalines **1** from **2** with 2-Aminopyridines

Compound	Substituent X	Substituent R	Conditions Temp (°C)	Conditions Time (h)	Mp (°C)	Yield (%)	Regioisomeric Product Ratio 9(8)– : 8(9)–
1a (R = H)		H	100-120	48	289-291 dec [a]	3	–
1a (R = 2-CH_3)	H	2-CH_3	100-120	72	263-265 dec	5	–
1a (R = 3-CH_3)		3-CH_3	100-120	48	273-275 dec [b]	3	–
1b (R = H)	9(8)-Cl	H	90-120	48	262-263 dec	13	2 : 1
1b (R = 3-CH_3)		3-CH_3	90-120	48	274-275 dec	22	3 : 1
1c (R = H)		H	80-100	48	264-266 dec	28	1 : 0
1c (R = 1-CH_3)		1-CH_3	80-100	48	250-251 dec	4	1 : 0
1c (R = 2-CH_3)	9(8)-COPh	2-CH_3	80-100	48	230-231 dec	30	5 : 3
1c (R = 3-CH_3)		3-CH_3	80-100	48	229-231 dec	31	6 : 1
1c (R = 4-CH_3)		4-CH_3	80-100	48	267-268 dec	21	4 : 1
1d (R = H)		H	80-100	48	305-308 dec	24	4 : 1
1d (R = 3-CH_3)	9(8)-NO_2	3-CH_3	80-100	48	301 dec	45	5 : 3
1d (R = 4-OCH_2Ph)		4-OCH_2Ph	80-100	48	290-293 dec	24	3 : 1

[a] Lit [5] mp 293-294°. [b] Lit [5] mp 284-285°.

Table 2

Analytical and Spectral Data of Pyridoimidazoquinoxalines **1**

Compound	Formula	Analysis (%) Calcd./Found C	H	N	^{1}H-NMR (δ ppm)	IR (cm^{-1})
1a (R = H)	$C_{13}H_8N_4$	70.90	3.66	25.44	7.07 (m, 2-H, 1H) 7.75-7.89 (m, 3,4,8,9-H, 4H)	3050, 1640
		70.67	3.46	25.44	8.27 (d, 10-H, 1H) 8.32 (d, 7-H, 1H) 8.93 (d, 1-H, 1H)	1620, 1500
1a (R = 2-CH_3)	$C_{14}H_{10}N_4$	71.78	4.30	23.92	2.58 (s, 2-CH_3, 3H) 7.59 (d, 3-H, 1H) 7.73 (d, 4-H, 1H)	3000, 1640
		71.52	4.07	23.72	7.77-7.87 (m, 8,9-H, 2H) 8.26 (d, 7-H, 1H) 8.36 (d, 10-H, 1H) 8.71 (s, 1-H, 1H)	1620, 1500 1380
1a (R = 3-CH_3)	$C_{14}H_{10}N_4$	71.78	4.30	23.92	2.55 (s, 3-CH_3, 3H) 6.83 (d, 2-H, 1H) 7.53 (d, 4-H, 1H)	3050, 1640
		71.43	4.12	23.87	7.72-7.85 (m, 8,9-H, 2H) 8.22 (d, 7-H, 1H) 8.32 (d, 10-H, 1H) 8.76 (d, 1-H, 1H)	1620, 1500 1380
1b (R = H)	$C_{13}H_7N_4Cl$	61.31	2.77	22.00	7.19 (dd, 2-H, 1H) 7.81 (d, 4-H, 1H) 7.88 (d, 8-H, 1H)	3050, 1640
		61.16	2.54	21.75	7.95 (dd, 3-H, 1H) 8.25 (d, 7-H, 1H) 8.30 (s, 10-H, 1H) 9.08 (d, 1-H, 1H) for 9-Cl-**1b** (R = H) and 7.22 (dd, 2-H, 1H) 7.82 (d, 4-H, 1H) 7.92 (d, 9-H, 1H) 7.98 (dd, 3-H, 1H) 8.25 (d, 7-H, 1H) 8.30 (s, 10-H, 1H) 9.10 (d, 1-H, 1H) for 8-Cl-**1b** (R = H)	1620, 1500
1b (R = 3-CH_3)	$C_{14}H_9N_4Cl$	62.58	3.38	20.85	2.55 (s, 3-CH_3, 3H) 7.05 (d, 2-H, 1H) 7.62 (s, 4-H, 1H)	3050, 1640
		62.37	3.15	20.83	7.85 (d, 8-H, 2H) 8.23 (d, 7-H, 1H) 8.28 (s, 10-H, 1H) 8.97 (d, 1-H, 1H) for 9-Cl-**1b** (R = 3-CH_3) and 2.55 (s, 3-CH_3, 3H) 7.06 (d, 2-H, 1H) 7.68 (s, 4-H, 1H) 7.80 (d, 9-H, 2H) 8.26 (d, 7-H, 1H) 8.28 (s, 10-H, 1H) 9.00 (d, 1-H, 1H) for 8-Cl-**1b** (R = 3-CH_3)	1620, 1500 1380
1c (R = H)	$C_{20}H_{12}N_4O$	74.06	3.73	17.27	7.07 (dd, 2-H, 1H) 7.57 (t, *m*-Ph, 2H) 7.68 (m, *p*-Ph, 1H)	3040, 1650
		74.25	3.55	17.18	7.80 (dd, 3-H, 1H) 7.82 (d, 4-H, 1H) 7.93 (d, *o*-Ph, 2H) 8.32 (d, 8-H, 1H) 8.44 (d, 7-H, 1H) 8.68 (s, 10-H, 1H) 8.90 (d, 1-H, 1H)	1620, 1600 1490
1c (R = 1-CH_3)	$C_{21}H_{14}N_4O$	74.54	4.17	16.56	3.36 (s, 1-CH_3, 3H) 6.82 (dd, 2-H, 1H) 7.59 (dd, *m*-Ph, 2H)	3020, 1635
		74.51	4.08	16.44	7.68 (m, *p*-Ph, 1H) 7.70 (dd, 3-H, 1H) 7.72 (d, 4-H, 1H) 7.95 (d, *o*-Ph, 2H) 8.33 (d, 8-H, 1H) 8.45 (d, 7-H, 1H) 8.69 (s, 10-H, 1H)	1560, 1490 1380

Table 2 (continued)

Compound	Formula	Analysis (%) Calcd./Found C	H	N	^{1}H-NMR (δ ppm)	IR (cm^{-1})
1c (R = 2-CH_3)	$C_{21}H_{14}N_4O$	74.54	4.17	16.56	2.49 (s, 1-CH_3, 3H) 7.57 (dd, *m*-Ph, 2H) 7.65 (m, *p*-Ph, 1H)	3020, 1645
		74.29	4.10	16.28	7.62-7.69 (m, 3-H, 1H) 7.77 (d, 4-H, 1H) 7.93 (d, *o*-Ph, 2H)	1560, 1480
					8.30 (d, 8-H, 1H) 8.43 (d, 7-H, 1H) 8.72 (s, 10-H, 1H)	1420
					8.74 (s, 1-H, 1H) for 9-COPh-**1c** (R = 2-CH_3)	
					and	
					2.49 (s, 1-CH_3, 3H) 7.55 (dd, *m*-Ph, 2H) 7.63 (m, *p*-Ph, 1H)	
					7.62-7.69 (m, 3-H, 1H) 7.75 (d, 4-H, 1H) 7.92 (d, *o*-Ph, 2H)	
					8.28 (d, 9-H, 1H) 8.37 (d, 7-H, 1H) 8.67 (s, 10-H, 1H)	
					8.70 (s, 1-H, 1H) for 8-COPh-**1c** (R = 2-CH_3)	
1c (R = 3-CH_3)	$C_{21}H_{14}N_4O$	74.54	4.17	16.56	2.59 (s, 3-CH_3, 3H) 6.85 (dd, 2-H, 1H) 7.57 (dd, *m*-Ph, 2H)	3040, 1650
		74.31	4.01	16.39	7.65 (t, *p*-Ph, 1H) 7.93 (d, *o*-Ph, 2H) 7.94 (s, 4-H, 1H)	1620, 1490
					8.28 (d, 8-H, 1H) 8.35 (d, 7-H, 1H) 8.69 (s, 10-H, 1H)	1390
					8.83 (s, 1-H, 1H) for 9-COPh-**1c** (R = 3-CH_3)	
					and	
					2.59 (s, 3-CH_3, 3H) 6.85 (dd, 2-H, 1H) 7.57 (dd, *m*-Ph, 2H)	
					7.65 (t, *p*-Ph, 1H) 7.93 (d, *o*-Ph, 2H) 7.94 (s, 4-H, 1H)	
					8.30 (d, 9-H, 1H) 8.41 (d, 7-H, 1H) 8.65 (s, 10-H, 1H)	
					8.83 (s, 1-H, 1H) for 8-COPh-**1c** (R = 3-CH_3)	
1c (R = 4-CH_3)	$C_{21}H_{14}N_4O$	74.54	4.17	16.56	2.75 (s, 4-CH_3, 3H) 6.99 (dd, 2-H, 1H) 7.56 (dd, *m*-Ph, 2H)	3020, 1655
		74.36	4.01	16.32	7.58 (d, 3-H, 1H) 7.67 (m, *p*-Ph, 1H) 7.96 (d, *o*-Ph, 2H)	1640, 1560
					8.27 (d, 8-H, 1H) 8.38 (d, 7-H, 1H) 8.72 (s, 10-H, 1H)	1390
					8.81 (s, 1-H, 1H) for 9-COPh-**1c** (R = 4-CH_3)	
					and	
					2.75 (s, 4-CH_3, 3H) 6.99 (dd, 2-H, 1H) 7.56 (dd, *m*-Ph, 2H)	
					7.58 (d, 3-H, 1H) 7.67 (m, *p*-Ph, 1H) 7.93 (d, *o*-Ph, 2H)	
					8.30 (d, 9-H, 1H) 8.45 (d, 7-H, 1H) 8.68 (s, 10-H, 1H)	
					8.78 (s, 1-H, 1H) for 8-COPh-**1c** (R = 4-CH_3)	
1d (R = H)	$C_{13}H_7N_5O_2$	58.87	2.66	26.40	7.29 (dd, 2-H, 1H) 7.90 (d, 4-H, 1H) 8.08 (dd, 3-H, 1H)	3050, 1650
		58.83	2.58	26.16	8.43 (d, 7-H, 1H) 8.61 (d, 8-H, 1H) 9.10 (s, 10-H, 1H)	1600, 1540
					9.20 (d, 1-H, 1H) for 9-NO_2-**1d** (R = H)	1500
					and	
					7.25 (dd, 2-H, 1H) 7.88 (d, 4-H, 1H) 8.03 (dd, 3-H, 1H)	
					8.49 (d, 7-H, 1H) 8.55 (d, 9-H, 1H) 9.07 (s, 10-H, 1H)	
					9.18 (d, 1-H, 1H) for 8-NO_2-**1d** (R = H)	
1d (R = 3-CH_3)	$C_{14}H_9N_5O_2$	60.21	3.25	25.08	2.58 (s, 3-CH_3, 3H) 7.16 (d, 2-H, 1H) 7.70 (s, 4-H, 1H)	3050, 1650
		60.03	3.09	24.89	8.38 (d, 7-H, 1H) 8.57 (d, 8-H, 1H) 9.04 (s, 10-H, 1H)	1600, 1540
					9.07 (d, 1-H, 1H) for 9-NO_2-**1d** (R = 3-CH_3)	1500, 1380
					and	
					2.58 (s, 3-CH_3, 3H) 7.12 (d, 2-H, 1H) 7.68 (s, 4-H, 1H)	
					8.47 (d, 7-H, 1H) 8.51 (d, 9-H, 1H) 9.01 (s, 10-H, 1H)	
					9.02 (d, 1-H, 1H) for 8-NO_2-**1d** (R = 3-CH_3)	
1d (R = 4-OCH_2Ph)	$C_{20}H_{13}N_5O_3$	64.69	3.53	18.86	5.46 (s, CH_2, 2H) 7.21 (dd, 2-H, 1H) 7.41-7.63 (m, Ph, 5H)	3050, 1650
		64.33	3.53	18.61	7.62 (d, 3-H, 1H) 8.46 (s, 7-H, 1H) 8.60 (d, 8-H, 1H)	1600, 1540
					8.81 (d, 1-H, 1H) 9.11 (s, 10-H, 1H)	1500
					for 9-NO_2-**1d** (R = 4-OCH_2Ph)	
					and	
					5.46 (s, CH_2, 2H) 7.18 (dd, 2-H, 1H) 7.41-7.63 (m, Ph, 5H)	
					7.62 (d, 3-H, 1H) 8.42 (s, 7-H, 1H) 8.52 (d, 9-H, 1H)	
					8.79 (d, 1-H, 1H), 9.08 (s, 10-H, 1H)	
					for 8-NO_2-**1d** (R = 4-OCH_2Ph)	

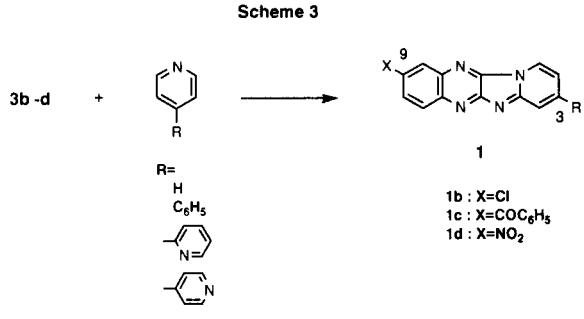
Table 3

Reaction Conditions, Yields, and Physical Properties of Pyrido- and Isoquinolinoimidazoquinoxalines **1** and **4** from **3** with Pyridines and Isoquinoline

Compound	Substituent		Conditions		Mp	Yield
	X	R	Temp (°C)	Time (h)	(°C)	(%)
1b (R = 3-Ph)	-Cl	3-Ph	90-120	48	358-360 dec	15
1c(R = 3-Ph)		3-Ph	80-100	48	324-326 dec	46
1c (R = 3-(4'-pyridyl))	-COPh	3-(4'-pyridyl)	80-100	48	>360	45
1c (R = 3-(2'-pyridyl))		3-(2'-pyridyl)	80-100	48	322-324 dec	25
1d (R = H)		H	80	48	307-308 dec	51
1d (R = 4-Ph)	$-NO_2$	4-Ph	100	48	342-343 dec	25
1d (R = 2-CH_3) + **1d** (R = 4-CH_3) [a]		2-CH_3 + 4-CH_3	100	48	309-312 dec	42
4c	-COPh		80-100	48	299-300	13
4d	$-NO_2$		80-100	48	>360	33

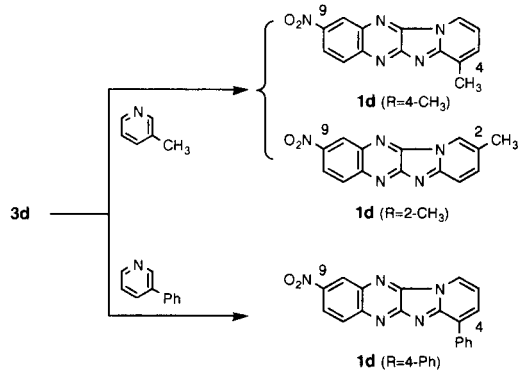
[a] A mixture of **1d** (R = 2-CH_3) and **1d** (R = 4-CH_3) was obtained in the ratio of 3:5.

Scheme 3



corresponding 3,9-disubstituted products in moderate yields (Scheme 3, Table 3) and their analytical and spectral data are collected in Table 4. It is found that the reactivity of these cyclization was mostly higher than that of the former reactions of dichloroquinoxalines **2** with 2-aminopyridines from a viewpoint of yields.

Scheme 4



Although the reaction of **3d** with 2-substituted pyridines such as 2-methylpyridine hardly took place, that with 3-substituted pyridines produced the expected pyridoimidazoquinoxalines. In the latter case, two directions in the ring closure are possible because of their structural dissymmetry. 3-Phenylpyridine cyclized with **3d** preferentially at its 1,2-position to afford 9-nitro-4-phenylpyridoimidazoquinoxaline (**1d**, R = 4-Ph). Whereas 3-methylpyridine yielded a mixture of 2- and 4-methylpyridoimidazoquinoxalines **1d** (R = 2-Me) and **1d** (R = 4-Me) (Scheme 4). It should be noted that this tendency is the reverse of that in cyclizations of aminochlorodicyanopyrazine, where 3-phenylpyridine cyclizes both at the 1,2- and the 1,6-positions and 3-methylpyridine cyclizing exclusively at the 1,2-positions [2]. The difference in the ring-closing direction will be investigated in the near future.

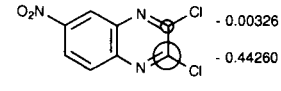


Figure 3. Estimated LUMO Coefficients for 2d

The reactions of **3c** and **3d** with isoquinoline were next carried out and isoquinoline cyclized at the 1,2-position to give isoquinolino[1',2':1,2]imidazo[4,5-*b*]quinoxalines **4c** and **4d**, respectively (Scheme 5).

The fluorescent properties of the thus obtained products are now under investigation and will be reported soon.

Scheme 5

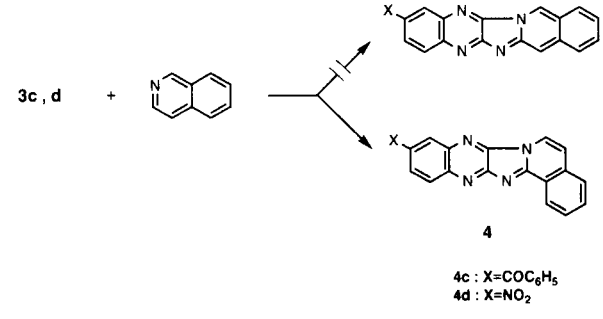


Table 4

Analytical and Spectral data of Pyrido- and Isoquinolinoimidazoquinoxalines **1** and **4**

Compound	Formula	Analysis (%) Calcd./Found C	H	N	^{1}H-NMR (δ ppm)	IR (cm^{-1})
1b (R = 3-Ph)	$C_{19}H_{11}N_4Cl$	68.99	3.35	16.94	7.37 (d, 2-H, 1H) 7.52-7.82 (m, Ph, 5H) 7.76 (d, 8-H, 1H)	3020, 1650
		69.13	3.01	16.65	7.98 (s, 4-H, 1H) 8.29 (d, 7-H, 1H) 8.34 (s, 10-H, 1H)	1600, 1500
					8.93 (d, 1-H, 1H)	1200
1c (R = 3-Ph)	$C_{26}H_{16}N_4O$	77.99	4.03	13.99	7.38 (d, 2-H, 1H) 7.56-7.68 (m, 9-COPh-*m,p*, 3H)	3020, 1650
		78.19	3.74	14.06	7.56-7.81 (m, 3-Ph, 5H) 7.94 (d, 9-COPh-*o*, 2H)	1620, 1500
					8.02 (s, 4-H, 1H) 8.32 (d, 8-H, 1H) 8.45 (d, 7-H, 1H)	1200
					8.68 (s, 10-H, 1H) 8.93 (d, 1-H, 1H)	
1c (R = 3-(4'-pyridyl))	$C_{25}H_{15}N_5O$	74.80	3.77	17.45	7.67 (m, 9-COPh-*m*, 2H) 7.70 (d, 2-H, 1H)	3020, 1640
		74.83	3.93	17.59	7.78 (m, 9-COPh-*p*, 1H) 7.91 (d, 9-COPh-*o*, 2H)	1580, 1500
					8.06 (d, 3'-H, 1H) 8.28 (d, 8-H, 1H) 8.42 (d, 7-H, 1H)	1200
					8.45 (s, 4-H, 1H) 8.65 (s, 10-H, 1H) 8.82 (d, 2'-H, 2H)	
					9.28 (d, 1-H, 1H)	
1c (R = 3-(2'-pyridyl))	$C_{25}H_{15}N_5O$	74.80	3.77	17.45	7.59 (dd, 5'-H, 1H) 7.65 (m, 9-COPh-*m*, 2H)	3020, 1640
		74.55	3.76	17.35	7.78 (m, 9-COPh-*p*, 1H) 7.90 (d, 9-COPh-*o*, 2H)	1580, 1500
					8.03 (d, 3'-H, 1H) 8.08 (d, 4'-H, 2H) 8.28 (d, 8-H, 1H)	1200
					8.41 (d, 7-H, 1H) 8.46 (d, 2-H, 1H) 8.55 (s, 4-H, 1H)	
					8.60 (s, 10-H, 1H) 8.87 (d, 6' -H, 1H) 9.25 (d, 1-H, 1H)	
1d (R = 4-Ph)	$C_{19}H_{11}N_5O_2$	66.86	3.25	20.52	7.42 (dd, 2H, 1H) 7.52-7.62 (m, *m, p*-Ph, 3H)	3045, 1645
		67.00	3.17	20.35	8.16-8.21 (m, *o*-Ph, 2H) 8.28 (d, 3-H, 1H) 8.42 (d, 7-H, 1H)	1580, 1545
					8.62 (d, 8-H, 1H) 9.15 (s, 10-H, 1H) 9.24 (d, 1-H, 1H)	1490
1d (R = 2-CH_3)	$C_{14}H_9N_5O_2$	60.21	3.25	25.08	2.55 (s, 2-CH_3, 3H) 7.83 (d, 4-H, 1H) 7.89 (d, 3-H, 1H)	3020, 1650
+		60.40	3.20	25.45	8.40 (d, 7-H, 1H) 8.58 (d, 8-H, 1H) 9.06 (s, 10-H, 1H)	1600, 1545
1d (R = 4-CH_3)					9.08 (d, 1-H, 1H) for **1d** (R = 2-CH_3)	1490, 1190
					and	
					2.55 (s, 4-CH_3, 3H) 7.83 (d, 4-H, 1H) 7.96 (d, 3-H, 1H)	
					8.42 (d, 7-H, 1H) 8.59 (d, 8-H, 1H) 9.06 (s, 10-H, 1H)	
					9.06 (s, 1-H, 1H) for **1d** (R = 4-CH_3)	
4c	$C_{24}H_{14}N_4O$	76.99	3.77	14.96	7.53 (d, 11-H, 1H) 7.66-7.90 (m, PhCO, 5H)	3045, 1640
		76.56	3.66	14.94	7.92 (dd, 8-H, 1H) 8.02 (dd, 9-H, 1H)	1580, 1500
					8.11 (d, 7-H, 1H) 8.26 (d, 3-H, 1H) 8.44 (d, 4-H, 1H)	1200
					8.54 (s, 1-H, 1H) 8.81 (d, 12-H, 1H) 8.84 (d, 10-H, 1H)	
4d	$C_{17}H_9N_5O_2$	64.76	2.88	22.21	7.32 (d, 11-H, 1H) 7.82-7.95 (m, 7-10-H, 4H)	3055, 1645
		64.50	3.01	22.35	8.47 (d, 4-H, 1H) 8.62 (d, 3-H, 1H) 9.02 (d, 12-H, 1H)	1580, 1540
					9.22 (s, 1-H, 1H)	1490, 1200

EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. The ir spectra were taken on a JASCO A-100 spectrometer as potassium bromide pellets. The ^{1}H-nmr spectra were recorded on a JEOL GX-270 spectrometer in dimethyl sulfoxide-d_6 or deuteriochloroform as the solvent. Chemical shifts are given in δ ppm downfield from tetramethylsilane as the internal standard. 2-Aminopyridines and pyridines are commercially obtained.

2,3-Dichloroquinoxalines **2a-d**. General Procedure.

According to the reported procedures, quinoxaline-2,3-diones were prepared in good yields from the reactions of *o*-phenylenediamines and oxalic acid or its dihydrate [8].

2,3-Dichloroquinoxalines **2a-d** were obtained by chlorination of quinoxaline-2,3-diones with thionyl chloride. For example the procedure for 2,3-dichloroquinoxaline (**2a**) is described as follows: To a suspension of quinoxaline-2,3-dione (14.0 g, 0.086 mole) in dioxane (100 ml) were added DMF (3 ml) and thionyl chloride (20 ml). The mixture was heated at 100° for 3 hours with stirring and then evaporated to dryness under reduced pressure to leave a solid. The residual solid was recrystallized from chloroform to give white needles of **2a** (14.5 g, 85%), mp 145-146° (lit [8] 152-153° and lit [6] 148-150°).

Anal. Calcd. for $C_8H_4N_2Cl_2$: C, 48.28; H, 2.03; N, 14.07. Found: C, 48.39; H, 1.91; N, 13.83.

2,3,6-Trichloroquinoxaline (**2b**).

This compound was obtained as light yellow needles (53% yield), mp 143-144°.

Anal. Calcd. for $C_8H_3N_2Cl_3$: C, 41.15; H, 1.30; N, 12.00. Found: C, 41.46; H, 1.14; N, 12.03.

6-Benzoyl-2,3-dichloroquinoxaline (**2c**).

This compound was obtained as light yellow needles (71% yield), mp 160-161°.

Anal. Calcd. for $C_{15}H_8N_2OCl_2$: C, 59.43; H, 2.66; N, 9.24. Found: C, 59.33; H, 2.54; N, 9.24.

2,3-Dichloro-6-nitroquinoxaline (**2d**).

This compound was obtained as light orange needles (53% yield), mp 147-149°.

Anal. Calcd. for $C_8H_3N_3O_2Cl_2$: C, 39.37; H, 1.24; N, 17.22. Found: C, 39.47; H, 1.10; N, 17.37.

Synthesis of Pyrido[1',2':1,2]imidazo[4,5-*b*]quinoxalines **1a-d** from **2a-d** with 2-Aminopyridines. General Procedure.

A solution of **2** (0.02 mole) and 2-aminopyridine (0.06 mole) in DMF (50 ml) was heated at 100° for 48 hours. After removal of the solvent under reduced pressure, the resulting solid was washed with least amount of cold methanol and hexane and then recrystallized from ethanol to give **1**. Preparative and physical data of the products are summarized in Table 1 and their analytial and spectral data in Table 2.

Synthesis of 2-Amino-3-chloroquinoxalines **3b-d**. General Procedure.

Anhydrous ammonia gas was bubbled into a solution of **2** (0.01 mole) in DMF (50-200 ml) with cooling at 0° for 15 minutes. Then the reaction mixture was evaporated to dryness *in vacuo* and recrystallized from acetone to give 2-amino-3-chloroquinoxaline **3**.

2-Amino-3,6-dichloroquinoxaline (**3b**).

This compound was obtained as light yellow needles (50% yield), mp 138-140°; ir: 3400 cm^{-1} (NH_2); ^{1}H-nmr: δ 1.55 (s, NH_2, 2H), 7.75 (d, 7-H, 1H), 7.98 (d, 8-H, 1H), 8.02 (s, 5-H, 1H).

Anal. Calcd. for $C_8H_5N_3Cl_2$: C, 44.89; H, 2.35; N, 19.63. Found: C, 44.80; H, 2.12; N, 19.55.

2-Amino-6-benzoyl-3-chloroquinoxaline (**3c**).

This compound was obtained as light yellow needles (52% yield), mp 260-263°; ir: 3400 (NH_2), 1620 cm^{-1} (C=O); ^{1}H-nmr: δ 1.55 (s, NH_2, 2H), 7.63-7.85 (m, Ph, 5H), 8.24 (d, 7-H, 1H), 8.27 (d, 8-H, 1H), 8.30 (s, 5-H, 1H).

Anal. Calcd. for $C_{15}H_{10}N_3OCl$: C, 63.50; H, 3.55; N, 14.81. Found: C, 63.44; H, 3.35; N, 14.72.

2-Amino-3-chloro-6-nitroquinoxaline (**3d**).

This compound was obtained as light orange needles (62% yield), mp 279-280° dec; ir: 3000 cm^{-1} (NH_2); ^{1}H-nmr: δ 1.55 (s, NH_2, 2H), 7.50 (d, 8-H, 1H), 8.34 (d, 7-H, 1H), 8.56 (s, 5-H, 1H).

Anal. Calcd. for $C_8H_5N_4O_2Cl$: C, 42.78; H, 2.24; N, 24.94. Found: C, 42.83; H, 2.41; N, 24.99.

Synthesis of Pyrido- and Isoquinolino[1',2':1,2]imidazo[4,5-*b*]-quinoxalines **1b-d** and **4c,d** from **3** with Pyridines and Isoquinoline. General Procedure.

A solution of **3** (2 mmoles) and pyridine or isoquinoline (7 mmoles) in DMF (20 ml) was heated at 80° for 48 hours. The resulting precipitate was collected on a filter and recrystallized from dimethylacetamide to yield the corresponding pyrido- or isoquinolinoimidazoquinoxaline **1** or **4**. Preparative and physical data of the products are summarized in Table 3 and their analytical and spectral data in Table 4.

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