Synthesis and Conversion of 2-(Pyrazol-1-yl)quinoxaline 4-Oxides

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The reaction of 6-chloro-2-hydrazinoquinoxaline 4-oxide **1b** with acetylacetone or benzoylacetone gave 6-chloro-2-(3,5-dimethylpyrazol-1-yl)quinoxaline 4-oxide **5a** or 6-chloro-2-(3-methyl-5-phenylpyrazol-1-yl)quinoxaline 4-oxide **5b**, respXectively. Compound **5a** or **5b** was converted into the pyrrolo[1,5-*a*]quinoxaline **6a** or **6b**, triazolo[4,3-*a*]quinoxaline **9a** or **9b**, and tetrazolo[1,5-*a*]quinoxaline **10**.

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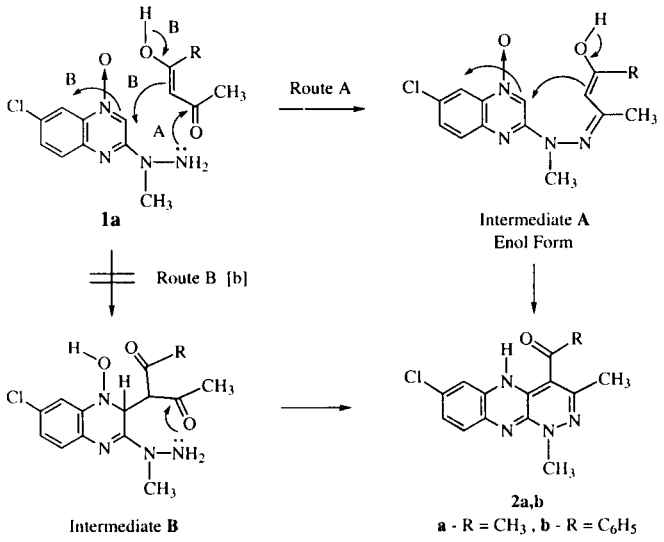
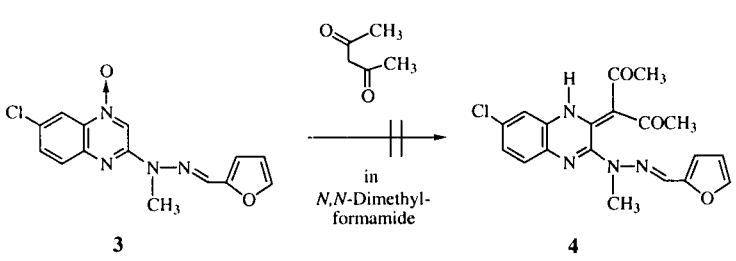
In a previous paper [1], we reported that the reaction of 6-chloro-2-(1-methylhydrazino)quinoxaline 4-oxide **1a** with β-diketones such as acetylacetone and benzoylacetone in *N,N*-dimethylformamide gave 4-acetyl- and 4-benzoyl-7-chloro-1,3-dimethyl-1,5-dihydropyridazino[3,4-*b*]quinoxalines **2a** and **2b** (Scheme 1), respectively, wherein intermediates **A** and **B** were postulated to be produced by dehydration between the NH_2 moiety of the C_2-(1-methylhydrazino) group and the carbonyl group of a β-diketone (route A) and by addition of the active methylene carbon in a β-diketone into the α-carbon of the *N*-oxide moiety (route B), respectively. Unfortunately, neither intermediate **A** nor **B** was isolated in this reaction. However, a reaction mechanism *via* an intermediate **B** in Scheme 1 was found to be unfavorable by the following result. Namely, a blockade of the NH_2 function in the C_2-(1-methylhydrazino) group with an aldehyde did not effect the above reaction. In fact, the reaction of 6-chloro-2-[2-(2-furyl)methylene-1-methylhydrazino]-quinoxaline 4-oxide **3** [2] with acetylacetone in *N,N*-dimethylformamide did not afford compound **4** (Scheme 2), but recovered the starting material **3**. On the contrary, a reaction mechanism *via* an intermediate **A** (enol form) in Scheme 1 was found to be acceptable by an indirect evidence obtained from the following investigation. That is, a change of the C_2-(1-methylhydrazino) group in compound **1a** into the hydrazino group provides 6-chloro-2-hydrazinoquinoxaline 4-oxide **1b** [3,4], whose reaction with acetylacetone in *N,N*-dimethylformamide furnishes a proof for the formation of an intermediate **A** (keto form), actually producing 6-chloro-2-(3,5-dimethylpyrazol-1-yl)quinoxaline 4-oxide **5a** (Scheme 3). Thus, the results shown in Schemes 2 and 3 prefer the reaction mechanism *via* an intermediate **A** (enol form) to that *via* an intermediate **B** in Scheme 1. This paper describes the synthesis of the pyrazolylquinoxaline 4-oxides **5a,b** (Scheme 4) supporting the reaction mechanism *via* an intermediate **A** in Scheme 1, together with the conversion of the pyrazolylquinoxaline 4-oxides **5a,b** into the pyrrolo-, triazolo-, and tetrazoloquinoxalines **6a,b**, **9a,b** and **10** confirming the structure of the pyrazolylquinoxalines **5a,b** (Schemes 4 and 5).

Scheme 1 [a]

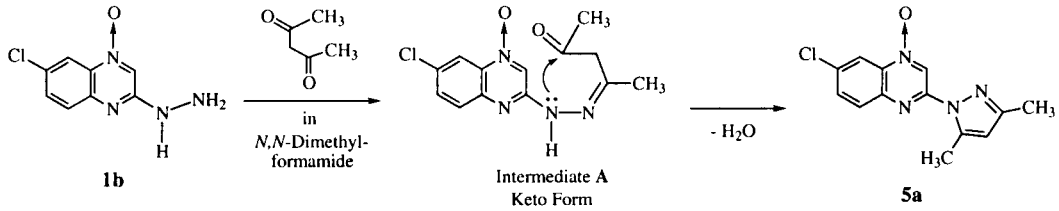


[a] Already reported by us [1]. [b] This route is denied in the present investigation.

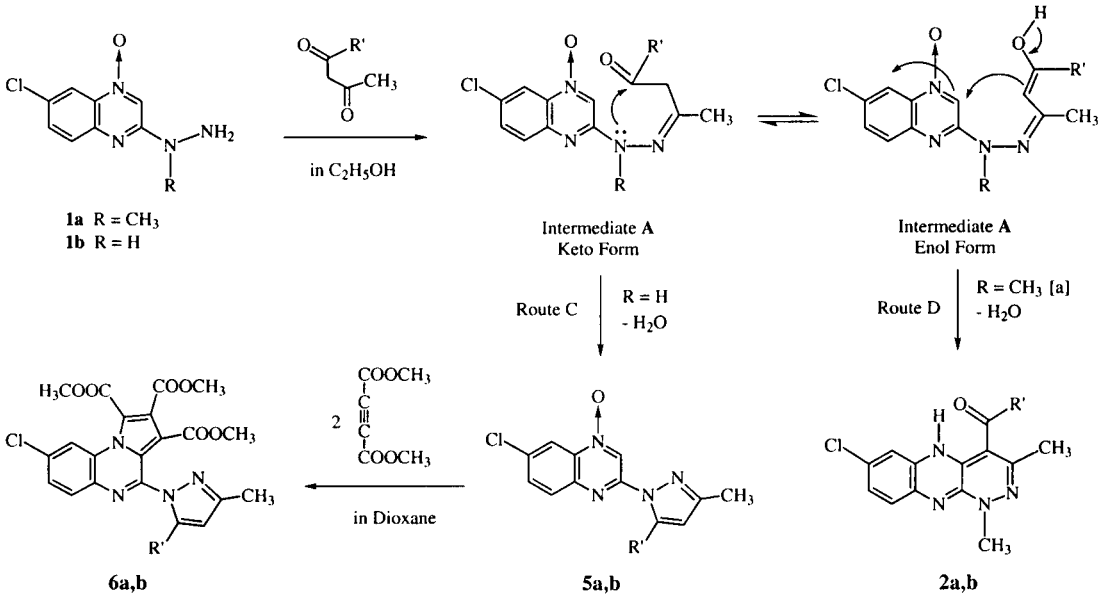
Scheme 2



Scheme 3

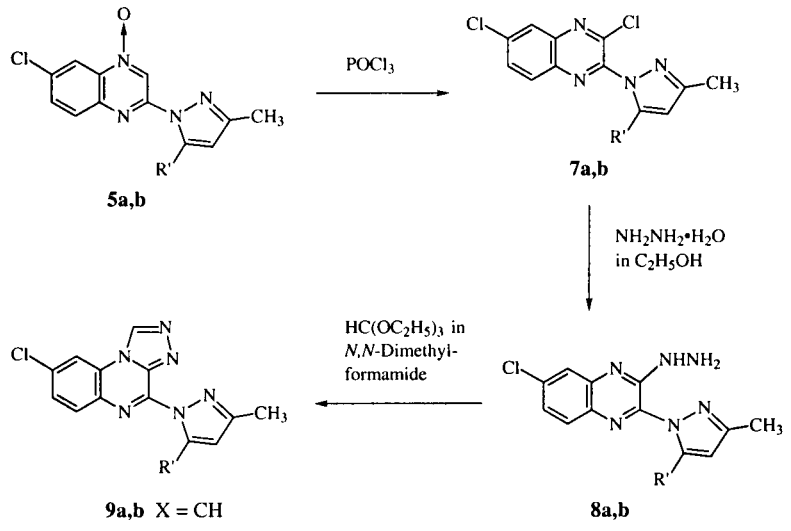


Scheme 4



[a] Already reported by us [1]. **2a,b**, **5a,b**, **6a,b** : **a** - R' = CH_3 , **b** - R' = C_6H_5

Scheme 5



5a,b, **7a,b**, **8a,b**, **9a,b** : **a** - R' = CH_3 , **b** - R' = C_6H_5

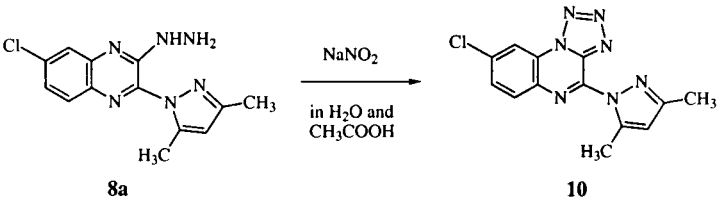
In the conversion of compound **1b** into the pyrazolylquinoxaline 4-oxide **5a** (Scheme 3), a change of a solvent from *N,N*-dimethylformamide to ethanol was found to improve the yield of compound **5a** (50% in *N,N*-dimethylformamide, 68% in ethanol) so that the transformation of compound **1b** into the pyrazolylquinoxaline 4-oxides **5a,b** was henceforth carried out in ethanol.

The reaction of 6-chloro-2-hydrazinoquinoxaline 4-oxide **1b** with acetylacetone or benzoylacetone in ethanol gave 6-chloro-2-(3,5-dimethylpyrazol-1-yl)-quinoxaline 4-oxide **5a** or 6-chloro-2-(3-methyl-5-phenylpyrazol-1-yl)quinoxaline 4-oxide **5b**, respectively (Scheme 4), presumably *via* the cyclization of an intermediate **A** (keto form) into a pyrazole ring by an intramolecular dehydration in the side chain (route C). However, when the substituent R of an intermediate **A** is methyl group, the cyclization of an intermediate **A** (keto form) into a pyrazole ring is impossible, and hence the cyclization of an intermediate **A** (enol form) into a pyridazino-[3,4-*b*]quinoxaline ring (route D) takes place *via* attack of the active methylene carbon to the α-carbon of the *N*-oxide moiety. Thus, the pyridazino[3,4-*b*]quinoxalines **2a,b** were produced from 6-chloro-2-(1-methylhydrazino)quinoxaline 4-oxide **1a**.

Preservation of the *N*-oxide moiety in compounds **5a,b** was assured by the following reactions. The reaction of compound **5a** and **5b** with 2-fold molar amount of dimethyl acetylenedicarboxylate resulted in the 1,3-dipolar cycloaddition reaction and then ring transformation [5,6] to afford trimethyl 8-chloro-4-(3,5-dimethylpyrazol-1-yl)pyrrolo[1,2-*a*]quinoxaline-1,2,3-tricarboxylate **6a** or trimethyl 8-chloro-4-(3-methyl-5-phenylpyrazol-1-yl)-pyrrolo[1,2-*a*]quinoxaline-1,2,3-tricarboxylate **6b**, respectively [7]. The reaction of compound **5a** and **5b** with phosphoryl chloride provided 3,6-dichloro-2-(3,5-dimethylpyrazol-1-yl)quinoxaline **7a** and 3,6-dichloro-2-(3-methyl-5-phenylpyrazol-1-yl)quinoxaline **7b** [7,8], whose reaction with hydrazine hydrate gave 6-chloro-3-hydrazino-2-(3,5-dimethylpyrazol-1-yl)quinoxaline **8a** and 6-chloro-3-hydrazino-2-(3-methyl-5-phenylpyrazol-1-yl)quinoxaline **8b**, respectively (Scheme 5). The reaction of compound **8a** and **8b** with triethyl orthoformate afforded 8-chloro-4-(3,5-dimethylpyrazol-1-yl)-1,2,4-triazolo[4,3-*a*]quinoxaline **9a** and 8-chloro-4-(3-methyl-5-phenylpyrazol-1-yl)-1,2,4-triazolo[4,3-*a*]quinoxaline **9b** [9], respectively, while the reaction of compound **8a** with nitrous acid provided 8-chloro-4-(3,5-dimethylpyrazol-1-yl)tetrazolo[1,5-*a*]quinoxaline **10** [10] (Scheme 6).

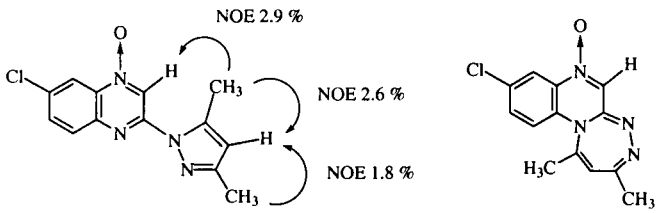
The structure of new compounds **5-10** were supported by the analytical and spectral data. Especially, for compound **5a** preserving the *N*-oxide moiety was ascertained by the nOe between the C_3-H proton of the quinoxaline ring and the C_5-CH_3 protons of the pyrazole ring (Chart). These results rule out the possible formation of triazepinoquinoxaline **5a'** (Chart) from the reaction of compound **1b** with acetylacetone.

Scheme 6



8a **10**

Chart



5a **5a'**

Quinoxaline C_3 - H	δ 9.05 ppm	[not obtained]
Pyrazole C_3 - CH_3	δ 2.39 ppm	
Pyrazole C_4 - H	δ 6.43 ppm	
Pyrazole C_5 - CH_3	δ 2.56 ppm	

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 FT/IR-200 spectrometer. The nmr spectra were measured with a Varian 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.

6-Chloro-2-(3,5-dimethylpyrazol-1-yl)quinoxaline 4-oxide **5a**.

A solution of compound **1b** (10 g, 47.5 mmoles) and acetylacetone (7.13 g, 71.3 mmoles) in ethanol (250 ml) was refluxed on a boiling water bath for 2 hours to precipitate colorless prismic needles of compound **5a**. After the reaction mixture was allowed to stand overnight, the colorless needles were collected by suction filtration and then washed with ethanol to provide an analytically pure sample of compound **5a** (8.91 g, 68%), mp 195-196°; ir: ν cm^{-1} 1570, 1540, 1525; ms: m/z 274 (M^+), 276 (M^+ + 2); pmr (deuteriotrifluoroacetic acid): 9.05 (s, 1H, C_3-H), 8.45 (d, J = 2.0 Hz, 1H, C_5-H), 7.95 (d, J = 9.0 Hz, 1H, C_8-H), 7.82 (dd, J = 2.0, 9.0 Hz, 1H, C_7-H), 6.43 (s, 1H, pyrazole C_4-H), 2.56 (s, 3H, pyrazole CH_3), 2.39 (s, 3H, pyrazole CH_3).

Anal. Calcd. for $C_{13}H_{11}ClN_4O$: C, 56.84; H, 4.04; Cl, 12.91; N, 20.39. Found: C, 56.77; H, 4.06; Cl, 12.89; N, 20.37.

6-Chloro-2-(3-methyl-5-phenylpyrazol-1-yl)quinoxaline 4-oxide **5b**.

A solution of compound **1b** (10 g, 47.5 mmoles) and benzoylacetone (11.55 g, 71.3 mmoles) in ethanol (500 ml) was refluxed on a boiling water bath for 2 hours. The solution was allowed to stand overnight to precipitate colorless prismic needles of

compound **5b**, which were collected by suction filtration and then washed with ethanol/*n*-hexane (1:1) to give an analytically pure sample of compound **5b** (9.26 g, 58%), mp 143-144°; ir: ν cm^{-1} 1610, 1570, 1545, 1505; ms: m/z 336 (M^+), 338 (M^+ + 2); pmr (deuteriodimethyl sulfoxide): 8.91 (s, 1H, C_3-H), 8.35 (d, J = 2.0 Hz, 1H, C_5-H), 7.81 (dd, J = 2.0, 9.0 Hz, 1H, C_7-H), 7.43 (d, J = 9.0 Hz, 1H, C_8-H), 7.44-7.41 (m, 2H, pyrazole C_5-phenyl), 7.40-7.32 (m, 3H, pyrazole C_5-phenyl), 6.58 (s, 1H, pyrazole C_4-H), 2.31 (s, 3H, pyrazole C_3-CH_3).

Anal. Calcd. for $C_{18}H_{13}ClN_4O$: C, 64.20; H, 3.89; Cl, 10.53; N, 16.64. Found: C, 64.17; H, 3.98; Cl, 10.37; N, 16.53.

Trimethyl 8-Chloro-4-(3,5-dimethylpyrazol-1-yl)pyrrolo-[1,2-*a*]quinoxaline-1,2,3-tricarboxylate **6a**.

A solution of compound **5a** (2 g, 7.30 mmoles) and dimethyl acetylenedicarboxylate (2.25 g, 15.8 mmoles) in dioxane (50 ml) was refluxed in an oil bath for 2 hours. Evaporation of the solvent *in vacuo* gave an oily residue, which was crystallized from ethanol to afford colorless prisms of compound **6a** (1.07 g, 31%), mp 208-209°; ir: ν cm^{-1} 1730, 1610; ms: m/z 470 (M^+), 472 (M^+ + 2); pmr (deuteriotrifluoroacetic acid): 8.02 (d, J = 8.5 Hz, 1H, C_6-H), 8.00 (d, J = 2.0 Hz, 1H, C_9-H), 7.70 (dd, J = 2.0, 8.5 Hz, 1H, C_7-H), 6.56 (s, 1H, pyrazole C_4-H), 4.15 (s, 3H, ester CH_3), 3.99 (s, 3H, ester CH_3), 3.73 (s, 3H, ester CH_3), 2.53 (s, 3H, pyrazole CH_3), 2.37 (s, 3H, pyrazole CH_3).

Anal. Calcd. for $C_{19}H_{17}ClN_4O_6$: C, 56.12; H, 4.07; Cl, 7.53; N, 11.90. Found: C, 56.11; H, 4.17; Cl, 7.51; N, 11.88.

Trimethyl 8-Chloro-4-(3-methyl-5-phenylpyrazol-1-yl)-pyrrolo[1,2-*a*]quinoxaline-1,2,3-tricarboxylate **6b**.

A solution of compound **5b** (2 g, 5.94 mmoles) and dimethyl acetylenedicarboxylate (1.86 g, 13.1 mmoles) in dioxane (50 ml) was refluxed in an oil bath for 2 hours. Evaporation of the solvent *in vacuo* afforded an oily residue, which was crystallized from ethanol to provide colorless cottony needles of compound **6b** (930 mg, 29%), mp 168-169°; ir: ν cm^{-1} 1735, 1718; ms: m/z 532 (M^+), 534 (M^+ + 2); pmr (deuteriotrifluoroacetic acid): 8.06 (d, J = 1.0 Hz, 1H, C_9-H), 8.00 (d, J = 8.5 Hz, 1H, C_6-H), 7.71 (dd, J = 1.0, 8.5 Hz, 1H, C_7-H), 7.38 (t, J = 6.5, Hz, 1H, pyrazole C_5-phenyl), 7.29-7.22 (m, 4H, pyrazole C_5-phenyl), 6.86 (s, 1H, pyrazole C_4-H), 4.13 (s, 3H, ester CH_3), 3.98 (s, 3H, ester CH_3), 3.77 (s, 3H, ester CH_3), 2.68 (s, 3H, pyrazole C_3-CH_3).

Anal. Calcd. for $C_{27}H_{21}ClN_4O_6$: C, 60.85; H, 3.97; Cl, 6.65; N, 10.51. Found: C, 60.55; H, 4.03; Cl, 6.71; N, 10.49.

3,6-Dichloro-2-(3,5-dimethylpyrazol-1-yl)quinoxaline **7a**.

A solution of compound **5a** (5 g) in phosphoryl chloride (30 ml) was refluxed in an oil bath for 1 hour. Evaporation of phosphoryl chloride *in vacuo* left an oily residue, which was dissolved in dioxane (50 ml) with heating. The dioxane solution was poured onto crushed ice with stirring to precipitate pale yellow crystals, which were collected by suction filtration. Recrystallization from ethanol/water afforded yellow prismic needles of compound **7a** (4.7 g, 88%), mp 131-132°; ir: ν cm^{-1} 1602, 1570; ms: m/z 292 (M^+), 294 (M^+ + 2); pmr (deuteriodimethyl sulfoxide): 8.27 (dd, J = 2.0, 0.5 Hz, 1H, C_5-H), 8.14 (dd, J = 0.5, 9.0 Hz, 1H, C_8-H), 7.98 (dd, J = 2.0, 9.0 Hz, 1H, C_7-H), 6.17 (q, J = 0.8 Hz, 1H, pyrazole C_4-H), 2.30 (d, J = 0.8 Hz, 3H, pyrazole CH_3), 2.21 (s, 3H, pyrazole CH_3).

Anal. Calcd. for $C_{13}H_{10}Cl_2N_4$: C, 53.26; H, 3.44; Cl, 24.19; N, 19.11. Found: C, 53.16; H, 3.49; Cl, 24.25; N, 19.00.

3,6-Dichloro-2-(3-methyl-5-phenylpyrazol-1-yl)quinoxaline **7b**.

A solution of compound **5b** (10 g) in phosphoryl chloride (50 ml) was refluxed in an oil bath for 1 hour. Evaporation of phosphoryl chloride *in vacuo* left an oily residue, which was dissolved in dioxane (80 ml) with heating. The dioxane solution was poured onto crushed ice with stirring to precipitate colorless crystals, which were collected by suction filtration. Recrystallization from ethanol/water provided colorless cottony needles of compound **7b** (8.40 g, 80%), mp 120-121°; ir: ν cm^{-1} 1602, 1550, 1500; ms: m/z 354 (M^+), 356 (M^+ + 2); pmr (deuteriodimethyl sulfoxide): 8.27 (d, J = 2.0 Hz, 1H, C_5-H), 8.06 (d, J = 8.5 Hz, 1H, C_8-H), 7.96 (dd, J = 2.0, 8.5 Hz, 1H, C_7-H), 7.28-7.24 (m, 3H, pyrazole C_5-phenyl), 7.19-7.14 (m, 2H, pyrazole C_5-phenyl), 6.67 (s, 1H, pyrazole C_4-H), 2.31 (s, 3H, pyrazole C_3-CH_3).

Anal. Calcd. for $C_{18}H_{12}Cl_2N_4$: C, 60.86; H, 3.40; Cl, 19.96; N, 15.77. Found: C, 60.90; H, 3.52; Cl, 19.83; N, 15.79.

6-Chloro-3-hydrazino-2-(3,5-dimethylpyrazol-1-yl)quinoxaline **8a**.

A solution of compound **7a** (5 g, 17.1 mmoles) and hydrazine hydrate (2.14 g, 42.8 mmoles) in ethanol (150 ml) was refluxed on a boiling water bath for 2 hours to precipitate yellow needles. After the reaction mixture was allowed to stand overnight, the yellow needles were collected by suction filtration. Recrystallization from *N,N*-dimethylformamide/ethanol gave yellow cottony needles of compound **8a** (4.08 g, 83%), mp 196-197°; ir: ν cm^{-1} 3310, 3270, 3190, 1610; ms: m/z 288 (M^+), 290 (M^+ + 2); pmr (deuteriotrifluoroacetic acid): 7.98 (d, J = 2.0 Hz, 1H, C_5-H), 7.98 (d, J = 8.5 Hz, 1H, C_8-H), 7.74 (dd, J = 2.0, 8.5 Hz, 1H, C_7-H), 6.58 (s, 1H, pyrazole C_4-H), 2.56 (s, 3H, pyrazole CH_3), 2.52 (s, 3H, pyrazole CH_3) (NH protons were deuterized); pmr (deuteriodimethyl sulfoxide): 9.38 (br, 1H, hydrazine NH), 7.74 (d, J = 8.5 Hz, 1H, C_8-H), 7.64 (d, J = 2.0 Hz, 1H, C_5-H), 7.38 (dd, J = 2.0, 8.5 Hz, 1H, C_7-H), 6.26 (s, 1H, pyrazole C_4-H), 4.70 (br, 2H, hydrazine NH_2), 2.55 (s, 3H, pyrazole CH_3), 2.26 (s, 3H, pyrazole CH_3).

Anal. Calcd. for $C_{13}H_{13}ClN_6$: C, 54.08; H, 4.54; Cl, 12.28; N, 29.11. Found: C, 54.13; H, 4.60; Cl,12.41; N, 29.33.

6-Chloro-3-hydrazino-2-(3-methyl-5-phenylpyrazol-1-yl)-quinoxaline **8b**.

A solution of compound **7b** (5 g, 14.1 mmoles) and hydrazine hydrate (1.77 g, 35.3 mmoles) in ethanol (150 ml) was refluxed on a boiling water bath for 2 hours to precipitate a small amount of yellow needles. Evaporation of the solvent *in vacuo* gave yellow needles, which were collected by suction filtration. Recrystallization from *N,N*-dimethylformamide/ethanol/water provided yellow powders of compound **8b** (4.10 g, 83%), mp 160-161°; ir: ν cm^{-1} 3385, 3305, 3195, 1610, 1578, 1550; ms: m/z 350 (M^+), 352 (M^+ + 2); pmr (deuteriotrifluoroacetic acid): 7.92 (d, J = 2.0 Hz, 1H, C_5-H), 7.92 (d, J = 8.5 Hz, 1H, C_8-H), 7.70 (dd, J = 2.0, 8.5 Hz, 1H, C_7-H), 7.44 (t, J = 7.5, Hz, 1H, pyrazole C_5-phenyl), 7.31 (dd, J = 7.5, 7.5 Hz, 2H, pyrazole C_5-phenyl), 7.24 (d, J = 7.5 Hz, 2H, pyrazole C_5-phenyl), 6.83 (s, 1H, pyrazole C_4-H), 2.63 (s, 3H, pyrazole C_3-CH_3) (NH protons were deuterized).

Anal. Calcd. for $C_{18}H_{15}ClN_6$: C, 61.63; H, 4.31; Cl, 10.11; N, 23.96. Found: C, 61.49; H, 4.46; Cl, 10.32; N, 23.79.

8-Chloro-4-(3,5-dimethylpyrazol-1-yl)-1,2,4-triazolo[4,3-*a*]-quinoxaline **9a**.

A solution of compound **8a** (1.5 g) and triethyl orthoformate (20 ml) in *N,N*-dimethylformamide (20 ml) was refluxed in an oil bath

for 2 hours. Evaporation of the solvent *in vacuo* gave yellow crystals, whose recrystallization from *N,N*-dimethylformamide/ethanol/water provided yellow prisms of compound **9a** (1.25 g, 81%), mp 290-291°; ir: ν cm^{-1} 3080, 1610, 1565, 1550, 1518; ms: m/z 298 (M^+), 300 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 10.18 (s, 1H, C_1-H), 8.68 (d, J = 2.0 Hz, 1H, C_9-H), 8.01 (d, J = 8.5 Hz, 1H, C_6-H), 7.73 (dd, J = 2.0, 8.5 Hz, 1H, C_7-H), 6.26 (q, J = 0.8 Hz, 1H, pyrazole C_4-H), 2.53 (d, J = 0.8 Hz, 3H, pyrazole CH_3), 2.25 (s, 3H, pyrazole CH_3).

Anal. Calcd. for $C_{14}H_{11}ClN_6$: C, 56.29; H, 3.71; Cl, 11.87; N, 28.13. Found: C, 56.38; H, 3.80; Cl, 11.72; N, 28.17.

8-Chloro-4-(3-methyl-5-phenylpyrazol-1-yl)-1,2,4-triazolo[4,3-*a*]-quinoxaline **9b**.

A solution of compound **8b** (1.5 g) and triethyl orthoformate (20 ml) in *N,N*-dimethylformamide (20 ml) was refluxed in an oil bath for 2 hours. Evaporation of the solvent *in vacuo* gave yellow crystals, whose recrystallization from *N,N*-dimethylformamide/ethanol/water afforded yellow powders of compound **9b** (1.10 g, 71%), mp 276-277°; ir: ν cm^{-1} 1610, 1580, 1562, 1530, 1510; ms: m/z 360 (M^+), 362 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 10.18 (s, 1H, C_1-H), 8.70 (dd, J = 1.0, 2.0 Hz, 1H, C_7-H), 7.68 (d, J = 2.0 Hz, 1H, C_6-H), 7.68 (d, J = 1.0 Hz, 1H, C_9-H), 7.35-7.30 (m, 2H, pyrazole C_5-phenyl), 7.27-7.24 (m, 3H, pyrazole C_5-phenyl), 6.70 (s, 1H, pyrazole C_4-H), 2.34 (s, 3H, pyrazole C_3-CH_3).

Anal. Calcd. for $C_{19}H_{13}ClN_6$: C, 63.25; H, 3.63; Cl, 9.83; N, 23.29. Found: C, 62.98; H, 3.83; Cl, 9.95; N, 23.12.

8-Chloro-4-(3,5-dimethylpyrazol-1-yl)tetrazolo[1,5-*a*]quinoxaline **10**.

A solution of sodium nitrite (538 mg, 7.80 mmoles) in water (10 ml) was added to a suspension of compound **8a** (1.5 g, 5.20 mmoles) in acetic acid (30 ml) with stirring in an ice-water bath. The mixture was heated on a boiling water bath for 30 minutes to give a clear solution. Then, water (50 ml) was added to the solution to precipitate yellow crystals, and additional heating was carried out for 30 minutes. After the reaction mixture was cooled to room temperature, the above yellow crystals were collected by suction filtration. Recrystallization from *N,N*-dimethylformamide/ethanol provided yellow needles of compound **10** (1.15 g, 74%), mp 208-209° (once melted and then changed into red needles), second mp 302-303°; ir: ν cm^{-1} 1610, 1582, 1570, 1558, 1510; ms: m/z 299 (M^+), 301 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 8.69 (d, J = 2.0 Hz, 1H, C_9-H), 8.24 (d, J = 9.0 Hz, 1H, C_6-H), 7.97 (dd, J = 2.0, 9.0 Hz, 1H, C_7-H), 6.76 (s, 1H, pyrazole C_4-H), 3.01 (s, 3H, pyrazole CH_3), 2.76 (s, 3H, pyrazole CH_3).

Anal. Calcd. for $C_{13}H_{10}ClN_7$: C, 52.10; H, 3.36; Cl, 11.83; N, 32.71. Found: C, 52.20; H, 3.53; Cl, 12.01; N, 32.44.

REFERENCES AND NOTES

[1] Y. Kurasawa, A. Takano, K. Harada, A. Takada, H. S. Kim, and Y. Okamoto, *Khim. Geterotsikl. Soedin.*, **9**, 1245 (1995).

[2] Y. Kurasawa, T. Kureyama, N. Yoshishiba, R. Katoh, A. Takada, H. S. Kim, and Y. Okamoto, *J. Heterocyclic Chem.*, **30**, 537 (1993).

[3] H. S. Kim, Y. Kurasawa, and A. Takada, *J. Heterocyclic Chem.*, **26**, 1511 (1989).

[4] H. S. Kim, Y. Kurasawa, C. Yoshii, M. Masuyama, A. Takada, and Y. Okamoto, *J. Heterocyclic Chem.*, **27**, 1111 (1990).

[5] H. S. Kim, Y. Kurasawa, and A. Takada, *J. Heterocyclic Chem.*, **26**, 871 (1989).

[6] H. S. Kim, Y. Kurasawa, C. Yoshii, M. Masuyama, A. Takada, and Y. Okamoto, *J. Heterocyclic Chem.*, **27**, 1119 (1990).

[7] Y. Kurasawa, A. Takada, and H. S. Kim, *J. Heterocyclic Chem.*, **32**, 1085 (1995).

[8] Y. Kurasawa, T. Hosaka, Y. Matsumoto, A. Ishikura, K. Ikeda, A. Takada, H. S. Kim, and Y. Okamoto, *J. Heterocyclic Chem.*, **31**, 1697 (1994).

[9] Y. Kurasawa, N. Yoshishiba, T. Kureyama, T. Okano, A. Takada, H. S. Kim, and Y. Okamoto, *J. Heterocyclic Chem.*, **29**, 1653 (1992).

[10] Y. Kurasawa, T. Kureyama, N. Yoshishiba, T. Okano, A. Takada, H. S. Kim, and Y. Okamoto, *J. Heterocyclic Chem.*, **30**, 781 (1993).