A New Synthesis of 1,5-Dihydropyridazino[3,4-*b*]quinoxalines and 2-(Pyrazol-4-yl)quinoxalines

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Dedicated to the memory of Professor Nicholas Alexandrou

The reaction of 6-chloro-2-(1-methylhydrazino)quinoxaline 1-oxide **3** with acetylenedicarboxylates gave the 8-chloro-1-methyl-1,5-dihydropyridazino[3,4-*b*]quinoxaline-3,4-dicarboxylates **4a,b** and 2-(pyrazol-4-yl)quinoxaline 1-oxides **5a,b**. The formation of compounds **4a,b** would follow the 1,3-dipolar cycloaddition reaction, subsequent 1,2-hydrazino migration, and then dehydrative cyclization, while the production of compounds **5a,b** would proceed *via* the addition of the hydrazino group to acetylenedicarboxylate leading to the construction of a pyrazole ring, followed by rearrangement of the pyrazole ring. Compounds **5a,b** were deoxidized with phosphoryl chloride/*N,N*-dimethylformamide to change into the 4-(quinoxalin-2-yl)pyrazole-3-carboxylates **8a,b**.

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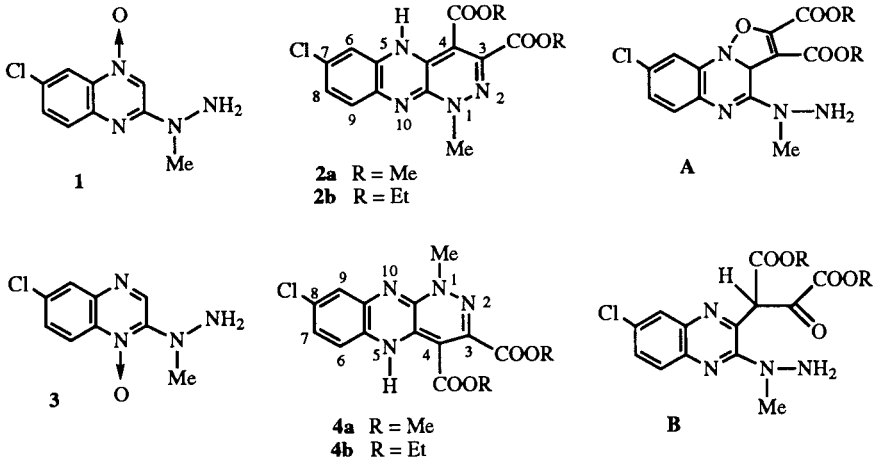
In previous papers [1,2], we reported that the 1,3-dipolar cycloaddition reaction of 6-chloro-2-(1-methylhydrazino)-quinoxaline 4-oxide **1** with acetylenedicarboxylates afforded the 7-chloro-1-methyl-1,5-dihydropyridazino[3,4-*b*]-quinoxaline-3,4-dicarboxylates **2a,b** (Chart 1) *via* the formation of an isoxazole intermediate **A**, subsequent cleavage of the isoxazole ring, and then dehydrative cyclization in an intermediate **B**. In continuation of the above type of investigation, we studied the reaction of acetylenedicarboxylates with 6-chloro-2-(1-methylhydrazino)quinoxaline 1-oxide **3** (regioisomer of compound **1** in the *N*-oxide position). As the result, we have found that this reaction provided the 8-chloro-1-methyl-1,5-dihydropyridazino[3,4-*b*]-quinoxaline-3,4-dicarboxylates **4a,b** (regioisomer of compounds **2a,b** in the chlorine atom position) and 2-(pyrazol-4-yl)quinoxaline 1-oxides **5a,b**. The formation of compounds **4a,b** would be due to the 1,3-dipolar cycloaddition reaction, following 1,2-hydrazino migration, and then dehydrative cyclization, while the production of compounds **5a,b** was owing to the addition of the hydrazino group to acetylenedicarboxylate giving a pyrazole ring, followed by the rearrangement of the pyrazole ring. This paper describes a new synthesis of the 1,5-dihydropyridazino[3,4-*b*]quinoxalines **4a,b** and 2-(pyrazol-4-yl)-quinoxalines **5a,b** together with the mechanism for the formation of compounds **4a,b** and **5a,b**.

Chart 1



The reaction of 2,6-dichloroquinoxaline **6** with peroxysulfuric acid gave 2,6-dichloroquinoxaline 1-oxide **7** [3], whose reaction with methylhydrazine afforded 6-chloro-2-(1-methylhydrazino)quinoxaline 1-oxide **3**. The reaction of compound **3** with dimethyl or diethyl acetylenedicarboxylate in dioxane at 70-80° provided dimethyl or diethyl 8-chloro-1-methyl-1,5-dihydropyridazino[3,4-*b*]-quinoxaline-3,4-dicarboxylate **4a** or **4b** and 6-chloro-2-(3-alkoxycarbonyl-5-hydroxy-1-methyl-1*H*-pyrazol-4-yl)quinoxaline 1-oxide **5a** or **5b**, respectively (Table 1). On the other hand, the reaction of compound **3** with dimethyl or diethyl acetylenedicarboxylate in ethanol at 40-50° precipitated compound **5a** or **5b**, respectively.

Table 1

Yield of Compounds **4a,b** and **5a,b**

Reaction Condition			
Solvent	Temperature	Product (Yield)	
Dioxane	70-80°	**4a** (50%)	**5a** (6%)
		4b (47%)	**5b** (10%)
EtOH	40-50°	---	**5a** (30%)
		---	**5b** (25%)

Table 2

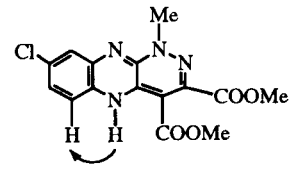
Carbon Chemical Shifts for Compounds **2a**, **2b**, **4a**, and **4b** in Deuteriodimethyl Sulfoxide

Carbon	Chemical Shift (δ ppm) Compound 2a	Compound 2b	Compound 4a	Compound 4b
C_3	142.5	142.6	142.8	143.1
C_4	90.8	90.5	90.3	90.1
C_{4a}	142.3	142.5	142.2	142.7
C_{5a}	129.9	129.7	129.2	129.1
C_6	116.1	116.0	117.5	117.7
C_7	128.0	127.9	123.7	123.7
C_8	125.2	125.0	127.6	128.0
C_9	125.2	125.1	123.0	123.0
C_{9a}	138.1	138.0	140.4	140.5
C_{10a}	150.0	149.9	150.4	150.4
NMe	39.8	39.8	39.6	[a]
Ester C=O	164.3	164.1	164.2	164.0
	164.2	163.6	164.0	163.6
Ester CH_2	---	61.4	---	61.4
	---	60.8	---	60.7
Ester Me	52.6	13.9	52.4	13.8
	52.2	13.9	52.0	13.8

[a] Overlapped with the carbon signals due to deuteriodimethyl sulfoxide.

The structural assignment of compounds **4a,b** were based on the NOE between the N_5-H and C_6-H protons (Chart 2) and on the comparison of the carbon chemical shifts between compounds **2a,b** and **4a,b** (Table 2). The chemical shifts of the C_3, C_4, C_{4a}, and C_{10a} carbons composing the pyridazine ring were closely similar among compounds **2a, 2b, 4a,** and **4b**. On the other hand, the mass

Chart 2



NOE (8.1%)

4a

spectra of compounds **5a,b** showed the molecular ion peak (M^+) and subsequent fragment ion peak (M^+ - O) (Table 3), indicating that compounds **5a,b** reserved the *N*-oxide moiety. Compound **5a** or **5b** was conveniently deoxidized

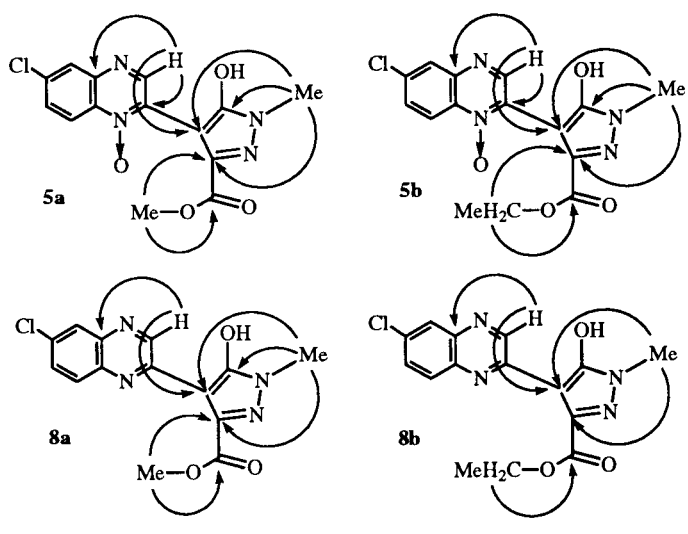
Table 3

High Resolution Mass Spectral Data for Compounds 5a and 5b

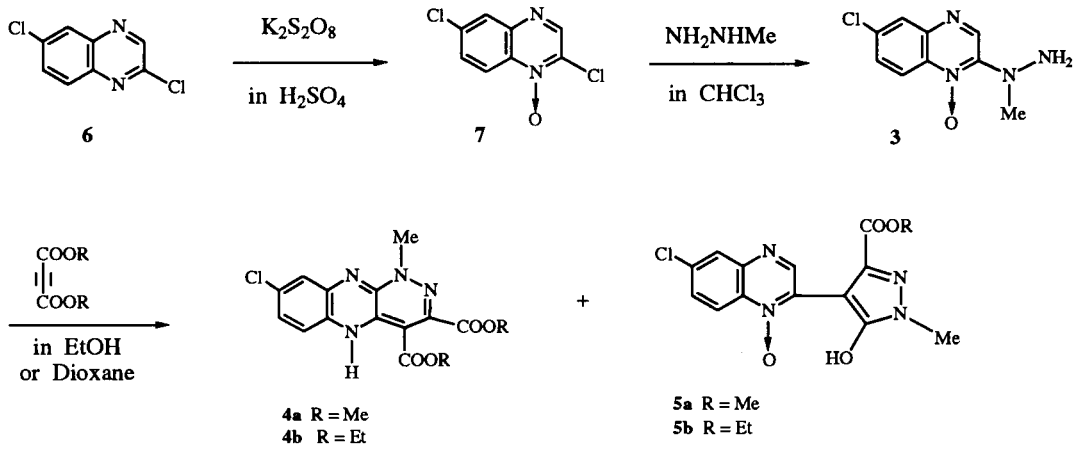
Compound	R	Formula	m/z Calcd./Found	
5a	Me	$C_{14}H_{11}ClN_4O_4$	334.0469 (334.0511)	(M^+)
		$C_{14}H_{11}ClN_4O_3$	318.0520 (318.0474)	(M^+ - O)
5b	Et	$C_{15}H_{13}ClN_4O_4$	348.0625 (348.0655)	(M^+)
		$C_{15}H_{13}ClN_4O_3$	332.0676 (332.0702)	(M^+ - O)

under heating in phosphoryl chloride/*N*,*N*-dimethylformamide to give methyl or ethyl 4-(6-chloroquinoxalin-2-yl)-5-hydroxy-1-methyl-1*H*-pyrazole-3-carboxylate **8a** or **8b**, respectively (Scheme 2). The structure of compounds **5a,b** and **8a,b** was further supported by the carbon chemical shifts (Table 4) obtained from the HMBC and HMQC spectra together with the ^2J-^4J coupling data (Chart 3), especially showing the ^3J coupling between the quinoxaline

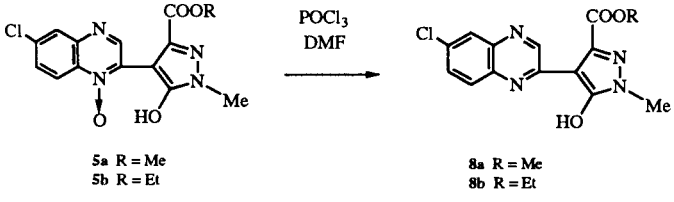
Chart 3



Scheme 1



Scheme 2



142.5 ppm) presumably due to the deuteration on the nitrogen of the pyrazole ring in the deuteriotrifluoroacetic acid solution of compounds **5a,b**. In addition, compounds **5a,b** and **8a,b** were found to exist as the OH form pyrazole (Scheme 3), but not as the NH or CH form pyrazole, from the comparison of the C_5 carbon chemical shifts with those of compounds **9-12** [compounds **9,10** (OH form pyrazole C_5: δ 155.6-154.5 ppm), compounds **5a,b,8a,b** (OH form pyrazole C_5: δ 159.0-155.4 ppm)] (Chart 4, Table 4).

Table 4

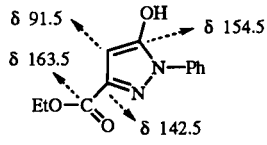
Carbon Chemical Shifts for Compounds **5a**, **5b**, **8a**, and **8b** in Deuteriotrifluoroacetic Acid

	Chemical Shift (δ ppm)			
Carbon	Compound **5a**	Compound **5b**	Compound **8a**	Compound **8b**
Quinoxaline Ring				
C_2	136.5	136.5	144.3	143.1
C_3	143.4	143.5	143.7	144.1
C_{4a}	133.6	133.6	135.6	136.0
C_5	121.1	121.1	124.7	125.0
C_6	144.4	144.3	141.0	140.9
C_7	135.3	135.5	136.7	136.7
C_8	121.1	121.2	123.6	123.4
C_{8a}	137.8	137.7	132.4	132.1
Pyrazole Ring				
C_3	136.2	136.5	137.0	137.4
C_4	94.9	94.9	97.6	97.7
C_5	155.4	155.4	159.0	159.0
NMe	33.1	33.0	32.6	32.7
Ester C=O	161.1	160.8	163.1	162.9
Ester CH_2	---	64.5	---	65.4
Ester Me	53.3	12.1	53.8	12.1

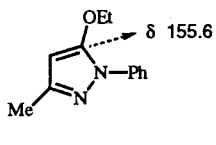
C_3-H proton and pyrazole C_4 carbon. The chemical shifts of the pyrazole C_4 and C_5 carbons in compounds **5a,b** measured in deuteriotrifluoroacetic acid [C_4 (δ ~94.9 ppm), C_5 (δ ~155.4 ppm)] were similar to those of compound **9** (Chart 4) measured in deuteriodimethyl sulfoxide [C_4 (δ 91.5 ppm), C_5 (δ 154.5 ppm)] [4], while the chemical shifts of the pyrazole C_3 carbons were slightly different between compounds **5a,b** (δ 136.5-136.2 ppm) and compound **9** (δ

Thus, the formation of compounds **5a,b** would be explained by the reaction mechanism *via* intermediates **C-F** (Scheme 4), including the pyrazole ring formation (**C**), elimination and addition of the pyrazole ring (**D, E**), and then prototropy (**F**). On the other hand, the production of compounds **4a,b** may be elucidated by the reaction mechanism *via* intermediates **G-I** (Scheme 5), involving the 1,3-dipolar cycloaddition reaction affording an isoxazole

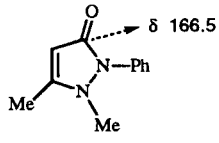
Chart 4



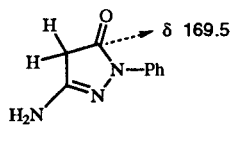
9 in DMSO-d_6



10 in DMSO-d_6

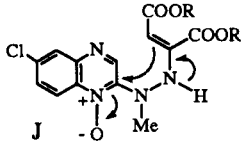


11 in DMSO-d_6

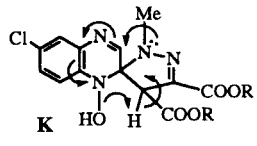


12 in DMSO-d_6

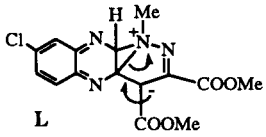
Chart 5



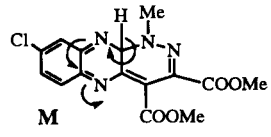
J



K

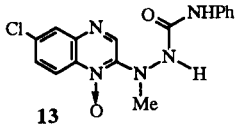


L

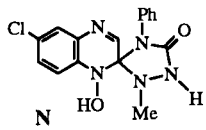


M

Chart 6

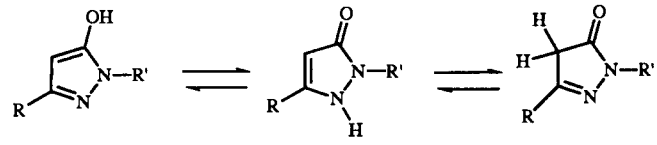


13



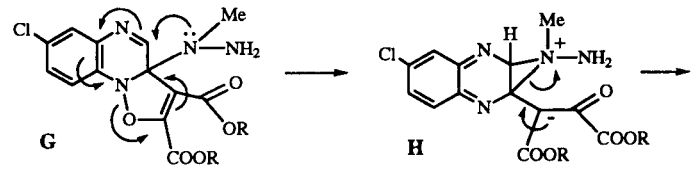
N

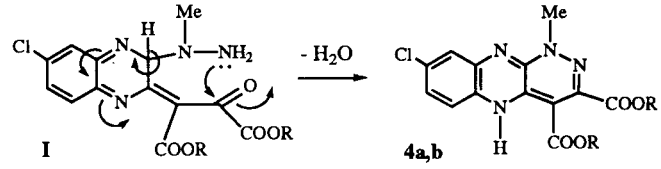
Scheme 3



OH Form NH Form CH Form

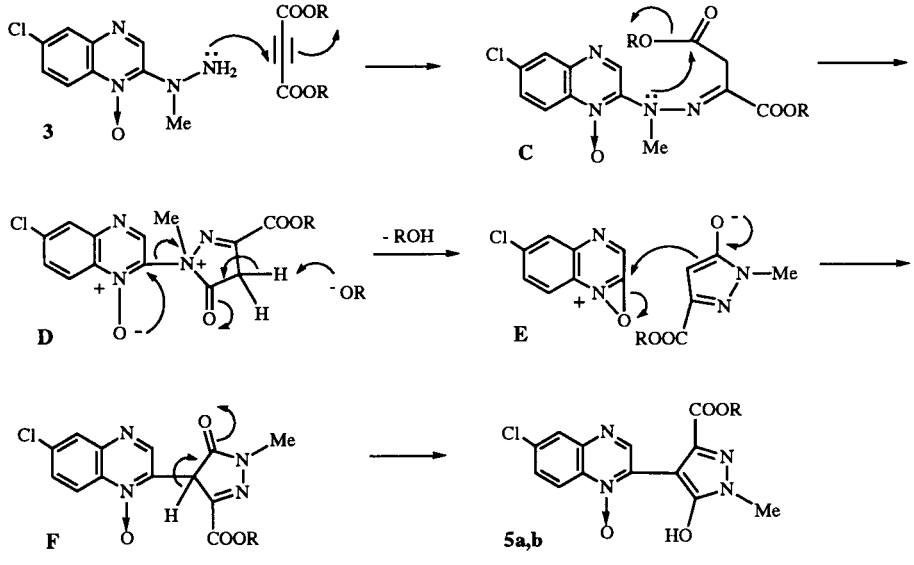
Scheme 5





intermediate **G**, subsequent 1,2-hydrazino migration *via* intermediates **H** [5-7] and **I**, and then dehydrative cyclization to compounds **4a,b**. Moreover, the mechanism *via* intermediates **J-M** (Chart 5) would be eliminated, since compound **13** [8] (Chart 6) synthesized from compound **3** was not converted into spiro compound **N** under reflux in dioxane or ethanol.

Scheme 4



EXPERIMENTAL

All melting points were determined on a Yazawa micro melting point BY-2 apparatus and are uncorrected. The ir spectra (potassium bromide) were recorded with a JASCO IRA-1 spectrophotometer. The nmr spectra were measured with an XL-400 spectrometer at 400 MHz. The chemical shifts are given in the δ scale. The mass spectra (ms) were determined with a JEOL JMS-01S spectrometer. Elemental analyses were performed on a Perkin-Elmer 240B instrument.

2,6-Dichloroquinoxaline 1-Oxide **7**.

Compound **6** (22.6 g, 113.6 mmoles) was added portionwise to concentrated sulfuric acid (100 ml) with stirring in an ice bath to give a brown solution. Then, potassium peroxodisulfate (33.75 g, 125.0 mmoles) was added portionwise to the above sulfuric acid solution, and stirring was continued for 24 hours. The whole reaction mixture was poured onto crushed ice to precipitate pale yellow crystals, which were extracted with chloroform 2-3 times. The combined chloroform solution was dried over sodium sulfate and then evaporated *in vacuo* to afford pale yellow crystals. Recrystallization from chloroform/ethanol provided pale yellow needles **7**, which were collected by suction filtration (13.01 g, 53%), mp 185-186°; ir: ν cm^{-1} 1585, 1550, 1510; ms: m/z 214 (M^+), 216 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 9.08 (s, 1H, C_3-H), 8.42 (d, J = 9.0 Hz, 1H, C_8-H), 8.26 (d, J = 2.0 Hz, 1H, C_5-H), 7.90 (dd, J = 9.0 , 2.0 Hz, 1H, C_7-H).

Anal. Calcd. for $C_8H_4Cl_2N_2O$: C, 44.68; H, 1.87; Cl, 32.98; N, 13.03. Found: C, 44.79; H, 1.69; Cl, 32.94; N, 13.25.

6-Chloro-2-(1-methylhydrazino)quinoxaline 1-Oxide **3**.

A solution of compound **7** (10 g, 46.5 mmoles) and methylhydrazine (5.35 g, 116.3 mmoles) in chloroform (150 ml) was refluxed on a boiling water bath for 1 hour. Evaporation of the solvent *in vacuo* gave yellow crystals **3**. Recrystallization from chloroform afforded yellow needles **3**, which were collected by suction filtration (7.94 g). Evaporation of the filtrate *in vacuo* provided yellow crystals **3**, whose recrystallization from chloroform gave yellow needles **3** (1.11 g), total yield, 9.05 g, (87%). Compound 3 had mp 174-175°; ir: ν cm^{-1} 3300, 3200, 3040, 1640, 1600, 1555; ms: m/z 224 (M^+), 226 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 9.06 (s, 1H, C_3-H), 8.30 (d, J = 9.0 Hz, 1H, C_8-H), 8.03 (d, J = 2.0 Hz, 1H, C_5-H), 7.73 (dd, J = 9.0, 2.0 Hz, 1H, C_7-H), 5.13 (s, 2H, NH_2), 3.42 (s, 3H, CH_3).

Anal. Calcd. for $C_9H_9ClN_4O$: C, 48.12; H, 4.04; Cl, 15.78; N, 24.94. Found: C, 48.21; H, 4.14; Cl, 15.56; N, 24.86.

Dimethyl 8-Chloro-1-methyl-1,5-dihydropyridazino[3,4-*b*]quinoxaline-3,4-dicarboxylate **4a** and 6-Chloro-2-(5-hydroxy-3-methoxycarbonyl-1-methyl-1*H*-pyrazol-4-yl)quinoxaline 1-Oxide **5a**.

A solution of compound **3** (4 g, 17.8 mmoles) and dimethyl acetylenedicarboxylate (3.04 g, 21.4 mmoles) in dioxane (80 ml) was heated at 70-80° with stirring in an oil bath for 2 hours. Evaporation of the solvent *in vacuo* gave a mixture of compounds **4a** and **5a** as yellow crystals. Recrystallization from dioxane/ethanol afforded yellow needles **5a**, which were collected by suction filtration (0.38 g, 6%). Evaporation of the filtrate *in vacuo* provided yellow crystals. Recrystallization from ethanol gave yellow needles **4a**, which were collected by suction filtration (3.11 g, 50%).

Compound **4a** had mp 179-180°; ir: ν cm^{-1} 3350, 1720, 1685; ms: m/z 348 (M^+), 350 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 10.24 (s, 1H, NH), 7.01 (d, J = 8.5 Hz, 1H, C_6-H), 6.75 (dd, J = 8.5, 2.0 Hz, 1H, C_7-H), 6.69 (d, J = 2.0 Hz, 1H, C_9-H), 3.70 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.11 (s, 3H, NCH_3).

Anal. Calcd. for $C_{15}H_{13}ClN_4O_4$: C, 51.66; H, 3.76; Cl, 10.17; N, 16.07. Found: C, 51.66; H, 3.75; Cl, 10.39; N, 16.29.

Compound **5a** had mp 275-276°; ir: ν cm^{-1} 1705; ms: m/z 334 (M^+), 336 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 9.24 (s, 1H, C_3-H), 8.35 (d, J = 9.5 Hz, 1H, C_8-H), 8.02 (d, J = 1.5 Hz, 1H, C_5-H), 7.72 (dd, J = 9.5, 1.5 Hz, 1H, C_7-H), 3.63 (s, 3H, OCH_3), 3.60 (s, 3H, NCH_3).

Anal. Calcd. for $C_{14}H_{11}ClN_4O_4$: C, 50.24; H, 3.31; Cl, 10.59; N, 16.74. Found: C, 50.19; H, 3.45; Cl, 10.63; N, 16.83.

Diethyl 8-Chloro-1-methyl-1,5-dihydropyridazino[3,4-*b*]quinoxaline-3,4-dicarboxylate **4b** and 6-Chloro-2-(3-ethoxycarbonyl-5-hydroxy-1-methyl-1*H*-pyrazol-4-yl)quinoxaline 1-Oxide **5b**.

A solution of compound **3** (4 g, 17.8 mmoles) and diethyl acetylenedicarboxylate (3.64 g, 21.4 mmoles) in dioxane (80 ml) was heated at 70-80° with stirring in an oil bath for 2 hours. Evaporation of the solvent *in vacuo* gave a mixture of compounds **4b** and **5b** as yellow crystals. Recrystallization from dioxane/ethanol afforded yellow needles **5b**, which were collected by suction filtration (650 mg, 10%). Evaporation of the filtrate *in vacuo* provided yellow crystals. Recrystallization from ethanol gave yellow needles **4b**, which were collected by suction filtration (3.13 g, 47%).

Compound **4b** had mp 160-161°; ir: ν cm^{-1} 1740, 1650; ms: m/z 376 (M^+), 378 ($M^+ + 2$), pmr (deuteriodimethyl sulfoxide): 10.03 (br, 1H, NH), 7.00 (d, J = 8.0 Hz, 1H, C_6-H), 6.75 (dd, J = 8.0, 2.5 Hz, 1H, C_7-H), 6.71 (d, J = 2.5 Hz, 1H, C_9-H), 4.14 (q, J = 7.0 Hz, 2H, CH_2), 4.11 (q, J = 7.0 Hz, 2H, CH_2), 3.11 (s, 3H, NCH_3), 1.22 (t, J = 7.0 Hz, 3H, CH_3), 1.16 (t, J = 7.0 Hz, 3H, CH_3).

Anal. Calcd. for $C_{17}H_{17}ClN_4O_4$: C, 54.19; H, 4.55; Cl, 9.41; N, 14.87. Found: C, 54.30; H, 4.59; Cl, 9.64; N, 14.95.

Compound **5b** had mp 283-284°; ir: ν cm^{-1} 1700; ms: m/z 348 (M^+), 350 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 9.24 (s, 1H, C_3-H), 8.32 (d, J = 9.5 Hz, 1H, C_8-H), 8.00 (d, J = 2.0 Hz, 1H, C_5-H), 7.70 (dd, J = 9.5, 2.0 Hz, 1H, C_7-H), 4.08 (q, J = 7.0 Hz, 2H, CH_2), 3.59 (s, 3H, NCH_3), 1.00 (t, J = 7.0 Hz, 3H, CH_3).

Anal. Calcd. for $C_{15}H_{13}ClN_4O_4$: C, 51.66; H, 3.76; Cl, 10.16; N, 16.07. Found: C, 51.73; H, 3.84; Cl, 9.94; N, 16.06.

6-Chloro-2-(5-hydroxy-3-methoxycarbonyl-1-methyl-1*H*-pyrazol-4-yl)quinoxaline 1-Oxide **5a**.

A solution of compound **3** (1 g, 4.45 mmoles) and dimethyl acetylenedicarboxylate (758 mg, 5.34 mmoles) in ethanol (50 ml) was heated at 40-50° on a water bath for 2 hours to precipitate yellow needles **5a**, which were collected by suction filtration (350 mg). Evaporation of the filtrate *in vacuo* afforded an oily product. Crystallization from ethanol provided yellow needles **5a**, which were collected by suction filtration (90 mg), total yield, 440 mg (30%).

6-Chloro-2-(3-ethoxycarbonyl-5-hydroxy-1-methyl-1*H*-pyrazol-4-yl)quinoxaline 1-Oxide **5b**.

A solution of compound **3** (1 g, 4.45 mmoles) and diethyl acetylenedicarboxylate (908 mg, 5.34 mmoles) in ethanol (50 ml) was heated at 40-50° on a water bath for 2 hours to precipitate yellow needles **5b**, which were collected by suction filtration (340 mg). Evaporation of the solvent *in vacuo* gave an oily product.

Crystallization from ethanol afforded yellow needles **5b**, which were collected by suction filtration (40 mg), total yield, 380 mg (25%).

Methyl 4-(6-Chloroquinoxalin-2-yl)-5-hydroxy-1-methyl-1*H*-pyrazole-3-carboxylate **8a** and Ethyl 4-(6-Chloroquinoxalin-2-yl)-5-hydroxy-1-methyl-1*H*-pyrazole-3-carboxylate **8b**.

General Procedure.

A solution of compound **5a** (1 g) or **5b** (1 g) in phosphoryl chloride (10 ml)/*N,N*-dimethylformamide (15 ml) was heated on a boiling water bath for 2 hours. The reaction mixture was poured onto crushed ice. The product was extracted with chloroform 2-3 times, and combined chloroform solution was dried over sodium sulfate. Evaporation of the solvent *in vacuo* gave red needles **8a** (360 mg, 38%) or **8b** (300 mg, 31%).

Compound **8a** was recrystallized from chloroform to give red needles, mp 302-303°; ir: ν cm^{-1} 1710, 1605; ms: m/z 318 (M^+), 320 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 10.22 (s, 1H, $C_{3'}$-H), 7.92 (d, J = 2.0 Hz, 1H, $C_{5'}$-H), 7.73 (d, J = 9.0 Hz, 1H, $C_{8'}$-H), 7.66 (dd, J = 2.0, 9.0 Hz, 1H, $C_{7'}$-H), 3.70 (s, 3H, OCH_3), 3.49 (s, 3H, NCH_3).

Anal. Calcd. for $C_{14}H_{11}ClN_4O_3$: C, 52.76; H, 3.48; Cl, 11.12; N, 17.58. Found: C, 52.84; H, 3.57; Cl, 11.16; N, 17.67.

Compound **8b** was recrystallized from chloroform/ethanol to afford red needles, mp 251-252°; ir: ν cm^{-1} 1700, 1600; ms: m/z 332 (M^+), 334 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 10.17 (s, 1H, $C_{3'}$-H), 7.88 (d, J = 2.0 Hz, 1H, $C_{5'}$-H), 7.66 (d, J = 9.0 Hz, 1H, $C_{8'}$-H), 7.61 (dd, J = 2.0, 9.0 Hz, 1H, $C_{7'}$-H), 4.14 (q, J = 7.0 Hz, 2H, CH_2), 3.45 (s, 3H, NCH_3), 1.00 (t, J = 7.0 Hz, 3H, CH_3).

Anal. Calcd. for $C_{15}H_{13}ClN_4O_3$: C, 54.16; H, 3.94; Cl, 10.66; N, 16.84. Found: C, 54.08; H, 3.95; Cl, 10.50; N, 16.80.

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