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Preparation and Ring Conversion of Furo[2,3-*b*]quinoxaline[1)]

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The reaction of 3-ethoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline with the Vilsmeier reagent gave 3-(N,N-dimethylaminocarbonyl)furo[2,3-*b*]quinoxaline, which was converted to various quinoxaline derivatives, 3-methyl-2-oxo-1,2-dihydroquinoxaline, quinoxalinylpyrazolin-5-ones, and pyrazolo[3′,4′: 3,4]pyridazino[5,6-*b*]quinoxalines.

Keywords——Vilsmeier reagent; hydrazines; quinoxalinylpyrazolin-5-ones; pyrazolo[3′,4′: 3,4]pyridazino[5,6-*b*]quinoxalines; azodicarboxylate; chlorination; hydrogen bonding

The tautomeric behavior of 3-ethoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (Ia) has been studied by ultraviolet (UV) and nuclear magnetic resonance (NMR) spectroscopy,[2)] and its equilibrium is considered to be as shown in Chart 1. On the basis of this tautomerism, it can be postulated that the compound will react with electrophilic reagents, while it will hardly react with nucleophilic reagents such as amines and hydrazines. Among electrophilic reagents, the Vilsmeier reagent (N,N-dimethylformamide and phosphorus oxychloride) was found to react with Ia to provide a furo[2,3-*b*]quinoxaline, but not a formylated compound (II). This paper describes the synthesis and ring conversions of the furo[2,3-*b*]quinoxaline.[3)]

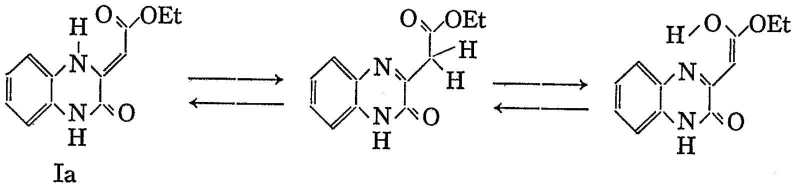


Chart 1

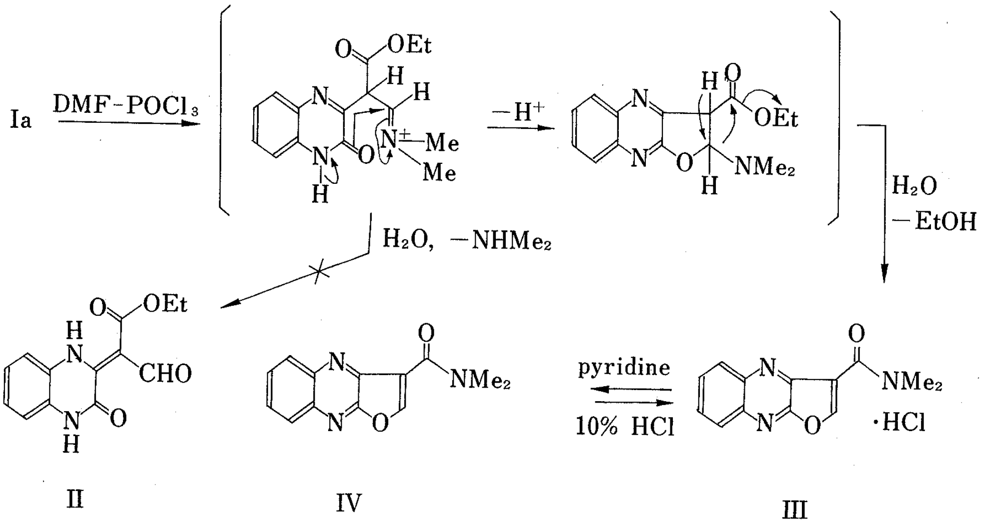


Chart 2

The reaction of Ia with the Vilsmeier reagent afforded yellow needles (III). The structure of III was assigned as 3-(N,N-dimethylaminocarbonyl)furo[2,3-*b*]quinoxaline hydrochloride on the basis of the analytical and spectral data. Free base (IV) was obtained by treatment of III with pyridine in ethanol. When IV was treated with 10% hydrochloric acid under cooling, III was obtained. The mechanism of formation of III was assumed to be as shown in Chart 2.

Heating of III with sodium acetate in acetic acid afforded furo[2,3-*b*]quinoxaline-3-carboxylic acid (V). Compound III was also converted to V by heating with pyridine in acetic acid. On the other hand, the reaction of III with 10% sodium hydroxide or 10% hydrochloric acid provided 3-methyl-2-oxo-1,2-dihydroquinoxaline (VI).[4] In 80% aqueous acetic acid solution, III was converted to V and VI. These results indicate that III is hydrolyzed to V initially, then its furan ring is cleaved by hydration in aqueous media at an extreme pH.[5-7] Moreover, the reaction of III with sodium ethoxide provided Ia, but not 3-ethoxycarbonylfuro[2,3-*b*]quinoxaline. In 80% aqueous ethanol solution, Ia and V were obtained from III. Similarly, in 80% aqueous methanol solution, 3-methoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (Ib) and V were obtained from III. Since V precipitated in aqueous alcohol solutions, it was not hydrolyzed to VI. The above reactions were formulated as shown in Chart 3. The yields are summarized in Table I.

In relation to the above results, the reaction of III with hydrazines was examined. The reaction of III with 1,1-dimethylhydrazine gave 3-(N,N-dimethylhydrazinocarbonyl)furo[2,3-*b*]quinoxaline (VII), whose structure was established by the analytical and spectral data.

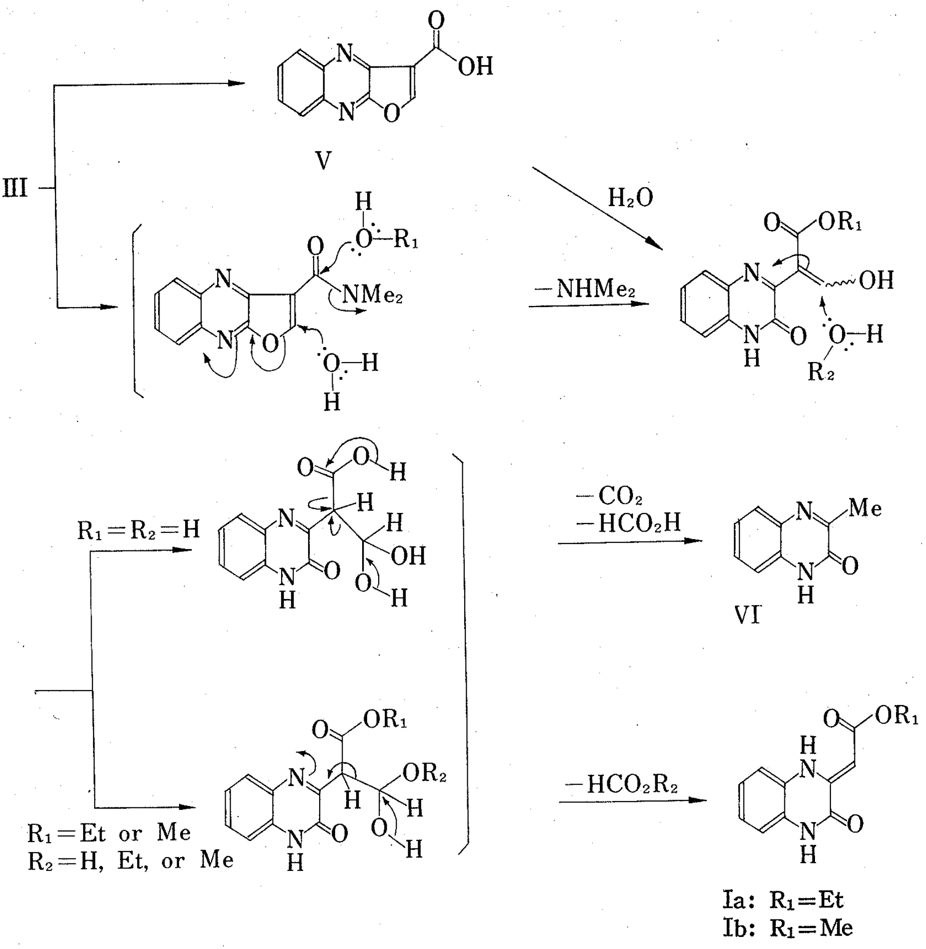


Chart 3

Table I. Conversion of III to Quinoxaline Derivatives

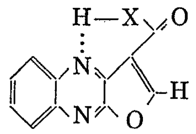
Reaction medium	Product (Yield %)
AcONa/AcOH	V(86)
Pyridine-AcOH	V(78)
10% NaOH	VI(95)
10% HCl	VI(60)
80% aq. AcOH	VI(17) V(39)
EtONa/EtOH	Ia(95)
80% aq. EtOH	Ia(80) V(19)
80% aq. MeOH	Ib(40) V(57)

The infrared (IR) absorption band of the 3-carbonyl group in VII was observed at 1735 cm^{-1}, which is much higher than that of ordinary hydrazinocarbonyl groups. Compound IV exhibited IR absorption due to the 3-carbonyl group at 1755 cm^{-1}, and V showed absorptions at 1790 and 1760 cm^{-1} (Table II); such absorption bands are characteristic of the 3-carbonyl groups on furo[2,3-*b*]quinoxaline rings. In the NMR spectra, the signals of the 2-protons of IV, V, and VII were observed at δ 7.90, 9.73, and 9.50 ppm, respectively. The difference of these chemical shifts may be attributed to anisotropy of the 3-carbonyl groups.[8] In V and VII, the 3-carbonyl group and the furan ring are fixed in the same plane, since an intramolecular hydrogen bond is formed between the 4-N atom and NH or OH proton, as shown in Chart 4. However, there is no such fixation in IV. On the other hand, the reaction of III with hydrazine hydrate, methylhydrazine, or phenylhydrazine produced 4-(3',4'-dihydro-3'-oxoquinoxalin-2'-yl)pyrazolin-5-one (VIIIa), 4-(3',4'-dihydro-3'-oxoquinoxalin-2'-yl)-2-methylpyrazolin-5-one (VIIIb), and 4-(3',4'-dihydro-3'-oxoquinoxalin-2'-yl)-2-phenylpyrazolin-5-one (VIIIc), respectively. The methyl and phenyl groups of VIIIb and VIIIc were assumed to be in the 2-position on the basis of the NMR spectral data, as shown in Table III. The signals of the 3-protons of VIIIb and VIIIc were observed as sharp singlets, but the signal of the 3-proton of VIIIa was a broad singlet. Furthermore, the chemical shifts of the 3-protons varied in

Table II. IR and NMR Data for IV, V, and VII

Compound	δ (DMSO-d_6)	$\nu_{C=O}$ (KBr)
IV	7.90 (1H, s, 2-H)	1775
V	9.73 (1H, s, 2-H)	1790, 1760[a]
VII	9.50 (1H, s, 2-H)	1735

a) branched.



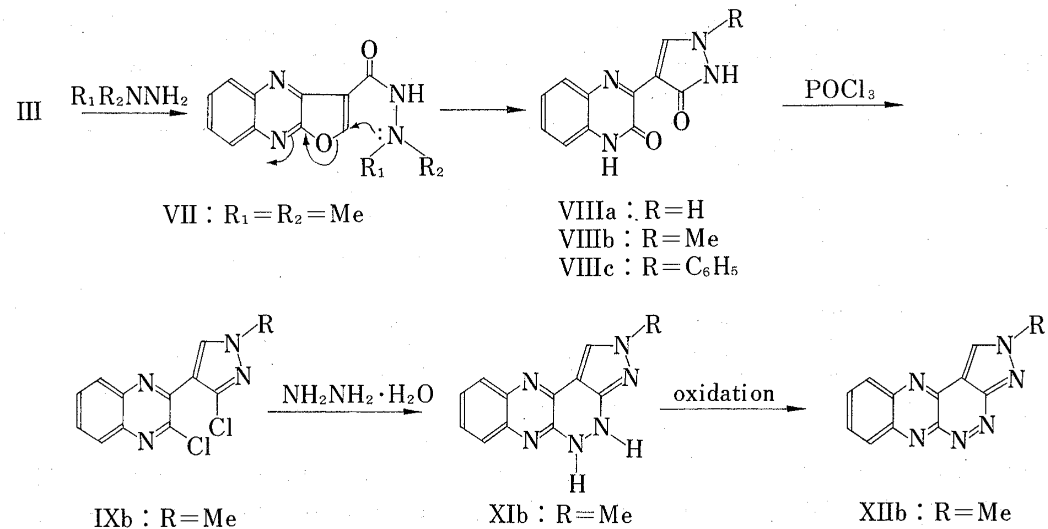
V: X=O
VII: X=N-NMe$_2$

Chart 4

Table III. IR and NMR Data for VIII, IX, X, and XII

Compound	δ (DMSO-d_6)	δ (TFA)[a]	$\nu_{C=O}$ (KBr)
VIIIa	8.30 (1H, br.s, 3-H)	9.27 (1H, s, 3-H)	1675 (3'-C=O) 1620 (5-C=O)
VIIIb	8.07 (1H, s, 3-H)	9.19 (1H, s, 3-H)	1683 (3'-C=O) 1620 (5-C=O)
VIIIc	8.43 (1H, s, 3-H)	9.38 (1H, s, 3-H)	1675 (3'-C=O) 1620 (5-C=O)
Xc		9.40 (1H, s, 3-H)	— 1605 (5-C=O)
IXb		8.68 (1H, s, 5-H)	
IXc		8.77 (1H, s, 5-H)	
XIIb		9.43 (1H, s, 1-H)[b]	
XIIc		9.63 (1H, s, 1-H)[b]	

a) Trifluoroacetic acid.
b) Measured in TFA-d_1.



VII : $R_1 = R_2 = Me$

VIIIa : R=H
VIIIb : R=Me
VIIIc : $R = C_6H_5$

IXb : R=Me
IXc : $R = C_6H_5$

XIb : R=Me
XIc : $R = C_6H_5$

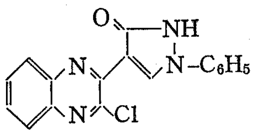
XIIb : R=Me
XIIc : $R = C_6H_5$

Chart 5

these three compounds, suggesting differences of the substituents on the 2-N atom. Similar results were obtained in the other compounds IX (5-protons) and XII (1-protons) (Table III).

Chlorination of VIIIb with phosphorus oxychloride gave 3-chloro-4-(3′-chloroquinoxalin-2′-yl)-1-methylpyrazole (IXb) predominantly, whereas the chlorination of VIIIc afforded 3-chloro-4-(3′-chloroquinoxalin-2′-yl)-1-phenylpyrazole (IXc) and 4-(3′-chloroquinoxalin-2′-yl)-2-phenylpyrazolin-5-one (Xc) in about a 1 : 1 ratio. The structural assignment of Xc was based on the NMR and IR spectral data (Table III). The absorption band due to the 5-carbonyl group was observed at 1605 cm^{-1}, and the signal of the 3-proton was observed at δ 9.40 ppm. These data were similar to those of VIIIc. Further chlorination of Xc provided IXc.

Refluxing of IXb and IXc in hydrazine hydrate produced 4,5-dihydro-2-methylpyrazolo-[3′4′ : 3,4]pyridazino[5,6-*b*]quinoxaline (XIb) and 4,5-dihydro-2-phenylpyrazolo[3′,4′ : 3,4]pyridazino[5,6-*b*]quinoxaline (XIc), respectively. Compounds XIb and XIc were oxidized under aeration to 2-methylpyrazolo[3′,4′ : 3,4]pyridazino[5,6-*b*]quinoxaline (XIIb) and 2-phenylpyrazolo[3′,4′ : 3, 4]pyridazino[5,6-*b*]quinoxaline (XIIc), respectively. Compound XIc was resistant to this oxidation as compared with XIb. However, the oxidation of XIb and XIc with dibenzyl azodicarboxylate afforded XIIb and XIIc, respectively, in improved yields. These results are shown in Table IV.



Xc

Chart 6

TABLE IV. Oxidation of XI to XII

Compound	Oxidation method	Product (Yield %)
XIb	Aeration	XIIb (80)
	Dibenzyl azodicarboxylate	(86)
XIc	Aeration	XIIc (30)
	Dibenzyl azodicarboxylate	(80)

Experimental

All melting points are uncorrected. IR spectra were recorded from KBr discs on a JASCO IRA-1 spectrophotometer. NMR spectra were measured with a Varian T-60 spectrometer using tetramethylsilane as an internal reference. Chemical shifts are given in the δ scale, relative to the internal reference. Mass spectra (MS) were determined with a JMSOIS spectrometer (Japan Electron Optics Laboratory Co. Ltd.).

3-(N,N-Dimethylaminocarbonyl)furo[2,3-*b*]quinoxaline Hydrochloride (III)——$POCl_3$ (10 ml) was added dropwise to a solution of Ia (1 g, 4.31 mmol) in DMF (10 ml) with stirring. The solution was heated on a boiling water bath for 2 h to precipitate yellow needles (III). The reaction mixture was concentrated *in* *vacuo*, and poured onto crushed ice. The yellow needles that precipitated were collected by suction, and washed with EtOH. This sample was suitable for use in the subsequent reactions. Yield, 1 g (88%). MS *m/e*: 241 (M^+). IR ν_{max} cm^{-1}: 1730 (C=O).

Free Base (IV) was obtained by recrystallization of III from EtOH–pyridine as yellow needles, mp 219—221°C. MS *m/e*: 241 (M^+). IR ν_{max} cm^{-1}: 1755 (C=O). NMR (DMSO-d_6): 7.93—7.43 (4H, m, aromatic), 7.90 (1H, s, 2-H), 4.02 (3H, s, NMe), 3.50 (3H, s, NMe). *Anal* Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.46; H, 4.44; N, 17.40.

Furo[2,3-*b*]quinoxaline-3-carboxylic Acid (V)——A solution of III (300 mg, 1.08 mmol) and AcONa–$3H_2O$ (150 mg, 1.08 mmol) in AcOH (20 ml) was heated on a boiling water bath for 2 h to precipitate yellow crystals (V) during the reaction. The crystals were collected by suction (200 mg, 86%). Recrystallization from EtOH–AcOH gave yellow needles, mp 280—282°C. MS *m/e*: 214 (M^+). IR ν_{max} cm^{-1}: 1790, 1760 (C=O). NMR (DMSO-d_6): 9.73 (1H, s, 2-H), 8.17—7.47 (4H, m, aromatic). The OH proton was not observed, presumably due to the presence of moisture in the solvent. *Anal.* Calcd for $C_{11}H_6N_2O_3$: C, 61.68; H, 2.82; N, 13.08. Found: C, 61.42; H, 2.74; N, 12.87.

A solution of III (300 mg, 1.08 mmol) and pyridine (1 ml) in AcOH (20 ml) was heated on a boiling water bath for 2 h to precipitate V (180 mg, 78%).

Reaction of III in 10% NaOH, 10% HCl, and 80% aq. AcOH Solutions——A solution of III (1 g, 3.6 mmol) in 10% NaOH (30 ml) and EtOH (20 ml) was refluxed on a boiling water bath for 1 h. The reaction mixture was neutralized with 10% HCl, extracted with $CHCl_3$, and dried over Na_2SO_4. Removal of the solvent by evaporation afforded yellow crystals (VI). Recrystallization from EtOH gave yellow needles (547 mg, 95%).

In the reaction of III (1 g, 3.6 mmol) with 10% HCl (30 ml) and EtOH (20 ml), neutralization was carried out with K_2CO_3. The subsequent procedure was the same as above. Yield of VI, 345 mg (60%).

When a solution of III (1 g, 3.6 mmol) in AcOH (40 ml) and H_2O (10 ml) was heated on a boiling water bath for 1 h, V precipitated as a yellow powder (300 mg, 39%). Concentration of the filtrate gave a brown mixture, which was treated with EtOH–H_2O to afford VI (100 mg, 17%).

Reaction of III in Sodium Ethoxide, 80% aq. EtOH, and 80% aq. MeOH Solutions——Na (200 mg) was dissolved in abs. EtOH (50 ml), and compound III (1 g, 3.6 mmol) was added to the solution. The solution was refluxed on a boiling water bath for 1 h. Removal of the solvent gave an oily product, which was treated with AcOH to afford yellow crystals (Ia) (800 mg, 95%).

When a solution of III (1 g, 3.6 mmol) in EtOH (40 ml) and H_2O (10 ml) was refluxed on a boiling water bath for 1 h, V precipitated as a yellow powder (165 mg, 19%). Concentration of the filtrate *in vacuo* provided Ia (760 mg, 80%).

In the reaction of III (1 g, 3.6 mmol) in MeOH (40 ml) and H_2O (10 ml), V and Ib were obtained in 57% and 40% yields, respectively.

3-(N,N-Dimethylhydrazinocarbonyl)furo[2,3-*b*]quinoxaline (VII)——NH_2NMe_2 (80 mg, 1.33 mmol) was added to a solution of III (200 mg, 0.72 mmol) in EtOH (30 ml), and the mixture was refluxed for 1 h. Removal of the solvent by evaporation gave yellow crystals, which were treated with hexane–EtOH to give a yellow powder (VII) (170 mg, 92%). Recrystallization from EtOH afforded yellow needles, mp 230—232°C. MS *m/e*: 256 (M^+). IR ν_{max} cm^{-1}: 1735 (C=O). NMR (DMSO-d_6): 12.20 (1H, br.s, $\mathrm{CON\underline{H}NMe_2}$), 9.50 (1H, s, 2-H), 7.73—7.00 (4H, m, aromatic), 3.00 (6H, s, $\mathrm{CONH\underline{Me}_2}$). *Anal.* Calcd for $C_{13}H_{12}N_4O_2$: C, 60.93; H, 4.72; N, 21.87. Found: C, 60.98; H, 4.58; N, 22.14.

4-(3′,4′-Dihydro-3′-oxoquinoxalin-2′-yl)pyrazolin-5-one (VIIIa) and Its 2-Methyl (VIIIb) and 2-Phenyl (VIIIc) Derivatives——General Procedure: The appropriate hydrazine (2.8 mmol) was added to a solution of III (200 mg, 0.72 mmol) in EtOH (30 ml), and the solution was refluxed for 1 h to precipitate yellow-orange crystals (VIII). Concentration of the mother liquor gave additional VIII.

Compound VIIIa: Yield, 150 mg (90%). Recrystallization from AcOH followed by EtOH gave yellow needles, mp 305°C. MS *m/e*: 228 (M^+). IR ν_{max} cm^{-1}: 1675, 1620 (C=O). NMR (DMSO-d_6): 12.35 (1H, br.s, 2-NH), 8.30 (1H, br.s, 3-H), 7.67—7.00 (4H, m, aromatic). The 1-NH and 4′-NH protons were not observed, presumably due to the presence of moisture in the solvent. *Anal.* Calcd for $C_{11}H_8N_4O_2$: C, 57.89; H, 3.53; N, 24.55. Found: C, 57.66; H, 3.47; N, 24.42.

Compound VIIIb: Yield, 170 mg (85%). Recrystallization from AcOH–EtOH gave orange needles, mp 310°C. MS *m/e*: 242 (M^+). IR ν_{max} cm^{-1}: 1683, 1620 (C=O). NMR (DMSO-d_6): 8.07 (1H, s, 3-H), 7.67—7.00 (4H, m, aromatic), 3.40 (3H, s, 2-Me). The 1-NH and 4′-NH protons were not observed, presumably due to the presence of moisture in the solvent. *Anal.* Calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.33; H, 4.05; N, 23.44.

Compound VIIIc: Yield, 210 mg (96%). Recrystallization from EtOH gave orange needles, mp 313°C. MS *m/e*: 304 (M^+). IR ν_{max} cm^{-1}: 1675, 1620 (C=O). NMR (DMSO-d_6): 8.43 (1H, s, 3-H), 8.23—7.00 (9H, m, aromatic). The 1-NH and 4′-NH protons were not observed, presumably due to the presence of moisture in the solvent. *Anal.* Calcd for $C_{17}H_{12}N_4O_2$: C, 67.09; H, 3.98; N, 18.41. Found: C, 67.01; H, 3.70; N, 18.23.

Chlorination of VIIIb: $POCl_3$ (50 ml) was added to a solution of VIIIb (1 g, 4.1 mmol) in DMF (20 ml), and the mixture was heated on a boiling water bath for 4 h. The reaction mixture was concentrated *in vacuo*, and poured onto crushed ice to precipitate colorless crystals (IXb) (1.03 g, 90%). Recrystallization from

EtOH gave colorless needles, mp 138—140°C. MS *m/e*: 278 (M^+), 280 ($M^+ + 2$). NMR (CF_3COOH): 8.68 (1H, s, 5-H), 8.83—7.33(4H, m, aromatic), 4.33 (3H, s, N-Me). *Anal.* Calcd for $C_{12}H_8Cl_2N_4$: C, 51.64; H, 2.89; N, 20.07. Found: C, 51.52; H, 2.78; N, 20.29.

Chlorination of VIIIc: $POCl_3$ (100 ml) was added to a solution of VIIIc (1 g, 3.3 mmol) in DMF (20 ml), and the mixture was heated on a boiling water bath for 8 h. The reaction mixture was concentrated *in vacuo*, and poured onto crushed ice. The reaction product was extracted with $CHCl_3$, and the extract was dried aver Na_2SO_4. The solvent was evaporated off *in vacuo* to give a mixture of IXc and Xc. Compound IXc was taken up in a small amount of EtOH by heating, and insoluble Xc was separated by filtration of the hot EtOH solution.

Concentration of the above filtrate gave colorless crystals (IXc). Recrystallization from EtOH gave colorless needles (0.55 g, 50%), mp 164—167°C. MS *m/e*: 340 (M^+), 342 ($M^+ + 2$). NMR (CF_3COOH): 8.77 (1H, s, 5-H), 8.67—7.73 (9H, m, aromatic). *Anal.* Calcd for $C_{17}H_{10}Cl_2N_4$: C, 59.84; H, 2.95; N, 16.42. Found: C, 59.83; H, 2.81; N, 16.50.

Recrystallization of Xc from EtOH gave red needles (0.48 g, 45%), mp 196.5—198°C. MS *m/e*: 322 (M^+), 324 ($M^+ + 2$). NMR (CF_3COOH); 9.30 (1H, s, 3-H), 8.40—7.07 (9H, m, aromatic). *Anal.* Calcd for $C_{17}H_{11}ClN_4O$: C, 63.26; H, 3.44; N, 17.36. Found: C, 63.21; H, 3.24; N, 17.35.

Chlorination of Xc: $POCl_3$ (20 ml) was added to a solution of Xc (500 mg, 1.55 mmol) in DMF (10 ml), and the mixture was heated on a boiling water bath for 2 h. The reaction mixture was concentrated *in vacuo*, and poured onto crushed ice. The reaction product was extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to dryness *in vacuo* to give IXc (520 mg, 98%).

4,5-Dihydro-2-methylpyrazolo[3′,4′: 3,4]pyridazino[5,6-*b*]quinoxaline (XIb) and 4,5-Dihydro-2-phenylpyrazolo[3′,4′: 3,4]pyridazino[5,6-*b*]quinoxaline (XIc)——A solution of IXb (300 mg, 1.34 mmol) in hydrazine hydrate (20 ml) was heated at 150—160°C for 4 h to precipitate a red powder (XIb), which was collected by suction and washed with EtOH (180 mg, 80%). MS *m/e*: 238 (M^+). Since XIb was oxidized to some extent during the recrystallization, producing a mixture of XIb and XIIb, spectral and elemental analytical data were not obtained.

A solution of IXc (300 mg, 0.88 mmol) in hydrazine hydrate (20 ml) was heated at 150—160°C for 8 h to precipitate a red powder (XIc), which was collected by suction and washed with EtOH (230 mg, 87%). MS *m/e*: 300 (M^+). Since XIc was oxidized to some extent during the recrystallization, producing a mixture of XIc and XIIc, spectral and elemental analytical data were not obtained.

2-Methylpyrazolo[3′,4′: 3,4]pyridazino[5,6-*b*]quinoxaline (XIIb)——Method A: A solution of XIb (50 mg, 0.21 mmol) in EtOH (100 ml) was refluxed for 30 min under aeration. The color of the solution changed from red to yellow. Removal of the solvent by evaporation gave yellow crystals (XIIb) (40 mg, 80%). Recrystallization from EtOH–AcOH afforded yellow needles, mp>300°C. MS *m/e*: 236 (M^+). NMR (CF_3COOD): 9.43 (1H, s, 1-H), 9.00—7.57 (4H, m, aromatic), 4.80 (3H, s, 2-Me). *Anal.* Calcd for $C_{12}H_8N_6$: C, 61.00; H, 3.41; N, 35.58. Found: C, 60.87; H, 3.26; N, 35.78.

Method B: Dibenzyl azodicarboxylate (400 mg, 1.5 mmol) was added to a solution of XIb (70 mg, 0.29 mmol) in EtOH (50 ml), and the mixture was refluxed for 3 h. Removal of the solvent by evaporation gave XIIb (60 mg, 86%).

2-Phenylpyrazolo[3′,4′: 3,4]pyridazino[5,6-*b*]quinoxaline (XIIc)——Method A: A solution of XIc (100 mg, 0.33 mmol) in AcOH (100 ml) was refluxed for 3 h under aeration. The color of the solution changed from red to yellow. Removal of the solvent by evaporation gave yellow crystals (XIIc) (30 mg, 30%). Recrystallization from EtOH–AcOH afforded yellow needles, mp>300°C. MS *m/e*: 298 (M^+). NMR (CF_3COOD): 9.63 (1H, s, 1-H), 8.90—7.00 (9H, m, aromatic). *Anal.* Calcd for $C_{17}H_{10}N_6$: C, 68.44; H, 3.38; N, 28.18. Found: C, 68.30; H, 3.27; N, 28.21.

Method B: Dibenzyl azodicarboxylate (507 mg, 1.91 mmol) was added to a solution of XIc (130 mg, 0.43 mmol) in EtOH (100 ml), and the mixture was refluxed for 3 h. Removal of the solvent by evaporation gave XIIc (105 mg, 80%).

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References and Notes

1) A part of this work was reported by Y. Kurasawa and A. Takada in *Heterocycles*, **14**, 281 (1980).
2) R. Mondelli and L. Merlini, *Tetrahedron*, **22**, 2356 (1966).
3) C. Iijima and E. Hayashi, *Yakugaku Zasshi*, **92**, 729 (1972).
4) C.L. Lees and H.N. Lydon, *J. Chem. Soc.*, **1955**, 303.
5) R. Royer and E. Bisagni, *Bull. Soc. Chim. Fr.*, **1960**, 395.
6) K. Takagi and T. Ueda, *Chem. Pharm. Bull.*, **19**, 1971, 1218.
7) K. Takagi and M. Hubert-Habart, *Bull. Soc. Chim. Fr.*, **1977**, 369.
8) L.M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1969, pp. 88—92, and references cited therein.