Tetrahedron, 1964, Vol. 20, pp. 1107 to 1112. Pergamon Press Ltd. Printed in Northern Ireland

QUINOXALINE DERIVATIVES—III[1]

CYCLIZATION OF α-CYANO-*o*-NITROACETANILIDES TO QUINOXALINE N-OXIDES

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(*Received* 16 *December* 1963)

Abstract—Base catalysed intramolecular cyclization of α-cyano-*o*-nitroacetanilides (Ia–d) to the corresponding 2-cyano-3-hydroxyquinoxaline 1-oxides (IIa–d) is described, and a mechanism proposed. The cyanoquinoxaline N-oxides (IIa–d) on reduction are deoxygenated with simultaneous loss of the nitrile group, and when heated with concentrated aqueous alkali the nitrile group is replaced quantitatively by an hydroxyl group.

AROMATIC nitro compounds with a side chain in *ortho* position, invariably, can be cyclized to N-heterocyclic compounds. This ring formation often is accomplished by reduction of the nitro group followed by (or simultaneous) ring closure. However, in some cases the nitro group participates directly and mutual oxidation of the side chain and reduction of the nitro group is achieved catalytically, resulting in the formation of an N-heterocycle. For example, benzotriazine 1-oxides[2] have been obtained from *o*-nitrophenylurea derivatives, and 1-hydroxy benzotriazole[3] from *o*-nitrophenylhydrazine. Recently Loudon *et al.*[4] reported syntheses of quinoline, indole and benzimidazole derivatives; all involving nucleophilic attack on the nitro group by the side chain in *ortho* position. Tennant[5] reported the cyclization of *o*-nitroacetanilide derivatives (Ia; Ac or Bz for CN) to the corresponding 3-hydroxyquinoxaline 1-oxides (IIa; Ac or Bz for CN). These nitroacetanilides carry in the adjacent side chain an active methylene group, which in the presence of a base reacts with the nitro group to give quinoxaline N-oxide derivatives.

α-Cyano-*o*-nitroacetanilides (Ia–d), which have all the features necessary for intramolecular cyclization to 2-cyano-3-hydroxyquinoxaline 1-oxides (IIa–d), were prepared as follows. *o*-Nitroaniline was condensed with ethyl cyanoacetate to give α-cyano-*o*-nitroacetanilide (Ia), pyridine solution of which on treatment with 1N sodium hydroxide at room temperature gave in good yield, a product which analysed for $C_9H_5N_3O_2$. Higher temperature or stronger alkali resulted in the hydrolysis of the anilide (Ia). The structure of the product $C_9H_5N_3O_2$ was established as 2-cyano-3-hydroxyquinoxaline 1-oxide (IIa) on the basis of the following degradative studies.

(i) The N-oxide (IIa) on being heated with 20% aqueous potassium hydroxide yields quantitatively 2,3-dihydroxyquinoxaline 1-oxide (IIIa) (identical with a sample

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[1] Part II. Y. Ahmad, M. S. Habib, M. Iqbal and M. I. Qureshi, *J. Chem. Soc.* In press.

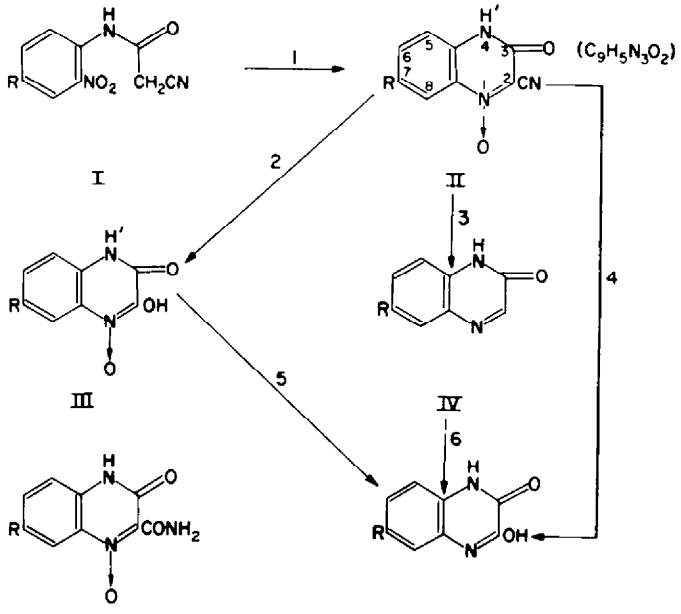
[2] F. J. Wolf, R. M. Wilson, Jr., K. Pfister, 3rd and M. Tishler, *J. Amer. Chem. Soc.* **76**, 4611 (1954); F. Arndt, *Ber. Dtsch. Chem. Ges.* **46**, 3522 (1913); F. Arndt and B. Rosenau, *Ibid.* **50**, 1248 (1917).

[3] T. Zincke and Ph. Schwarz, *Liebig's Ann.* **311**, 329 (1900).

[4] J. D. Loudon and I. Wellings, *J. Chem. Soc.* 3462, J. D. Loudon and G. Tennant, *Ibid.* 3466 (1960); 3470 (1963); 3092 (1962); 4268 (1963).

[5] G. Tennant, *J. Chem. Soc.* 2428 (1963).

supplied by Dr. Landquist[6]). The reaction mixture gave a strong test for cyanide ions, indicating this reaction to be a simple case of displacement of a CN by an OH group. This facile displacement is due to a highly developed electrophilic centre at $C_{(2)}$ of the quinoxaline molecule on account of the presence of strongly electron-attracting nitrile group at $C_{(2)}$, augmented by an oxide function at $N_{(1)}$. Tennant[5] in a similar reaction with N-oxides (IIa; Ac or Bz for CN) reported the isolation of

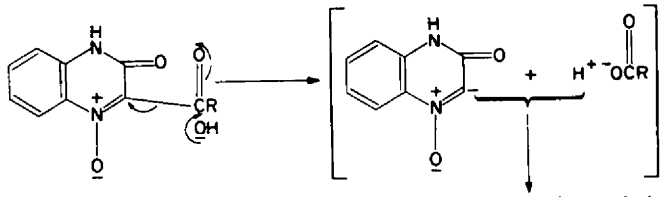


(a) R = H (b) R = Cl (c) R = EtO (d) R = MeO

3,4-dihydro-3-oxoquinoxalines⇌3-hydroxyquinoxalines.

Reagents: 1, pyridine + 1N NaOH; 2, 20% aq KOH (hot); 3, $Na_2S_2O_4$/aq ethanol (or AcOH); 4, H_2SO_4/AcOH (1:4); 5, Zn/AcOH. 6, H_2O_2/AcOH.

3-hydroxyquinoxaline 1-oxide (IIIa, H for OH). This difference in behaviour towards alkali in his case is probably due to the attack of hydroxyl ion on a different site in the molecule as indicated below; and is analogous to a reverse Claisen condensation.[7]



[6] J. K. Landquist, *J. Chem. Soc.* 2830 (1953).

[7] E. S. Gould, *Mechanism and Structure in Organic Chemistry* p. 337. Holt, Rinehart and Winston, New York (1959).

Attempts to obtain IIIa from N-oxide (IIa) with hydrogen peroxide and acetic acid (cf. Habib and Rees[8]) resulted in recovery of the starting material.

(ii) Deoxygenation of IIIa with zinc and acetic acid yields 2,3-dihydroxyquinoxaline (VIa), identical with an authentic sample, prepared from *o*-phenylenediamine and ethyl oxalate.

(iii) The cyanoquinoxaline N-oxide (IIa) smoothly methylates to IIa (H′ = Me), and the methylated product on being heated with 20% aqueous potassium hydroxide is converted to 3,4-dihydro-2-hydroxy-4-methyl-3-oxoquinoxaline 1-oxide (IIIa; H′ = Me). Again the nitrile has been replaced by an hydroxyl group in IIa (H′ = Me) and the compound has the same melting point as reported by Usherwood and Whiteley[9] for the product which they obtained by the action of sodium ethoxide on 3,4-dihydro-4-methyl-2-(N-methyl-N-phenylcarbamoyl)-3-oxoquinoxaline 1-oxide (IIIa; H′ = Me; CONMePh for OH) and to which they assigned the same constitution. The action of hot aqueous alkali on the N-oxide produced by Usherwood and Whiteley yields an identical product.

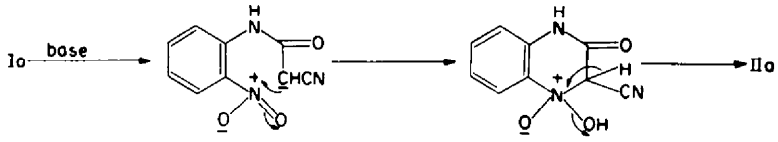
(iv) The N-oxide (IIa) on being heated with a mixture of acetic and concentrated sulphuric acids (1:1 by volume) for a long period affords 2,3-dihydroxyquinoxaline (VIa), but under milder conditions both VIa and 3-hydroxyquinoxaline-2-carboxyamide 1-oxide (Va) may be isolated. The constitution of Va was established by its deoxygenation to the known 3-hydroxyquinoxaline-2-carboxyamide. The ultimate formation of 2,3-dihydroxyquinoxaline probably takes place through the hydrolysis of the amide N-oxide (Va) to the corresponding acid followed by its decarboxylation to 3-hydroxyquinoxaline 1-oxide (IIIa; H for OH); which has already been reported[5]* to rearrange, under similar conditions, to VIa. This reaction is similar to the exclusive formation of 2,3-dihydroxyquinoxaline during an attempted[10] conversion of 3-hydroxyquinoxaline-2-carboxylic acid to its N-oxide, with hydrogen peroxide and acetic acid (steps involved being: N-oxidation → simultaneous decarboxylation → acid-catalysed rearrangement). It appears plausible that the hydrolysis of the N-oxide (IIa) precedes the rearrangement to VIa and this is supported by the fact that IIa is recovered unchanged on being heated with acetic anhydride alone (cf. Habib and Rees[8]).

(v) Attempted deoxygenation of the N-oxide (IIa) with sodium dithionite and acetic acid (or aqueous ethanol); zinc and acetic acid or by hydrogenation in the presence of Pd-C; results in each case, in the loss of nitrile group with simultaneous formation of 2-hydroxyquinoxaline (IVa), identical with the product of decarboxylation of 3-hydroxyquinoxaline-2-carboxylic acid.[14] Formation of IVa was further confirmed by its conversion to 2,3-dihydroxyquinoxaline with hydrogen peroxide in acetic acid. On the other hand 3-hydroxyquinoxaline-2-carboxyamide 1-oxide (Va), on reduction, yields the normal deoxygenated product.

* Compare Refs. 10 and 11.

[8] M. S. Habib and C. W. Rees, *J. Chem. Soc.* 3386 (1960).
[9] E. H. Usherwood and M. A. Whiteley, *J. Chem. Soc.* 1069 (1923).
[10] G. T. Newbold and F. S. Spring, *J. Chem. Soc.* 519 (1948).
[11] G. H. W. Cheeseman, *J. Chem. Soc.* 1246 (1961).
[12] A. F. Crowther, F. H. S. Curd, D. G. Davey and G. J. Stacey, *J. Chem. Soc.* 1260 (1949).
[13] W. Autenrieth and O. Hinsberg, *Ber. Dtsch. Chem. Ges.* **25**, 492 (1892).
[14] A. H. Gowenlock, G. T. Newbold and F. S. Spring, *J. Chem. Soc.* 622 (1945).

These conversions of the product $C_9H_5N_3O_2$ to quinoxaline derivatives of proven structure fully confirm the constitution as IIa and its formation from α-cyano-*o*-nitroacetanilide under the influence of a basic catalyst may be represented as follows:



Application of this cyclization has resulted in conversion of α-cyano-*o*-nitroacetanilides (Ib, c and d) to the corresponding 2-cyano-3-hydroxyquinoxaline 1-oxides (IIb, c and d). The structure of these N-oxides is based on their elementary analyses and degradation to simpler quinoxaline derivatives. All three N-oxides, on treatment with sodium dithionite in 50% aqueous ethanol, yield 2-hydroxyquinoxalines (IVb, c and d) which are oxidized to the corresponding 2,3-dihydroxyquinoxalines (VIb, c and d) with hydrogen peroxide in acetic acid. The structure of these 2,3-dihydroxyquinoxalines was confirmed by comparison with authentic samples, prepared by the condensation of 4-chloro-, 4-ethoxy-, and 4-methoxy-*o*-phenylenediamine with ethyl oxalate. The N-oxides (IIb, c and d) as usual, with hot 20% aqueous potassium hydroxide, yield 2,3-dihydroxyquinoxaline 1-oxides (IIIb, c and d) respectively. All these develop a red colour with a solution of ferric chloride in ethanol—characteristic of an hydroxamic structure—and on reduction with zinc and acetic acid afford the corresponding 2,3-dihydroxyquinoxalines (VIb, c and d).

EXPERIMENTAL

IR spectra were measured in Nujol mull.

α-*Cyano*-2-*nitroacetanilide* (Ia). *o*-Nitroaniline (1 mole) and ethyl cyanoacetate (2–3 moles) were heated together for 4–6 hr under gentle reflux, allowing the alcohol formed during the reaction to escape. Excess of the ester was removed (red. press.) and the residue crystallized from benzene as yellow plates of the *anilide* (Ia), yield 55%, m.p. 148–150°. (Found: N, 19·95. $C_9H_7N_3O_3$ requires: N, 20·5%). This general procedure was used for the preparation of the other substituted anilides described below.

4-*Chloro*-α-*cyano*-2-*nitroacetanilide* (Ib). 4-Chloro-2-nitroaniline gave, in 60% yield, the 4-*chloroanilide* (Ib), m.p. 191–192° (Found: Cl, 15·1; N, 17·1. $C_9H_6ClN_3O_3$ requires: Cl 14·9; N, 17·5%), which crystallized from ethanol as yellow needles.

α-*Cyano*-4-*ethoxy*-2-*nitroacetanilide* (Ic). 4-Ethoxy-2-nitroaniline afforded, in 64% yield, the 4-*ethoxyanilide* (Ic), m.p. 146–148° (Found: N, 16·65. $C_{11}H_{11}N_3O_4$ requires: N, 16·8%). It crystallized from benzene as yellow needles.

α-*Cyano*-4-*methoxy*-2-*nitroacetanilide* (Id). 4-Methoxy-2-nitroaniline gave in 60% yield, yellow plates (from benzene) of the 4-*methoxyanilide* (Id), m.p. 132–134° (Found: N, 17·85. $C_{10}H_9N_3O_4$ requires: N, 17·9%).

2-*Cyano*-3-*hydroxyquinoxaline* 1-*oxide* (IIa). A solution of α-cyano-2-nitroacetanilide (12·0 g) in pyridine (60 ml) was shaken with 1N NaOH (60 ml) for 1 hr. A dark red solution was formed, which was diluted with water and neutralized in the cold with HCl aq. The solid which separated was washed with dil. acid and water, dried (7·0 g; 64% yield) and crystallized from ethanol as yellow needles of the 1-*oxide* (IIa), m.p. 278° (dec.) (Found: C, 57·7; H, 3·0; N, 22·05. $C_9H_5N_3O_2$ requires: C, 57·7; H, 3·0; N, 22·45%). It was recovered unchanged on being heated with hydrogen peroxide and acetic acid at 90° for 8 hr.

7-Chloro-2-cyano-3-hydroxyquinoxaline 1-oxide (IIb). By the above general method, Ib gave in 65% yield, yellow needles (from ethanol) of the *7-chloro 1-oxide* (IIb), m.p. 285° (dec.) (Found: Cl, 16·05; N, 19·1. $C_9H_4ClN_3O_2$ requires: Cl, 16·0; N, 19·0%). On being heated with hydrogen peroxide and acetic acid at 90° for 8 hr it was recovered unchanged.

2-Cyano-7-ethoxy-3-hydroxyquinoxaline 1-oxide (IIc). Similarly Ic afforded in 63% yield, yellow needles (from ethyl acetate) of the *7-ethoxy 1-oxide* (IIc), m.p. 246–248°. (Found: C, 57·7; H, 3·65; N, 18·05. $C_{11}H_9N_3O_3$ requires: C, 57·15; H, 3·9; N, 18·2%).

2-Cyano-3-hydroxy-7-methoxyquinoxaline 1-oxide (IId). Similarly Id gave in 60% yield, yellow needles (from ethanol) of the *7-methoxy 1-oxide* (IId), m.p. 266–267° (Found: C, 55·25, H, 3·3. $C_{10}H_7N_3O_3$ requires: C, 55·25; H, 3·2%).

2,3-Dihydroxyquinoxaline 1-oxide (IIIa). A mixture of IIa (1·0 g) and 20% KOH (10 ml) was heated under reflux for 1–2 hr. Dilution with water and acidification gave a precipitate which crystallized from acetic acid as colourless needles of the 1-oxide (IIIa) in almost quantitative yield, m.p. 290–292° (Found: C, 53·8; H, 3·6. Calc. for $C_8H_6N_2O_3$: C, 53·9; H, 3·4%). It was identical (mixed m.p. and IR spectrum) with a sample supplied by Dr. Landquist.[8] On reduction with zinc and acetic acid it was converted to 2,3-dihydroxyquinoxaline (white micro-needles from acetic acid), m.p. >360°, identical (IR spectrum) with an authentic sample.[10]

Similarly, IIb, c and d, on treatment with alkali, gave, in almost quantitative yield, the corresponding 2,3-dihydroxyquinoxaline 1-oxides, all of which developed a blood red colour with ferric chloride in ethanol—characteristic of hydroxamic structure. The alkaline reaction mixture, in all cases, indicated the presence of a high concentration of free cyanide ions.

7-Chloro-2,3-dihydroxyquinoxaline 1-oxide (IIIb). From IIb the *7-chloro 1-oxide* (IIIb), m.p. >340° (dirty white needles from water) was obtained. (Found: C, 45·4; H, 2·5; N, 13·1. $C_8H_5ClN_2O_3$ requires: C, 45·2; H, 2·35; N, 13·2%). Zinc and acetic acid reduced it to 6-chloro-2,3-dihydroxyquinoxaline, m.p. >360° (colourless needles from acetic acid), identical (IR spectrum) with a synthetic sample.[12]

7-Ethoxy-2,3-dihydroxyquinoxaline 1-oxide (IIIc). Compound IIc afforded orange needles (from water) of the *7-ethoxy 1-oxide* (IIIc), m.p. 285–286° (Found: N, 12·9. $C_{10}H_{10}N_2O_4$ requires: N, 12·6%). Zinc and acetic acid reduced it to 6-ethoxy-2,3-dihydroxyquinoxaline (colourless needles from acetic acid), m. p. >350°, identical (IR spectrum) with a synthetic sample.[13]

2,3-Dihydroxy-7-methoxyquinoxaline 1-oxide (IIId). Compound IId gave colourless cubes (from acetic acid) of the *7-methoxy 1-oxide* (IIId), m.p. 325–327° (dec.) (Found: N, 13·25. $C_9H_8N_2O_4$ requires: N, 13·5%). Zinc and acetic acid reduced it to *2,3-dihydroxy-6-methoxyquinoxaline* (70%), m.p. >350° (colourless needles from acetic acid), identical (IR spectrum) with a synthetic sample (see below).

3,4-Dihydro-2-hydroxy-4-methyl-3-oxoquinoxaline 1-oxide (IIIa; H′ = Me). (a) Compound IIa (H′ = Me) on treatment with alkali, gave dirty white needles (from water) of the 4-methyl 1-oxide (IIIa; H′ = Me), m.p. 259–260° (dec.) (Found: C, 56·6; H, 4·3; N, 14·5. Calc. for $C_9H_8N_2O_3$: C, 56·25; N, 4·2; N, 14·6%). It developed a blood red colour with ferric chloride in ethanol.

(b) Compound IIIa[15] (H′ = Me; CONMePh for OH), on reaction with alkali, also gave the same, 4-methyl 1-oxide (IIIa; H′ = Me), m.p. 262–263° (dec.), undepressed on admixture with that obtained under (a). IR spectra of both the samples were identical. Usherwood and Whiteley[9] record m.p. 257° (dec) for this compound.

2,3-Dihydroxy-6-methoxyquinoxaline. 4-Methoxy-*o*-phenylenediamine (1·0 g) was heated under reflux with excess ethyl oxalate for 2–3 hr. The reaction mixture was diluted with ethanol and the resulting solid crystallized from acetic acid as colourless micro-needles of *2,3-dihydroxy-6-methoxyquinoxaline*, m.p. >350° (Found: N, 14·3. $C_9H_8N_2O_3$ requires: N, 14·6%).

2-Cyano-3,4-dihydro-4-methyl-3-oxoquinoxaline 1-oxide (IIa; H′ = Me). A mixture of IIa (1·0 g), anhydrous K_2CO_3 (2·0 g), methyl sulphate (1 ml) and acetone (50 ml) was heated under reflux for 3 hr. The filtered acetone solution, on concentration gave a solid (65%), which crystallized from ethanol as yellow needles of the *2-cyano-4-methyl 1-oxide* (IIa; H′ = Me), m.p. 210–211° (Found; C, 59·9; H, 3·8; N, 20·1. $C_{10}H_7N_3O_2$ requires: C, 59·7; H, 3·5; N, 20·9%).

2-Hydroxyquinoxaline (IVa). Compound IIa on treatment with sodium dithionite in acetic acid or 50% aqueous ethanol (as described below); zinc and acetic acid, or by hydrogenation over Pd-C

[15] M. S. Habib and C. W. Rees, *J. Chem. Soc.* 3371 (1960).

in ethanol, afforded in each case in almost quantitative yield 2-hydroxyquinoxaline, m.p. 270–272° (colourless needles from acetic acid), identical (IR spectrum and mixed m.p.) with a synthetic sample.[14] Formation of 2-hydroxyquinoxaline was further confirmed when on treatment with 30% hydrogen peroxide in acetic acid it gave 2,3-dihydroxyquinoxaline, m.p. >350° (white needles from acetic acid), identical (IR spectrum) with a synthetic sample.[10] All our attempts to deoxygenate IIa to 2-cyano-3-hydroxyquinoxaline were unsuccessful.

6-*Chloro-2-hydroxyquinoxaline* (IVb). A mixture of IIb (1·0 g), sodium dithionite (2·0 g) and 50% aqueous ethanol (70 ml) was heated under reflux for 1½ hr. The ethanol was removed (red. press.) and the filtrate, obtained after removal of a small amount (about 0·1 g) of a white solid X, was acidified with acetic acid and concentrated (red. press.) to about 10 ml. The solid which separated crystallized from ethanol as cream needles of 6-chloro-2-hydroxyquinoxaline (50%), m.p. 322–323° (dec) (Found: C, 52·5; H, 2·55; Cl, 19·0. Calc. for $C_8H_5ClN_2O$: C, 53·2; H, 2·7; Cl, 19·6%); Crowther *et al.*[11] record m.p. 305–306°. Its reaction with 30% hydrogen peroxide and acetic acid at 90° for 1 hr afforded 6-chloro-2,3 dihydroxyquinoxaline, white needles (from acetic acid) m.p. >350°, identical (IR spectrum) with a synthetic sample.[11] The white product (X) crystallized from ethanol–water as micro-crystals and gave a reasonable analysis for *7-chloro-2-cyano-3-hydroxyquinoxaline*, m.p. >340° (Found: C, 52·9; H, 3·2; Cl, 17·5. $C_9H_4ClN_3O$ requires: C, 52·55; H, 2·0; Cl, 17·3%).

6-*Ethoxy-2-hydroxyquinoxaline* (IVc). Similarly IIc on reduction yielded 6-*ethoxy-2-hydroxyquinoxaline* (80%), m.p. 240–242° (yellow cubes from dil. acetic acid) (Found: C, 63·2; H, 5·4; N, 14·65. $C_{10}H_{10}N_2O_2$ requires: C, 63·15; H, 5·3; N, 14·7%). On treatment with 30% hydrogen peroxide and acetic acid at 90°, it was converted to 6-ethoxy-2,3-dihydroxyquinoxaline, m.p. >350° (needles from acetic acid), identical (IR spectrum) with a synthetic sample.[13]

2-*Hydroxy-6-methoxyquinoxaline* (IVd). And IId on reduction with sodium dithionite in aqueous ethanol as above, gave 2-*hydroxy-6-methoxyquinoxaline* (55%), m.p. 271–272° (micro-crystals from acetic acid). (Found: C, 61·7; H, 4·9. $C_9H_8N_2O_2$ requires: C, 61·4; H, 4·6%). Its oxidation with 30% hydrogen peroxide in acetic acid afforded 2,3-dihydroxy-6-methoxyquinoxaline, m.p. >350° (needles from acetic acid), identical (IR spectrum) with a synthetic sample.

3-*Hydroxyquinoxaline-2-carboxyamide* 1-*oxide* (Va). Compound IIa (0·5 g), acetic acid (8 ml) and H_2SO_4 (2 ml) were heated under reflux for 2 hr. The mixture was diluted with water and chilled for 24 hr. The solid which separated was crystallized from acetic acid (charcoal) as white micro-needles of 2,3-dihydroxyquinoxaline (about 0·1 g), m.p. >350° (Found: C, 59·8; H, 3·8; N, 17·3. Calc. for $C_8H_6N_2O_2$: C, 59·3; H, 3·7; N, 17·3%), identical (IR spectrum) with a synthetic sample.[10] The filtrate on neutralization gave a solid (0·3 g), which on crystallization from ethanol (charcoal) gave colourless micro-needles of the *carboxyamide* 1-*oxide* (Va) m.p. >325° (Found: C, 53·2; H, 3·6; N, 20·05. $C_9H_7N_3O_3$ requires: C, 52·7; H, 3·45; N, 20·5%). If either the concentration of H_2SO_4 in the reaction mixture or the time of heating was increased more 2,3-dihydroxyquinoxaline was formed and proportionately the amount of the carboxyamide 1-oxide (Va) decreased, and either could be obtained to the exclusion of the other by varying the conditions of the reaction. The carboxyamide 1-oxide (Va) on deoxygenation by refluxing with sodium dithionite in 50% aqueous ethanol gave the known[14] 3-hydroxyquinoxaline-2-carboxyamide, yellow micro-needles, m.p. 309–311°, identical (IR spectrum) with a synthetic sample.[15]

Acknowledgement—We wish to thank Dr. S. Siddiqui, F.R.S., Chairman, P.C.S.I.R. for his interest and encouragement. Our thanks are due to Mr. M. Iqbal and Miss Bushra Bakhtiari for assistance in experimental work, and Mr. Rehmat Khan for IR spectra. Analyses were carried out by M/S. Weiler and Strauss, Oxford (through the courtesy of Dr. C. W. Rees); M/S. Pascher and Pascher, Germany; and Microanalytical Section, Central Laboratories, P.C.S.I.R., Karachi. We thank Dr. J. K. Landquist for a sample of 2,3-dihydroxy-quinoxaline 1-oxide.