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Synthesis of Condensed Quinoxalines. VI.[1] Synthesis of 1*H*-Pyrazolo[3,4-*b*]quinoxaline N-Oxides and Related Compounds

KEI YOSHIDA and HIROTAKA OTOMASU*

Faculty of Pharmaceutical Sciences, Hoshi University, Ebara 2–4–41, Shinagawa-ku, Tokyo 142, Japan

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Oxidation of 1*H*-pyrazolo[3,4-*b*]quinoxalines (**1a**: R=H, **1b**: R=CH_3) with *m*-chloroperbenzoic acid (MCPBA) gave the 4-oxides (**2a**, **b**). The structures of **2a**, **b** were confirmed by synthesis, by condensing 2-chloroquinoxaline-3-carbaldehyde 4-oxide (**6**) with appropriate hydrazines. Further oxidation of **2a** with MCPBA gave the 4,9-dioxide (**8**).

Treatment of 1,2-dihydro-2-oxoquinoxaline-3-carboxamide (**10**) and 1,2-dihydro-2-oxoquinoxaline-3-carbonitrile 4-oxide (**13**) with a mixture of $POCl_3$ and PCl_5 or $POCl_3$–dimethylformamide afforded 2-chloroquinoxaline-3-carbonitrile (**11**) and its 4-oxide (**14**), respectively. When **11** and **14** were reacted with hydrazines, the corresponding 3-amino-1*H*-pyrazolo[3,4-*b*]quinoxalines (**12a**, **b**) and their 4-oxides (**15a**, **b**) were obtained in high yields.

The reaction of ethyl 2-chloroquinoxaline-3-carboxylate (**16**) with hydrazine hydrate afforded a mixture of uncyclized products, *N,N'*-bis(2-ethoxycarbonyl-3-quinoxalinyl)hydrazine (**17**), ethyl 2-hydrazinoquinoxaline-3-carboxylate (**18**) and 2-hydrazinoquinoxaline-3-carbohydrazide (**19**).

Keywords——1*H*-pyrazolo[3,4-*b*]quinoxaline 4-oxide; 1*H*-pyrazolo[3,4-*b*]quinoxaline 4,9-dioxide; 3-amino-1*H*-pyrazolo[3,4-*b*]quinoxaline 4-oxide; 2-chloroquinoxaline-3-carbaldehyde 4-oxide; hydrazine; *N,N'*-bis(2-ethoxycarbonyl-3-quinoxalinyl)hydrazine; ethyl 2-hydrazinoquinoxaline-3-carboxylate; 2-hydrazinoquinoxaline-3-carbohydrazide

As a part of our continuing studies on the synthesis of condensed quinoxalines, 1*H*-pyrazolo[3,4-*b*]quinoxalines and their N-oxides were synthesized with a view to evaluating their biological activities. Some 1-substituted 1*H*-pyrazolo[3,4-*b*]quinoxalines (**1**: R=H, CH_3, C_6H_5) were prepared from 2-bromomethyl-3-chloroquinoxaline by treatment with hydrazines by Beyer,[2] but the N-oxides were not obtained. The present paper deals with the N-oxidation of **1a**, **b** and with synthesis of this ring system by taking advantage of the reactive functionalities at the 2 and 3 positions of quinoxaline.

The oxidation of **1a** with *m*-chloroperbenzoic acid (MCPBA) in chloroform solution formed a sole mono-oxide (**2a**) in 74% yield. The structure of **2a** was confirmed by the three-step synthesis outlined in Chart 1.

The similar oxidation of 2-chloro-3-methylquinoxaline (**3**) using MCPBA gave a single mono-oxide (**4**) in 82% yield. Treatment of **4** with sodium ethoxide afforded the 2-ethoxy derivative (**5**), which was identical with 2-ethoxy-3-methylquinoxaline 4-oxide prepared by the oxidation of 2-ethoxy-3-methylquinoxaline with hydrogen peroxide in acetic acid. The structural assignment of **5** was established by Newbold *et al.*[3] and Otomasu *et al.*[4] When the resulting product (**4**) was oxidized with selenium oxide in benzene, a yellow product (**6**) was obtained in 72% yield. The infrared (IR) spectrum of **6** showed a C=O absorption band at 1700 cm^{-1}, and the nuclear magnetic resonance (NMR) spectrum of **6** indicated the presence of an aldehyde proton, δ 10.54 (1H, s).

These spectral and analytical data were consistent with the 2-chloroquinoxaline-3-

carbaldehyde 4-oxide structure (**6**).

Compound **6** was easily reacted with hydrazine hydrate to give a yellow solid (**2a**). The NMR spectrum of **2a** showed signals at δ 8.74 (1H, s) and 14.8 (1H, br), which could be assigned to 3-H and 1-H, respectively, of the pyrazole ring. The compound thus obtained **2a** was identical with the foregoing sample prepared by the oxidation of **1a** with MCPBA on the basis of mixed fusion and comparison of NMR spectra. Similarly, the oxidation of **1b** with MCPBA afforded a mono-oxide (**2b**), which was identical with 1-methyl-*H*-pyrazolo[3,4-*b*]quinoxaline 4-oxide prepared by the condensation of **6** with methylhydrazine. The reaction of **6** with phenylhydrazine produced only the phenylhydrazone (**7**), but this was cyclized into a condensed pyrazolo compound (**2c**) in good yield by treatment with potassium hydroxide in dimethylformamide (DMF).

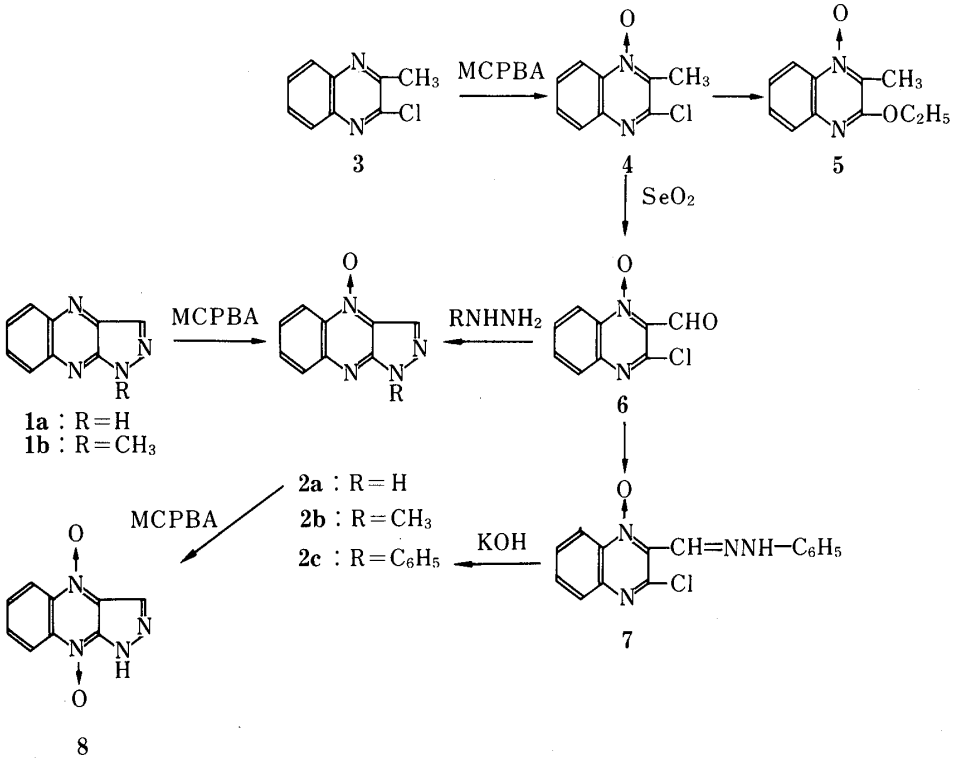

Chart 1

The mono-oxide **2a** was oxidized with MCPBA to give a slightly soluble dioxide (**8**) in 90% yield. The mass spectrum (MS) of **8** showed the molecular ion peak (M^+) at *m/e* 202 and two deoxygenated fragment peaks at 186 (M^+-O) and 170 (M^+-O_2). In the NMR spectrum of **8**, the signals of 1-H and 8-H appeared at δ 15.01 and 8.47, respectively, being shifted 0.2 ppm downfield from those of **2a**. These results were rationalized in terms of the magnetic anisotropy effect of the N–O bond at the 9-position. Based on these spectral data, the structure of **8** was concluded to be 1*H*-pyrazolo[3,4-*b*]quinoxaline 4,9-dioxide. Similar oxidations of **2b**, **c** did not give their dioxides.

The title compounds were also synthesized by alternative procedures. In a previous paper,[5] we reported that 2-chloro-3-cyano-substituted pyridine and quinoline compounds reacted with hydrazine hydrate to form 3-amino-1*H*-pyrazolo[3,4-*b*]pyridine and 3-amino-1*H*-pyrazolo[3,4-*b*]quinoline compounds, respectively. Using this procedure, 3-amino-1*H*-pyrazolo[3,4-*b*]quinoxaline and their N-oxides were prepared.

Ethyl 1,2-dihydro-2-oxoquinoxaline-3-carboxylate[6] (**9**) reacted with ammonium carbonate to form the carboxamide (**10**) in *ca.* 90% yield. When **10** was heated with a mixture of PCl_5 and $POCl_3$, chlorination and dehydration occurred and 2-chloroquinoxaline-3-

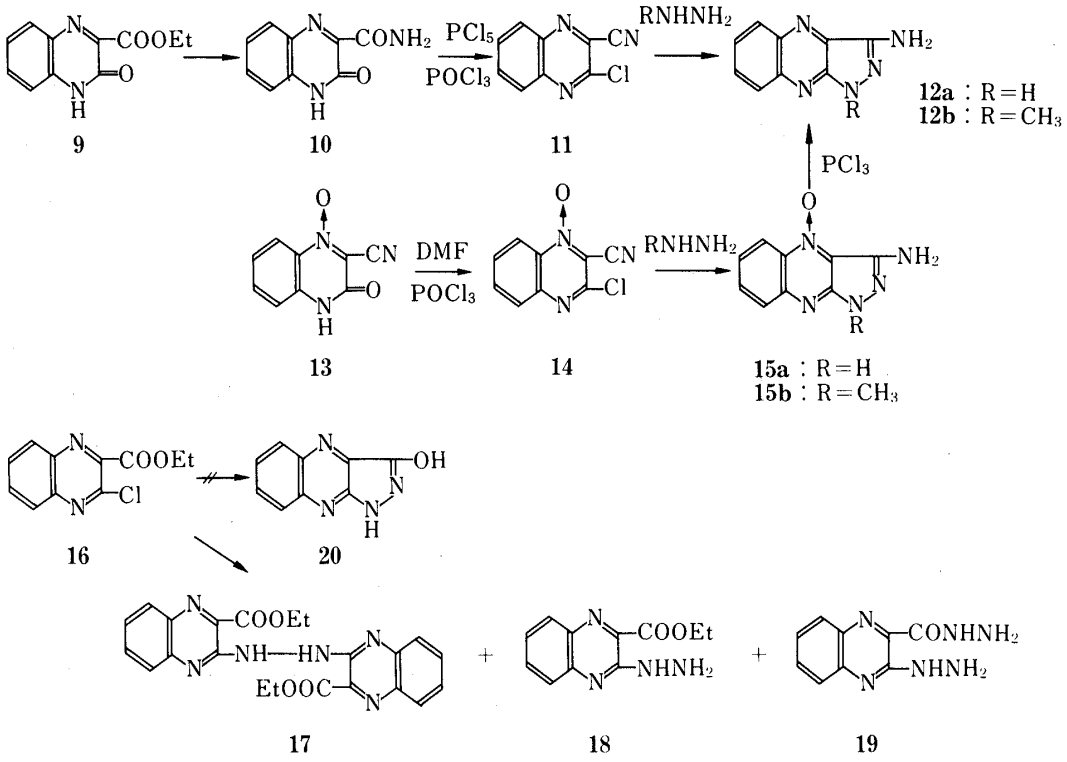

Chart 2

carbonitrile (**11**) was obtained in 85% yield. Refluxing of an ethanolic solution of **11** with hydrazine hydrate gave an orange-red solid (**12a**) in 83% yield. The IR spectrum of **12a** showed absorption bands due to NH_2 and NH groups at 3400, 3340 and 3200 cm^{-1}, and these were also apparent in the NMR spectrum as singlets (exchangeable with D_2O) at δ 6.12 (2H) and 12.21 (1H), respectively. Similarly, the reaction of **11** with methylhydrazine gave **12b** in 77% yield.

Confirmation of structure of **12a**, **b** was obtained by the following experiments. On treatment of 1,2-dihydro-2-oxoquinoxaline-3-carbonitrile 4-oxide[7] (**13**) with a mixture of $POCl_3$ and DMF in toluene solution followed by chromatography, the major product (**14**) was obtained in 45% yield. The reaction of **14** with appropriate hydrazines gave the products **15a**, **b** as in the reaction of **11**. Deoxygenation of **15a**, **b** with PCl_3 afforded the products **12a**, **b**, which were shown to be identical with the products obtained from the condensation of **11** with hydrazines.

Finally, the condensation of ethyl 2-chloroquinoxaline-3-carboxylate[8] (**16**) with hydrazine hydrate, which was expected to produce the homologous compound in a similar manner, was carried out. The reaction did not give the corresponding product (**20**) but a mixture of uncyclized products, *N,N'*-bis(2-ethoxycarbonyl-3-quinoxalinyl) hydrazine (**17**), ethyl 2-hydrazinoquinoxaline-3-carboxylate (**18**) and 2-hydrazinoquinoxaline-3-carbohydrazide (**19**). The formation ratio of these products depended on the reaction conditions. The structures of **17**—**19** were supported by the spectral and analytical data. Attempts to obtain a cyclized product under various conditions failed.

Experimental

All melting points were determined in a capillary and are uncorrected. The following instruments were used; IR spectra, Hitachi 215 spectrometer; MS, Hitachi RMS-4 and JEOL D-300 machines at 70 eV; NMR spectra, JEOL FX-100 spectrometer with tetramethylsilane as the internal standard.

1*H*-Pyrazolo[3,4-*b*]quinoxaline 4-Oxide (2a)——i) Oxidation of **1a**. MCPBA (85%, 0.12 g) was added to a suspension of **1a**[2] (0.1 g) in $CHCl_3$ (5 ml), and the mixture was stirred at 40 °C for 3 h. The precipitate was collected and recrystallized from MeOH to give 0.08 g (74%) of **2a** as yellow needles, mp > 300 °C. NMR (DMSO-d_6) δ: 7.84—7.94 (2H, m, H-6 and H-7), 8.22—8.63 (2H, m, H-5 and H-8), 8.75 (1H, s, H-3), 14.79 (1H, br, NH). *Anal.* Calcd for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.10. Found: C, 57.93; H, 3.10; N, 30.02.

ii) Condensation of **6** with hydrazine hydrate. Compound **6** (0.13 g) was added to hydrazine hydrate (1.5 ml) and the mixture was heated at 70 °C with stirring for 15 min. The separated product was recrystallized from MeOH to give yellow needles of **2a**. Yield, 70%. The IR and NMR spectra were superimposable on those of the above sample.

1-Methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline 4-Oxide (2b)——i) Oxidation of **1b**[2] (0.1 g) with MCPBA (85%, 0.12 g) as described for the preparation of **1a**, followed by recrystallization from MeOH gave yellow flakes, mp 189—190 °C. Yield, 78%. NMR (DMSO-d_6) δ: 4.12 (3H, s, CH_3), 7.65—7.99 (2H, m, H-6 and H-7), 8.05—8.55 (2H, m, H-5 and H-8), 8.65 (1H, s, H-3). *Anal.* Calcd for $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99. Found: C, 60.23; H, 3.92; N, 27.94.

ii) Condensation of **6** (0.18 g) with methylhydrazine (2 ml) as described for the preparation of **1a** gave yellow flakes of **2b**, which were identical with the above sample.

2-Chloro-3-methylquinoxaline 4-Oxide (4)——MCPBA (85%, 1.14 g) was added to a solution of **3** (1.0 g) in $CHCl_3$ (100 ml), and the mixture was stirred at room temperature for 6 h. The $CHCl_3$ solution was washed with aqueous $NaHCO_3$, dried over $MgSO_4$ and evaporated to dryness. The product was recrystallized from MeOH to give 0.89 g (82%) of **4** as colorless needles, mp 95—96 °C. NMR ($CDCl_3$) δ: 2.80 (3H, s, CH_3), 7.69—7.86 (2H, m, H-6 and H-7), 7.89—8.56 (2H, m, H-5 and H-8). *Anal.* Calcd for $C_9H_7ClN_2O$: C, 55.17; H, 3.46; N, 14.56. Found: C, 55.54; H, 3.62; N, 14.39.

2-Ethoxy-3-methylquinoxaline 4-Oxide (5)——A solution of Na (0.03 g) in EtOH (5 ml) was added to a solution of **5** (0.2 g) in EtOH (3 ml), and the mixture was refluxed for 30 min. The salt that separated was removed and the solution was evaporated to dryness. The product was recrystallized from EtOH to give colorless prisms, mp 86—87 °C, which were identical with an authentic sample[4] (mixed mp and IR spectral comparison).

2-Chloroquinoxaline-3-carbaldehyde 4-Oxide (6)——A mixture of **4** (1.0 g) and SeO_2 (0.7 g) and in benzene (30 ml) was refluxed under stirring, during which time a black precipitate formed. The mixture was filtered, the filtrate was evaporated, and the residual product was recrystallized from benzene to give 0.77 g (72%) of **6** as yellow needles, mp 165—166 °C. IR ν_{max}^{Nujol} cm^{-1}: 1700 (C=O). NMR ($CDCl_3$) δ: 7.70—8.12 (3H, m, H-6, H-7 and H-8), 8.44—8.54 (1H, m, H-5), 10.54 (1H, s, CHO). *Anal.* Calcd for $C_9H_5ClN_2O_2$: C, 68.69; H, 3.84; N, 21.34. Found: C, 68.85; H, 3.74; N, 21.50.

2-Chloroquinoxaline-3-carbaldehyde Phenylhydrazone 4-Oxide (7)——Compound **6** (1.0 g) was added to phenylhydrazine (5 ml) with stirring at room temperature. The precitate that formed immediately was corrected and recrystallized from MeOH to give 1.35 g (94%) of **7** as dark red needles, mp 220—221 °C (dec.). NMR (DMSO-d_6) δ: 6.89—8.02 (8H, m, Ar-H), 8.33—8.43 (1H, m, H-5), 8.53 (1H, s, CH=N), 11.45 (1H, s, NH). *Anal.* Calcd for $C_{15}H_{11}ClN_4O$: C, 60.36; H, 3.71; N, 18.77. Found: C, 60.21; H, 3.64; N, 18.74.

1-Phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline 4-Oxide (2c)——An aqueous solution of KOH (20%, 4 ml) was added to an ice-cooled solution of **7** (1.0 g) in DMF (20 ml) with stirring, and the stirring was continued for 30 min. The reaction mixture was poured into ice-water, and the resulting precipitate was collected and recrystallized from EtOH to give 0.8 g (91%) of **2c** as yellow needles, mp 190—191 °C. NMR (DMSO-d_6) δ: 7.40—8.36 (8H, m, Ar-H), 8.52—8.60 (1H, m, H-5), 8.89 (1H, s, H-3). *Anal.* Calcd for $C_{15}H_{10}N_4O$: C, 68.69; H, 3.84; N, 21.34. Found: C, 68.85; H, 3.74; N, 21.50.

1*H*-Pyrazolo[3,4-*b*]quinoxaline 4,9-Dioxide (8)——MCPBA (85%, 0.4 g) was added to a suspension of **2a** (0.1 g) in $CHCl_3$ (5 ml), and the mixture was warmed at 40 °C for 30 min. The precipitate was recrystallized from MeOH to give red needles, mp > 300 °C (dec.). Yield, 90% MS *m/e*: 202 (M^+), 186 ($M^+ - O$), 170 ($M^+ - O_2$). NMR (DMSO-d_6) δ: 7.79—7.82 (2H, m, H-6 and H-7), 8.49—8.59 (2H, m, H-5 and H-8), 8.71 (1H, s, H-3), 15.01 (1H, br, NH). Good agreement with the calculated values was not obtained on elemental analysis, possibly because of explosive burning.

1,2-Dihydro-2-oxoquinoxaline-3-carboxamide (10)——A mixture of **9**[6] (2.0 g) and $(NH_4)_2CO_3$ (4.0 g) in MeOH (20 ml) was allowed to stand overnight at room temperature under stirring. The solvent was removed, and the residual product was washed with water to give 1.6 g (89%) of **10** as pale yellow needles, mp 265 °C (dec.). (MeOH). IR ν_{max}^{Nujol} cm^{-1}: 3350—3150 (NH, NH_2), 1690 (C=O). *Anal.* Calcd for $C_9H_7N_3O_2$: C, 57.14; H, 3.73; N, 22.21. Found: C, 56.72; H, 3.99; N, 22.15.

2-Chloroquinoxaline-3-carbonitrile (11)——A mixture of **10** (5.4 g), PCl_5 (12 g) and $POCl_3$ (4.4 g) was heated at 110 °C for 1.5 h. The reaction mixture was poured into ice-water and the resulting precipitate was collected. The product was taken up in benzene and run through an Al_2O_3 column to give 4.5 g (85%) of **11** as colorless needles, mp 159—160 °C. MS *m/e*: 189 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 2220 w (CN). *Anal.* Calcd for $C_9H_4ClN_3$: C, 57.01; H, 2.12; N, 22.16. Found: C, 56.77; H, 2.45; N, 21.96.

3-Amino-1*H*-pyrazolo[3,4-*b*]quinoxaline (12a)——Hydrazine hydrate (0.26 g) was added to a solution of **11** (0.5 g) in EtOH (30 ml), and the mixture was refluxed for 30 min, then allowed to cool. The precipitate was collected, washed with water and recrystallized from EtOH to give 0.4 g (83%) of **12a** as orange-red leaflets, mp 292—293 °C.

MS *m/e*: 185 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 3400, 3340, 3210 (NH, NH_2). NMR (DMSO-d_6) δ: 6.12 (2H, s, NH_2), 12.2 (1H, s, NH). *Anal.* Calcd for $C_9H_7N_5$: C, 58.37; H, 3.81; N, 37.82. Found: C, 58.28; H, 3.57; N, 37.34.

3-Amino-1-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (12b)——Treatment of **11** (0.5 g) with methylhydrazine (0.28 g) as described above gave 0.4 g (77%) of **12b** as orange-red needles, mp 178 °C (EtOH). MS *m/e*: 199 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 3410, 3340, 3210 (NH, NH_2). *Anal.* Calcd for $C_{10}H_9N_5$: C, 60.29; H, 4.55; N, 35.16. Found: C, 60.63; H, 4.55; N, 34.81.

2-Chloroquinoxaline-3-carbonitrile 4-Oxide (14)——A mixture of **13**[7] (3.0 g), $POCl_3$ (16.7 g) and DMF (1.8 g) in toluene (40 ml) was refluxed for 2 h. After cooling, the reaction mixture was poured into ice-water, and the toluene layer was collected and evaporated to dryness. The residual product was taken up in benzene and run through an Al_2O_3 column to give 2.1 g (45%) of **14** as pale yellow leaflets, mp 192 °C. MS *m/e*: 205 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 2220 w (CN). NMR ($CDCl_3$) δ: 7.81—8.16 (3H, m, Ar-H), 8.42—8.53 (1H, m, H-5). *Anal.* Calcd for $C_9H_4ClN_3O$: C, 52.57; H, 1.96; N, 20.43. Found: C, 52.79; H, 2.49; N, 20.31.

3-Amino-1*H*-pyrazolo[3,4-*b*]quinoxaline 4-Oxide (15a)——Hydrazine hydrate (0.26 g) was added to a solution of **14** (0.5 g) in EtOH (30 ml) and the mixture was refluxed for 30 min, then allowed to cool. The precipitate was filtered off and recrystallized from EtOH to give **15a** as dark red needles, mp 276 °C. Yield, 0.46 g (93%). MS *m/e*: 201 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 3420, 3290, 3170 (NH, NH_2). NMR (DMSO-d_6) δ: 6.08 (2H, br, NH_2), 12.41 (1H, s, NH). *Anal.* Calcd for $C_8H_7N_5O$: C, 53.73; H, 3.51; N, 34.81. Found: C, 53.54; H, 3.42; N, 34.77.

3-Amino-1-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline 4-Oxide (15b)——Treatment of **14** (0.5 g) with methylhydrazine (0.28 g) as described above gave 0.39 g (75%) of **15b** as dark red needles, mp 203 °C (EtOH). MS *m/e*: 215 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 3470, 3290, 3180 (NH_2). NMR (DMSO-d_6) δ: 3.80 (3H, s, CH_3), 6.18 (2H, s, NH_2). *Anal.* Calcd for $C_{10}H_9N_5O$: C, 55.81; H, 4.22; N, 32.54. Found: C, 55.94; H, 4.45; N, 32.73.

Deoxygenation of 15a, b——A solution of **15a** (0.1 g) in PCl_3 (5 ml) was refluxed for 1 h. After cooling, the mixture was poured into ice-water. The aqueous solution was made alkaline with Na_2CO_3 and a brown precipitate was collected. Recrystallization from EtOH gave 0.03 g of orange-red leaflets, which were identical with an authentic sample of **12a**.

By a similar procedure, 0.045 g of **12b** was obtained from 0.1 g of **15b**.

Reaction of Ethyl 2-Chloroquinoxaline-3-carboxylate (16) with Hydrazine Hydrate——Hydrazine hydrate (0.32 g) was added to a solution of **16**[8] (1.0 g) in EtOH (40 ml) and the mixture was warmed at 70 °C for a while. Slightly soluble red crystals (**17**) immediately precipitated, and were collected. Yield, 0.45 g (25%). The mother liquor was concentrated to give **18**. Yield, 0.25 g (25%). In order to control the formation of **17**, the following procedure was carried out: a solution of **16** (1.0 g) in EtOH (20 ml) was added to a solution of hydrazine hydrate (0.63 g) in EtOH (20 ml) in small portions at 70 °C over a period of 30 min under stirring. In this case, the reaction mixture gave 0.86 g (95%) of another product (**19**) along with a small amount of **17**.

***N,N'*-Bis(2-ethoxycarbonyl-3-quinoxalinyl)hydrazine (17)**——Red needles, mp 183—184 °C (THF). MS *m/e*: 432 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 3350 (NH), 1760 (C=O). NMR (DMSO-d_6) δ: 1.44 (3H, t, J=7 Hz, CH_3CH_2), 4.51 (2H, q, J=7 Hz, CH_3CH_2), 10.71 (1H, br, NH). *Anal.* Calcd for $C_{22}H_{20}N_6O_4$: C, 61.10; H, 4.61; N, 19.44. Found: C, 61.14; H, 4.50; N, 19.21.

Ethyl 2-Hydrazinoquinoxaline-3-carboxylate (18)——Yellow needles, mp 141—142 °C (EtOH). MS *m/e*: 232 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 3390. 3310, 3200 (NH, NH_2). NMR (DMSO-d_6) δ: 1.37 (3H, t, J=7 Hz, CH_3CH_2), 4.41 (2H, q, J=7 Hz, CH_3CH_2), 4.66 (2H, br, NH_2), 8.75 (1H, br, NH). *Anal.* Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.14. Found: C, 56.96; H, 5.50; N, 24.15.

2-Hydrazinoquinoxaline-3-carbohydrazide (19)——Orange needles, mp 281—282 °C (dec.) (EtOH). MS *m/e*: 218 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 3330—3190 (br, NH_2, NH), 1662 (C=O). NMR (DMSO-d_6) δ: 4.66 (4H, br, $2NH_2$), 9.39 (1H, br, NH), 10.23 (1H, br, NH). *Anal.* Calcd for $C_9H_{10}N_6O$: C, 49.53; H, 4.62; N, 38.52. Found: C, 49.96; H, 4.69; N, 38.32.

References

1) Part V: H. Otomasu, H. Takahashi, and K. Yoshida, *Chem. Pharm. Bull.*, **21**, 492 (1973).
2) H. Beyer, *Z. Chem.*, **10**, 381 (1970).
3) G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, **1948**, 519.
4) H. Otomasu, R. Yamaguchi, K. Ishigo-oka, and H. Takahashi, *Yakugaku Zasshi*, **82**, 1434 (1962).
5) K. Yoshida and H. Otomasu, *Yakugaku Zasshi*, **96**, 33 (1976).
6) G. Kuhlung, *Ber.*, **24**, 2368 (1891).
7) Y. Ahmad, M. S. Habib, and Ziauddin, *Tetrahedron*, **20**, 1107 (1964).
8) A. H. Gowenlock, G. T. Newbold, and F. S. Spring, *J. Chem. Soc.*, **1945**, 622.