243. *Quinoxalines and Related Compounds. Part V.*[1] *Some Experiments with 1,2-Dihydro-2-oxoquinoxalines.*

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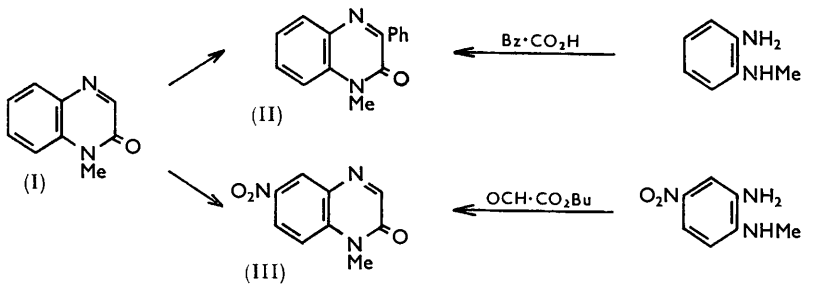
Although 1,2-dihydro-1-methyl-2-oxoquinoxaline (I) can be methylated and hydroxylated at position 3, conditions have now been found under which it undergoes phenylation at position 3 and nitration at position 6. A number of 3-methyl-, 3-hydroxy-, and 6-nitro-quinoxalines have been prepared by substitution procedures. *E.g.*, nitration of 2-hydroxyquinoxaline (1,2-dihydro-2-oxoquinoxaline) gave 2-hydroxy-6-nitroquinoxaline, previously a difficultly accessible compound.

1,2-DIHYDRO-1-METHYL-2-OXOQUINOXALINE (I) formed an aryl derivative when treated with an aqueous solution of benzene- or *p*-nitrobenzene-diazonium chloride. Proof that phenylation had taken place at position 3 was obtained by the identity of the product with 1,2-dihydro-1-methyl-2-oxo-3-phenylquinoxaline (II) synthesised unambiguously from *N*-methyl-*o*-phenylenediamine and phenylglyoxylic acid. This product was also obtained by methylation of 2-hydroxy-3-phenylquinoxaline with methyl sulphate and alkali. Stannous chloride and hydrochloric acid reduced the *p*-nitrophenyl derivative of 1,2-dihydro-1-methyl-2-oxoquinoxaline to the corresponding *p*-aminophenyl compound.



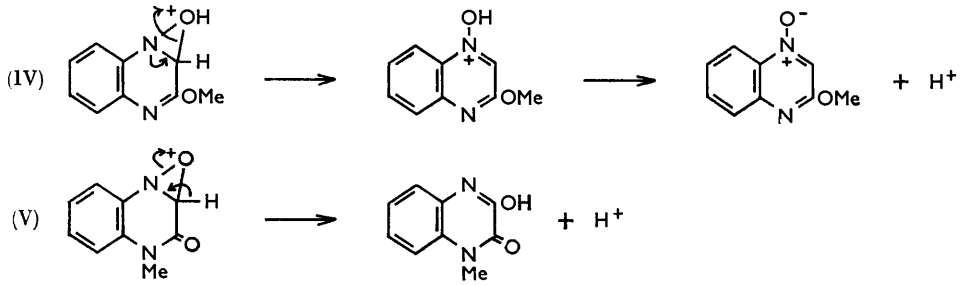
When a solution 1,2-dihydro-1-methyl-2-oxoquinoxaline in concentrated sulphuric acid was treated with potassium nitrate, 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (III) was obtained: under these conditions the base (pK_a −1·15) [1] will be predominantly in a protonated form. The structure of the nitration product was confirmed by synthesis from 2-methylamino-5-nitroaniline and butyl glyoxylate. The nitration of 2-hydroxyquinoxaline under similar conditions gave 2-hydroxy-6-nitroquinoxaline. This was converted into 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline by treatment with methyl iodide and methanolic sodium methoxide. Attempts to obtain this compound by methylation with methyl sulphate and alkali were not successful; reaction of the hydroxyquinoxaline with ethereal diazomethane gave the expected mixture [2] of *O*-methyl derivative (2-methoxy-6-nitroquinoxaline) and *CN*-dimethyl derivative (1,2-dihydro-1,3-dimethyl-6-nitro-2-oxoquinoxaline). This dimethylnitroquinoxaline was also obtained on nitration of 1,2-dihydro-1,3-dimethyl-2-oxoquinoxaline; it was prepared previously by condensation of 2-methylamino-5-nitroaniline and pyruvic acid [3] and also by methylation of 2-hydroxy-3-methyl-6-nitroquinoxaline, the major nitration product of 2-hydroxy-3-methylquinoxaline in sulphuric acid.[4]

A recent report [5] that 2-hydroxyquinoxaline undergoes nitration in acetic acid at

[1] Part IV, Cheeseman, *J.*, 1958, 108.
[2] Cheeseman, *J.*, 1955, 3308.
[3] Kehrmann and Messinger, *J. prakt. Chem.*, 1892 (2), **46**, 573.
[4] Otomasa and Nakajima, *Chem. Pharm. Bull. (Tokyo)*, 1958, **6**, 566; *Chem. Abs.*, 1959, **53**, 10,243.
[5] Kazuo Asano and Sotoo Asai, *Yakugaku Zasshi*, 1959, **79**, 567; *Chem. Abs.*, 1959, **53**, 21,979.

position 7 has been confirmed. Thus treatment of 2-hydroxyquinoxaline in acetic acid with one equivalent of fuming nitric acid gave 2-hydroxy-7-nitroquinoxaline. 2,3-Dihydroxy-6-nitroquinoxaline was a product of reaction when a ten-fold excess of nitric acid was used. The ready nitration of 2-hydroxyquinoxaline and related 1,2-dihydro-2-oxoquinoxalines is due to the cyclic NR·CO grouping (R = H or Me) and is in marked contrast with the resistance of quinoxaline itself to nitration: quinoxaline is said to resist nitration with fuming nitric and concentrated sulphuric acid at 100°,[5] and is converted [6] into a mixture of 5-nitro- and 5,6-dinitro-quinoxaline only after prolonged treatment with a mixture of fuming nitric and sulphuric acid at 90°. The nitration of other hydroxy-mono- and -di-azanaphthalenes leads to substitution at positions 3, 6, or 8 according to the conditions used,[7] and 2- and 4-hydroxypyridine both undergo ready electrophilic substitution at positions 3 and 5.[8] In 2-hydroxyquinoxaline, position 3 is deactivated by the adjacent ring-nitrogen atom. This nitrogen functions as the basic centre in the molecule, and clearly conjugate-acid formation will still further deactivate position 3 to electrophilic substitution. 2-Hydroxyquinoxaline is a very weak base (pK_a −1·4) [1] and so the different course of nitration in acetic and sulphuric acid may indicate that the principal species undergoing nitration in acetic acid is the free base and in sulphuric acid is the conjugate acid.

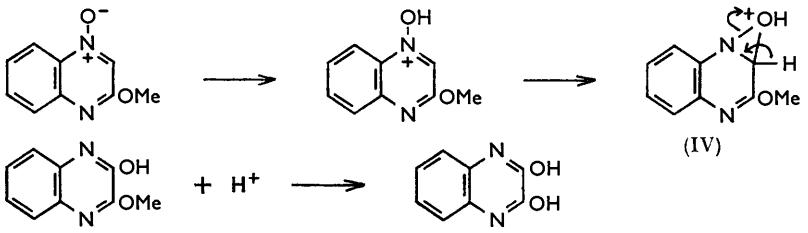
2-Hydroxy-6-nitroquinoxaline was readily converted into 2-chloro-6-nitroquinoxaline, and the 7-nitro-isomer into 2-chloro-7-nitroquinoxaline. Previous attempts to separate 2-chloro-6-nitroquinoxaline from mixtures of the two chloronitroquinoxalines have failed.[9,10,11] A mixture of 2-chloro-6- and -7-nitroquinoxaline, prepared by condensation of 4-nitro-1,2-phenylenediamine and butyl glyoxylate and subsequent chlorination,[9] has now been separated into the two pure chloronitroquinoxalines, and in this way confirmatory evidence for the structures of the corresponding hydroxynitroquinoxalines has been obtained.



Whereas oxidation of 1,2-dihydro-1-methyl-2-oxoquinoxaline with hydrogen peroxide and acetic acid gave 1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline in high yield, similar oxidation of 2-methoxyquinoxaline furnished mainly the 4-oxide. Under these conditions *N*-oxide formation may involve co-ordination of OH^+ with a ring nitrogen followed by elimination of a proton. Alternatively a cyclic intermediate of the type (IV) may be postulated. If, in the oxidation of 1,2-dihydro-1-methyl-2-oxoquinoxaline, a similar cyclic intermediate (V) is involved, hydroxylation subsequently requires the elimination, as a proton, of hydrogen linked to $C_{(3)}$. In *N*-oxide formation, it is the hydrogen linked to oxygen which is eliminated. The course of reaction may depend on the basicity of the ring-nitrogen atom involved: thus 2-methoxyquinoxaline (pK_a 0·28) [1] is a much

[6] Dewar and Maitlis, *J.*, 1957, 2518.
[7] Schofield, *Quart. Rev.*, 1950, **4**, 382.
[8] Albert, *J.*, 1960, 1020.
[9] Atkinson, Brown, and Simpson, *J.*, 1956, 26.
[10] Wolf, Pfister, Beutel, Wilson, Robinson, and Stevens, *J. Amer. Chem. Soc.*, 1949, **71**, 6.
[11] Horner, Schwenk, and Junghanns, *Annalen*, 1953, **579**, 212.

stronger base than 1,2-dihydro-1-methyl-2-oxoquinoxaline (pK_a −1·15).[1] 2-Methoxyquinoxaline 4-oxide and 2-ethoxyquinoxaline 4-oxide [12] rearrange under the influence of mineral acid into 2,3-dihydroxyquinoxaline and intermediates such as (IV) may be involved. Oxidation of 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline with hydrogen



peroxide and acetic acid similarly gave 1,2-dihydro-3-hydroxy-1-methyl-6-nitro-2-oxoquinoxaline. This compound was also prepared by condensation of 2-methylamino-5-nitroaniline and ethyl oxalate.

2-Hydroxyquinoxaline underwent base-catalysed addition to acrylonitrile. Presumably a *N*-cyanoethyl derivative was formed and this was hydrolysed readily by aqueous alkali to the parent quinoxaline.

In conclusion it may be noted that 1,2-dihydro-2-oxoquinoxalines appear to undergo electrophilic attack either at position 4 (H^+ or OH^+) or at positions 6 or 7 (NO_2^+). Nucleophilic attack, as exemplified by methylation with diazomethane ($CH_2^-{\cdot}N^+{\equiv}N$), occurs at position 3. Further substitution reactions of these compounds are being studied.

Experimental

1,2-*Dihydro*-1-*methyl*-2-*oxo*-3-*phenylquinoxaline*.—(*a*) An aqueous solution of benzenediazonium chloride (20 ml.; from 1·5 ml. of aniline) was added at 5° to a stirred solution of 1,2-dihydro-1-methyl-2-oxoquinoxaline (2·66 g.) in water (125 ml.). The mixture was stirred and kept at 5° for 4 hr., set aside at 0° for a further 7 days, and then distilled in steam until the distillate no longer contained phenol. The residual solution was cooled to 0° and the precipitate (0·64 g.) then filtered off and crystallised twice from 96% ethanol. This gave 1,2-*dihydro*-1-*methyl*-2-*oxo*-3-*phenylquinoxaline*, m. p. 138—139°, not depressed on admixture with an authentic sample prepared as described below (Found: C, 75·9; H, 5·0; N, 12·2. $C_{15}H_{12}N_2O$ requires C, 76·25; H, 5·1; N, 11·9%). The initial aqueous filtrate was neutralised with sodium acetate and then extracted with chloroform. Evaporation of the dried (Na_2SO_4) extracts gave unchanged 1,2-dihydro-1-methyl-2-oxoquinoxaline (1·5 g.), m. p. 113—119°.

(*b*) A solution of freshly distilled *N*-methyl-*o*-phenylenediamine (2·6 g.) in 2N-sulphuric acid (35 ml.) was added to an aqueous solution of phenylglyoxylic acid (0·025 mole) and the mixture set aside at room temperature for 3 hr. The precipitate was then filtered off and washed with water. Crystallisation from 96% ethanol (70 ml.) gave 1,2-dihydro-1-methyl-2-oxo-3-phenylquinoxaline (3·49 g., 69%) as pale yellow needles, m. p. 138—139°.

(*c*) A solution of 2-hydroxy-3-phenylquinoxaline [13] (2·22 g., 0·01 mole) in 2N-sodium hydroxide (20 ml.) and water (80 ml.) was shaken with methyl sulphate (2·52 g., 0·02 mole) for 30 min. The precipitate was then filtered off and washed with water. Crystallisation from 96% ethanol gave 1,2-dihydro-1-methyl-2-oxo-3-phenylquinoxaline (1·8 g., 76%), m. p. 138—139°.

Reaction of 1,2-*Dihydro*-1-*methyl*-2-*oxoquinoxaline and* p-*Nitrobenzenediazonium Chloride*.—An aqueous solution of *p*-nitrobenzenediazonium chloride (85 ml.; from 2·8 g. of *p*-nitroaniline) was added at 5° to a stirred solution of 1,2-dihydro-1-methyl-2-oxoquinoxaline (1·6 g.) in water (75 ml.). The mixture was set aside at room temperature for 36 hr., and the precipitate (2·55 g.)

[12] Newbold and Spring, *J.*, 1948, 519.
[13] Burton and Shoppee, *J.*, 1937, 546.

then filtered off. A second crop (0·15 g.) was collected after a further 72 hr. Crystallisation of the crude product from glacial acetic acid and then from benzene (65 parts) gave the p-*nitrophenyl derivative*, m. p. 247—248°, of 1,2-dihydro-1-methyl-2-oxoquinoxaline (Found: C, 64·4; H, 3·95; N, 14·8. $C_{15}H_{11}N_3O_3$ requires C, 64·0; H, 3·9; N, 14·9%).

Reduction of the p-*Nitrophenyl Derivative of* 1,2-*Dihydro*-1-*methyl*-2-*oxoquinoxaline*.—A suspension of the nitro-compound (1·4 g.) in concentrated hydrochloric acid (20 ml.) was stirred with a solution of stannous chloride dihydrate (6·8 g.) in concentrated hydrochloric acid (7 ml.) for 1 hr. The solid dissolved and then a crystalline complex separated. This was filtered off, suspended in boiling 0·2N-hydrochloric acid (50 ml.), and treated with hydrogen sulphide until no further precipitation of tin sulphide occurred. The hot mixture was filtered, and the filtrate freed from excess of hydrogen sulphide and then made alkaline. After cooling, the yellow precipitate (0·5 g.) was collected. Crystallisation from 96% ethanol (15 ml.) gave the p-*aminophenyl derivative* (0·42 g.), m. p. 156—157°, of 1,2-dihydro-1-methyl-2-oxoquinoxaline. The m. p. was raised to 158—159° by further crystallisation from 96% ethanol (Found: C, 71·9; H, 5·0; N, 16·6. $C_{15}H_{13}N_3O$ requires C, 71·7; H, 5·2; N, 16·7%).

1,2-*Dihydro*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline*.—(*a*) Powdered potassium nitrate (2·0 g., 0·02 mole) was added rapidly at 0° to a stirred solution of 1,2-dihydro-1-methyl-2-oxoquinoxaline (3·2 g., 0·02 mole) in concentrated sulphuric acid (20 ml.). The mixture was stirred at 0° for 30 min. and at room temperature for 2 hr., then slowly poured on crushed ice (*ca.* 500 ml.). The precipitate was filtered off and washed with water. Crystallisation from 96% ethanol (400 ml.) gave 1,2-*dihydro*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline* (3·3 g., 80%), m. p. 216—218°. The m. p. was raised to 219—220° by further crystallisation from 96% alcohol (120 parts) and was undepressed on admixture with an authentic sample prepared as described below (Found: C, 52·9; H, 3·7; N, 20·4. $C_9H_7N_3O_3$ requires C, 52·7; H, 3·4; N, 20·5%).

(*b*) A mixture of 2-methylamino-5-nitroaniline hydrochloride [14] (3·5 g.), butyl glyoxylate (2·86 g.), and N-hydrochloric acid (100 ml.) was shaken at room temperature for 1 hr. The precipitate was filtered off and extracted with boiling water (400 ml.). Insoluble material (1·3 g.) was removed and the extract was treated with charcoal, and then cooled. Yellow needles (1·0 g.) separated which, on crystallisation from 96% ethanol (80 ml.), gave 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (0·5 g.), m. p. 213—214°. The m. p. was raised to 219—220° by further crystallisation from 96% ethanol.

Nitration of 2-*Hydroxyquinoxaline*.—(a) *In sulphuric acid.* 2-Hydroxyquinoxaline (4·38 g., 0·03 mole) in concentrated sulphuric acid (50 ml.) was caused to react with potassium nitrate (3·0 g., 0·03 mole) similarly to 1,2-dihydro-1-methyl-2-oxoquinoxaline above. Crystallisation of the product from glacial acetic acid (200 ml.) gave 2-*hydroxy*-6-*nitroquinoxaline* (4·75 g., 83%), m. p. 298—302°. The analytical specimen was sublimed at 250°/1·0 mm. and crystallised from glacial acetic acid (60 parts); it had m. p. 300—302° (Found: C, 50·2; H, 2·4; N, 22·1. Calc. for $C_8H_5N_3O_3$: C, 50·3; H, 2·6; N, 22·0%). Horner, Schwenk, and Junghanns [11] give m. p. 294°.

(b) *In acetic acid.* Fuming nitric acid (0·88 ml., 0·02 mole) in glacial acetic acid (5 ml.) was added dropwise to a stirred solution of 2-hydroxyquinoxaline (2·92 g., 0·02 mole) in glacial acetic acid (85 ml.) at 18—20°. The mixture was left at room temperature overnight, then evaporated in a vacuum. Water was added to the residue and the pH adjusted to 5. The precipitate (3·3 g.) was filtered off, dried, and dissolved in acetone (450 ml.). 2-Hydroxy-7-nitroquinoxaline (1·1 g.), m. p. (mainly) 272—274°, separated from the cooled solution. Concentration of the mother-liquor yielded a further 0·6 g., m. p. (mainly) 268—274° (total yield, 45%). The analytical specimen was sublimed at 200°/0·1 mm. and crystallised from nitromethane (15 parts); it had m. p. 274—276° (Found: C, 50·4; H, 2·8; N, 22·0%). Atkinson, Brown, and Simpson [9] give m. p. 275—276°. 2,3-Dihydroxy-6-nitroquinoxaline was isolated from an experiment in which fuming nitric acid was used in ten-fold excess, and the reaction mixture was poured into water after 2 hr. It was characterised by conversion into 2,3-dichloro-6-nitroquinoxaline,[15] m. p. and mixed m. p. 152—153°.

Methylation of 2-*Hydroxy*-6-*nitroquinoxaline*.—(a) *With methyl iodide.* The hydroxyquinoxaline (1·4 g.) was dissolved in a solution of sodium methoxide (prepared from 0·23 g. of sodium and 50 ml. of methanol). Methyl iodide (0·62 ml.) was added and the mixture heated

[14] Pesin, Khaletskiĭ, and Chi-Chun Chao, *Zhur. obshchei Khim.*, 1957, **27**, 1570; *Chem. Abs.*, 1958, **52**, 3790.

[15] Curd, Davey, and Stacey, *J.*, 1949, 1271.

under reflux for 2 hr. After cooling, the precipitate of 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (1·1 g.), m. p. and mixed m. p. 214—216°, was filtered off.

(b) *With diazomethane.* Ethereal diazomethane (from *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide, 21·5 g.) was added to a stirred, ice-cooled suspension of the hydroxyquinoxaline (1·9 g.) in dry methanol (20 ml.). The mixture was stirred at 0° for 4 hr., and then left overnight at 0°. The precipitate (0·95 g.) was filtered off. Crystallisation (charcoal) from 96% ethanol and then from acetone gave 1,2-dihydro-1,3-dimethyl-6-nitro-2-oxoquinoxaline, m. p. 219—222°, undepressed on admixture with an authentic specimen prepared as described below. The initial filtrate was evaporated in a vacuum. Crystallisation of the residue from light petroleum (b. p. 60—80°) and then benzene gave *2-methoxy-6-nitroquinoxaline*, m. p. 169—170°, undepressed on admixture with a sample prepared as described below.

1,2-Dihydro-1,3-dimethyl-6-nitro-2-oxoquinoxaline.—(*a*) 1,2-Dihydro-1,3-dimethyl-2-oxoquinoxaline (5·22 g., 0·03 mole) in concentrated sulphuric acid (30 ml.) was caused to react with potassium nitrate (3·0 g., 0·03 mole) similarly to 1,2-dihydro-1-methyl-2-oxoquinoxaline above. Crystallisation (charcoal) of the product from acetone (350 ml.) gave 1,2-dihydro-1,3-dimethyl-6-nitro-2-quinoxaline (5·5 g., 84%), m. p. 220—223°. The m. p. was raised to 222—223° by crystallisation from 96% alcohol (200 parts) and undepressed on admixture with an authentic specimen prepared as described below (Found: C, 54·4; H, 4·2; N, 19·3. Calc. for $C_{10}H_9N_3O_3$: C, 54·8; H, 4·1; N, 19·2%).

(*b*) Pyruvic acid (1 ml.) was added to a solution of 2-methylamino-5-nitroaniline hydrochloride (1·75 g.) in N-hydrochloric acid (100 ml.). After 18 hr., the precipitate (0·6 g.; m. p. 218—220°) was filtered off and dried. Crystallisation from 96% alcohol (100 ml.) gave 1,2-dihydro-1,3-dimethyl-6-nitro-2-oxoquinoxaline, m. p. 222—223°.

2-Chloro-7-nitroquinoxaline.—A mixture of 2-hydroxy-7-nitroquinoxaline (0·8 g.), freshly distilled phosphoryl chloride (8 ml.), and phosphorus pentachloride (1·6 g.) was heated under reflux for 2 hr., then cooled and slowly poured into stirred ice-water. The precipitated 2-chloro-7-nitroquinoxaline (0·8 g.), m. p. 187—189°, was filtered off washed with sodium hydrogen carbonate solution and water, and then dried in a vacuum-desiccator over potassium hydroxide and phosphorus pentoxide. The m. p. was raised to 188—190° by crystallisation from benzene. Atkinson, Brown, and Simpson [9] give m. p. 185—186°.

2-Chloro-6-nitroquinoxaline.—(*a*) 2-Hydroxy-6-nitroquinoxaline (3·0 g.) was caused to react with phosphoryl chloride (30 ml.) and phosphorus pentachloride (6·0 g.) similarly to 2-hydroxy-7-nitroquinoxaline, above. The product (3·1 g., 94%), m. p. 208—209°, crystallised from benzene (20 parts) as pale yellow needles of unchanged m. p. (Found: C, 45·8; H, 2·3; N, 20·1; Cl, 16·95. Calc. for $C_8H_4ClN_3O_2$: C, 45·8; H, 1·9; N, 20·0; Cl, 16·9%). Horner, Schwenk, and Junghanns [11] give m. p. 202°.

(*b*) A mixture (6·25 g.) of 2-chloro-6- and -7-nitroquinoxaline (prepared by Atkinson, Brown, and Simpson's method [9]) was crystallised twice from benzene and then twice from 96% alcohol, and a fraction (0·90 g.), m. p. (mainly) 203—205°, thus obtained. The m. p. was raised to 208—209° by crystallisation from 96% alcohol (20 parts) and was undepressed on admixture with 2-chloro-6-nitroquinoxaline prepared as described above. Evaporation of the benzene mother-liquor gave a fraction (3·5 g.), m. p. (mainly) 163—165°. A portion (0·5 g.) was dissolved in benzene (20 ml.) and filtered through a column of aluminium oxide (100 g.; Spence, type H; mesh 100—200) prepared in benzene. Elution with benzene gave successively 2-chloro-7-nitroquinoxaline (0·23 g.; m. p. 187—188°), mixed solid of m. p. *ca.* 163—165°, and 2-chloro-6-nitroquinoxaline (0·02 g.; m. p. 202—204°). The analytical specimen of 2-chloro-7-nitroquinoxaline was crystallised from cyclohexane (150 parts) and had m. p. 188—190° (Found: N, 20·4; Cl, 17·35%).

2-Methoxy-6-nitroquinoxaline.—2-Chloro-6-nitroquinoxaline (1·05 g., 0·005 mole) was added to a solution of sodium methoxide prepared from sodium (0·23 g., 0·01 g.-atom) and methanol (20 ml.). The mixture was heated under reflux for 3 hr., then evaporated in a vacuum. Water was added to the residue, and the precipitate of 2-methoxy-6-nitroquinoxaline (0·95 g., 92%; m. p. 170—171°) was filtered off. Crystallisation from benzene (10 parts) gave pale yellow needles, m. p. 171—172° (Found: C, 52·3; H, 3·7; N, 20·2. $C_9H_7N_3O_3$ requires C, 52·7; H, 3·4; N, 20·5%).

1,2-Dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline.—(*a*) A mixture of 1,2-dihydro-1-methyl-2-oxoquinoxaline (8·0 g., 0·05 mole), glacial acetic acid (100 ml.), and hydrogen peroxide (30% w/v; 50 ml.) was set aside at room temperature for 7 days. The crystalline precipitate of

1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline (7·15 g., 81%), m. p. 285—286°, was then filtered off, washed with water, and dried at 100°.

(*b*) Methyl sulphate (120 ml.) was added dropwise to a stirred solution of 2,3-dihydroxyquinoxaline (48·6 g.) in 2N-sodium hydroxide (1200 ml.). The mixture was stirred for a further 2 hr., and the precipitate was then filtered off and triturated with excess of 2N-acetic acid. Filtration gave 1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline (27·0 g., 51%), m. p. (mainly) 279—281°. The m. p. was raised to 285—286° by crystallisation from glacial acetic acid (6 parts). The initial aqueous filtrate was extracted with chloroform, and the combined extracts were washed with water, dried (Na_2SO_4) and evaporated. Crystallisation of the residue (13·0 g.) from ethanol (600 ml.) gave 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline (10·3 g., 18%), m. p. 252—253°.

2-*Methoxyquinoxaline* 4-*Oxide*.—A mixture of 2-methoxyquinoxaline (4·8 g., 0·03 mole), glacial acetic acid (60 ml.), and hydrogen peroxide (30% w/v; 30 ml.) was heated at 55° for 14 hr., and then concentrated to small bulk in a vacuum. Water (15 ml.) was added and, after cooling to 0°, the product (3·5 g.) was filtered off. Crystallisation from methanol–N-sodium hydroxide (1 : 1; 35 ml.) gave 2-methoxyquinoxaline 4-oxide (1·83 g., 35%) as needles, m. p. 105—108°. The m. p. was raised to 106—108° by crystallisation from aqueous methanol (Found: C, 61·1; H, 4·65; N, 16·2. $C_9H_8N_2O_2$ requires C, 61·35; H, 4·6; N, 15·9%).

A mixture of 2-methoxyquinoxaline 4-oxide (0·36 g.), ethanol (3 ml.), and 2N-hydrochloric acid (3 ml.) was heated under reflux for 3½ hr. and then evaporated to dryness. The residue was extracted with 2N-sodium hydroxide, and insoluble matter filtered off. Acidification of the filtrate with acetic acid gave 2,3-dihydroxyquinoxaline (0·26 g.). This was identified by conversion [2] into 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline, m. p. and mixed m. p. 252—253°.

1,2-*Dihydro*-3-*hydroxy*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline*.—(*a*) A mixture of 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (1·0 g., 0·005 mole), glacial acetic acid (45 ml.), and hydrogen peroxide (30% w/v; 5 ml.) was set aside at room temperature for 7 days. The crystalline product (0·85 g.) was then filtered off. Crystallisation from glacial acetic acid (85 ml.) gave 1,2-*dihydro*-3-*hydroxy*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline* (0·6 g.), m. p. 350—352° (decomp.), not depressed on admixture with an authentic sample prepared as described below (Found: C, 49·0; H, 2·9; N, 18·6. $C_9H_7N_3O_4$ requires C, 48·9; H, 3·2; N, 19·0%).

(*b*) A mixture of 2-methylamino-5-nitroaniline (0·5 g.) and ethyl oxalate (5 ml.) was heated under reflux for 15 min., and then cooled. The precipitate (0·47 g.) was filtered off and washed with 96% alcohol. Crystallisation from glacial acid gave 1,2-dihydro-3-hydroxy-1-methyl-6-nitroquinoxaline (0·41 g.), m. p. 350—352° (decomp.).

Reaction of 2-*Hydroxyquinoxaline and Acrylonitrile*.—A solution of 2-hydroxyquinoxaline (7·3 g.), acrylonitrile (10 ml.), and 15N-sodium hydroxide (12 drops) in 96% ethanol (250 ml.) was heated under reflux for 20 hr., then concentrated to *ca.* 50 ml. After cooling to 0°, the crystalline precipitate was filtered off and triturated with 2N-sodium hydroxide (25 ml.). Filtration gave the (?1-)*cyanoethyl*-1,2-*dihydro*-2-*oxoquinoxaline* (5·4 g., 54%), m. p. (mainly) 203—208°. The m. p. was raised to 207—208° by crystallisation (charcoal) from 96% ethanol (220 ml.) (Found: C, 66·5; H, 4·4; N, 21·3. $C_{11}H_9N_3O$ requires C, 66·3; H, 4·5; N, 21·1%).

The cyano-compound (2·0 g.) and 2N-sodium hydroxide (20 ml.) were heated under reflux for 25 min., and then in an open flask for 5 min. to expel most of the ammonia. The mixture was acidified with 2N-acetic acid, and after cooling, the precipitate of 2-hydroxyquinoxaline (1·5 g.), m. p. (mainly) 263—265°, was filtered off.

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