449. *Heterocyclic* N-*Oxides. Part I. A New Synthesis of 2-Hydroxyquinoxaline 4-Oxides.*

By G. Tennant.

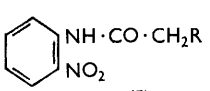
Derivatives of *o*-nitroacetanilide containing a suitably activated methylene group cyclise in warm aqueous alkali, giving the corresponding 2-hydroxyquinoxaline 4-oxide (II). In a similar but more complex reaction, the pyridinium salt (III), when treated with piperidine in methanol, affords 2-amino-3-hydroxyquinoxaline 1-oxide (II; R = NH_2).

Derivatives (IV) of 2-nitrobiphenyl containing an activated methylene group [*e.g.*, R = Bz in (IV)] give phenanthridine 5-oxides [1] when treated with methanolic potassium hydroxide. By an apparently related process, *o*-nitrophenylurea in warm aqueous alkali yields 3-hydroxybenzotriazine *N*-oxide,[2] whereas the closely related *o*-nitrophenylacetamide fails to cyclise under similar conditions.[1] In view of these results, it was of interest to study the action of aqueous alkali on the *o*-nitroacetanilide derivatives (I; R = Ac or Bz) which contain structural features both of the biphenyl compounds (IV) and of *o*-nitrophenylurea. If successful, cyclisation in this case should afford acyl derivatives of

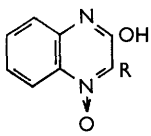
[1] Muth, Ellers, and Folmer, *J. Amer. Chem. Soc.*, 1957, **79**, 6500; Muth, Abraham, Linfield, Wotring, and Pacovsky, *J. Org. Chem.*, 1960, **25**, 736.

[2] Arndt, *Ber.*, 1913, **46**, 3522; Arndt and Rosenau, *Ber.*, 1917, **50**, 1248; Wolf, Wilson, Pfister, and Tishler, *J. Amer. Chem. Soc.*, 1954, **76**, 4611.

2-hydroxyquinoxaline 4-oxide (II), which might then be used as a source of the hitherto unknown quinoxalines (V; R = Ac or Bz) that might serve as intermediates for the syntheses of condensed quinoxalines.



(I)



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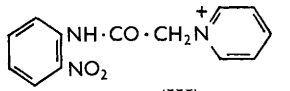


(III)

The anilides required were available by recorded methods. Brown *et al.*[3] obtained α-benzoyl-*o*-nitroacetanilide (I; R = Bz) in 40% yield by condensing *o*-nitroaniline with ethyl benzoylacetate in xylene at 150°; Sexton [4] similarly prepared the acetyl compound (I; R = Ac) in 19% yield from the amine and ethyl acetoacetate. By carrying out these condensations at a higher temperature and using the method of Weissberger and Kibler [5] the yield in both cases was raised to 50%.

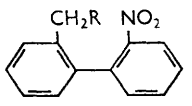
These anilides give deep red solutions in 20% aqueous potassium hydroxide from which sparingly soluble, highly coloured potassium salts tend to be precipitated. When either of these solutions is warmed the same acidic substance, readily recovered from the reaction mixture by acidification, is formed. It has the formula $C_8H_6N_2O_2$, but no infrared band characteristic of a nitro-group. Its properties corresponded with those described by Landquist [6] for 2-hydroxyquinoxaline 4-oxide (II; R = H). Thus it readily dissolved in dilute alkali giving a red solution which, shaken with dimethyl sulphate, afforded an *N*-methyl derivative.[6] Reduction of the *N*-methyl derivative and of the parent acid gave deoxy-compounds identified as the 1,2-dihydro-1-methyl-2-oxoquinoxaline [7] (VII; R = H) and 2-hydroxyquinoxaline,[8] respectively, by comparison with authentic samples. Oxidation with hydrogen peroxide in acetic acid afforded a product $C_8H_6N_2O_3$ which Landquist [6] considered to be 2,3-dihydroxyquinoxaline 1-oxide (II; R = OH). In support of this formula, the oxidation product gave a blood-red colour with ferric chloride in ethanol (hydroxamic grouping) and formed an acetyl derivative with an infrared band at 1800 cm.$^{-1}$ (cyclic :N·OAc).[9] This acetate was hydrogenated over palladium–charcoal to afford 2,3-dihydroxyquinoxaline.[10]

2-Acylquinoxaline *N*-oxides are possible intermediates in the reaction, since cyclisation of the respective anilides under controlled conditions afforded the *N*-oxides (II; R = Ac or Bz) in high yield. α-Acetyl-*o*-nitroacetanilide, however, as well as yielding the expected *N*-oxide (II; R = Ac), afforded two neutral by-products (X and Y) and a second acidic material (Z): the benzoyl compound gave only the *N*-oxide. The nature of these by-products is under investigation.

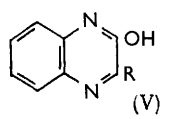
The structures assigned to the *N*-oxides were based on analysis and on degradation to known quinoxaline derivatives. Hydrolysis of the benzoyl compound with 20% aqueous potassium hydroxide gave the parent *N*-oxide (II; R = H) in high yield. In contrast, the acetyl compound, even in dilute alkali, gave none of this product, but afforded a high-melting solid in low yield; this was not further characterised. In warm mineral acid, however, both oxides were degraded to 2,3-dihydroxyquinoxaline and it was established that this product was also obtained from 2-hydroxyquinoxaline 4-oxide by similar treatment. This acid-catalysed rearrangement has been reported for 2-ethoxy- and 2-methoxy-quinoxaline 4-oxide [10,11] and it seems reasonable in the present case to assume

[3] Brown Figueras, Gledhill, Kibler, McCrossen, Parmarter, Vittum, and Weissberger, *J. Amer. Chem. Soc.*, 1957, **79**, 2919.
[4] Sexton, *J.*, 1942, 303.
[5] Weissberger and Kibler, *Org. Synth.*, 1945, **25**, 7.
[6] Landquist, *J.*, 1953, 2830.
[7] Cheeseman, *J.*, 1955, 1804.
[8] Perkin and Riley, *J.*, 1923, **123**, 2399.
[9] Loudon and Wellings, *J.*, 1960, 3462.
[10] Newbold and Spring, *J.*, 1948, 519.
[11] Cheeseman, *J.*, 1961, 1246.

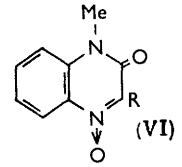
that hydrolysis of the acyl derivative precedes a similar rearrangement in the parent *N*-oxide (II; R = H) formed. Reduction of the oxides (II; R = Ac or Bz) afforded the amines (V) which were oxidised by hydrogen peroxide in acetic acid to the dihydroxyquinoxaline (V; R = OH). This resembles the similar oxidation of 2-hydroxyquinoxaline-3-carboxylic acid (V; R = CO_2H) which gives the same product.[10] These deoxy-derivatives could not be degraded to the known quinoxaline (V; R = H); the benzoyl compound was recovered unchanged after 5 hours' refluxing with acid or alkali, and the acetyl



(IV)



(V)



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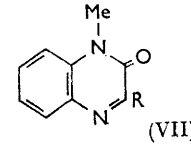

(VII)

derivative even under mild hydrolytic conditions afforded unidentified high-melting amorphous products. The easier hydrolysis of the benzoyl group in the *N*-oxide (II; R = Bz) than in the deoxy-derivative (V; R = Bz) is a measure of the facilitating influence of the electrophilic nitrogen atom in the former.

With methyl sulphate or methyl iodide, the oxides (II; R = Ac or Bz) formed methyl derivatives which were reduced to the amines obtained also by similar methylation of the quinoxalines (V). Each of these derivatives is assigned the *N*-methyl structure since, (*a*) the oxides (VI) afforded the known compound [6] (VII; R = OH) in warm mineral acid, and (*b*) the amines (VII; R = Ac or Bz) were oxidised to the same compound by hydrogen peroxide in acetic acid. The *N*-methyl structure was confirmed for the benzoyl compound (VII; R = Bz) by synthesis.

The scope of the reaction was extended to include the pyridinium derivative (III) which contains a strongly activated methylene group. This salt (m. p. 91°) was obtained by Löfgren and Fischer [12] from the chloroanilide (I; R = Cl) and an excess of pyridine. Repetition of their reaction afforded a product (m. p. 281°) which gave correct analyses for compound (III). The chloroanilide (I; R = Cl) was prepared in 86% yield by treating *o*-nitroaniline with chloroacetyl chloride (3 mol.) at 0° in the presence of alkali; no diacetylation resulted from the use of an excess of acid chloride. Treatment of the pyridine salt with aqueous alkali under various conditions gave low yields of amorphous products which were difficult to purify. Successful cyclisation was achieved, however, by using piperidine as the base. When warmed with this reagent in methanol, the salt afforded, in 50% yield, a high-melting amphoteric product $C_8H_7N_3O_2$ which is considered to be 2-amino-3-hydroxyquinoxaline 1-oxide (II; R = NH_2) on the following evidence. It was readily soluble in dilute alkali, and in dilute hydrochloric acid formed a sparingly soluble hydrochloride. The presence of a primary amino-group was indicated by bands at 3400 and 3200 $cm.^{-1}$ in the infrared spectrum. With a solution of ferric chloride in ethanol it gave the deep-blue colour characteristic of heterocyclic *N*-oxides having a 2-amino-substituent (cf. 2-aminopyridine 1-oxide [13,14]). Dithionite in acetic acid reduced it to 2-amino-3-hydroxyquinoxaline [15] (V; R = NH_2), this compound being further identified by conversion in nitrous acid into 2,3-dihydroxyquinoxaline.[16] With dimethyl sulphate and alkali the compound (II; R = NH_2) formed an *N*-methyl derivative which was reduced to the known compound [7] (VII; R = NH_2). Attempts to convert the amino-group of the *N*-oxide (II; R = NH_2) into hydroxyl by nitrous acid were unsuccessful.

[12] Löfgren and Fischer, *Svensk Kem. Tidskr.*, 1946, **58**, 219.
[13] Sharp and Spring, *J.*, 1951, 932.
[14] Newbold and Spring, *J.*, 1949, S.133.
[15] Stevens, Pfister, and Wolf, *J. Amer. Chem. Soc.*, 1946, **68**, 1035.
[16] Shiho and Tagami, *Pharm. Bull.* (*Japan*), 1957, **5**, 45.

Experiments are in progress to determine the scope and mechanism of this novel cyclisation.

Experimental

Infrared spectra were measured for Nujol suspensions by using a Perkin-Elmer Infracord spectrophotometer; bands noted below were either strong or very strong.

α-Benzoyl-o-nitroacetanilide (I; R = Bz).—As recommended by Weissberger and Kibler,[5] *o*-nitroaniline (69·0 g.) was condensed with ethyl benzoylacetate (1·1 mol.; 106·4 g.) in xylene (150 ml.) at 210—220° (bath-temp.), to give the anilide (52%), m. p. 112° (from ethanol).

α-Acetyl-o-nitroacetanilide[4] (I; R = Ac).—This anilide (54%), m. p. 69° (from ethanol), was prepared by condensing *o*-nitroaniline (69·0 g.) with ethyl acetoacetate (1·1 mol.; 71·5 g.) in xylene (150 ml.) at 210—220°.

2-Hydroxyquinoxaline 4-Oxide (II; R = H).—When warmed with 20% aqueous potassium hydroxide (100 ml.) for 1 hr., the anilide (I; R = Bz) (11·4 g.) afforded an orange solution which was extracted with chloroform, to remove non-acidic material, and the aqueous layer was acidified with dilute sulphuric acid. The buff precipitate was collected, washed with dilute sodium hydrogen carbonate solution and water, and extracted with N-sodium hydroxide (50 ml.). The insoluble red solid (0·05 g.) was discarded. Acidification of the filtrate gave 2-hydroxyquinoxaline 4-oxide as buff needles (5 g.), m. p. 276° (from acetic acid), $\nu_{max.}$ 2700 (broad) and 1660 cm.$^{-1}$ (Found: C, 59·0; H, 3·5; N, 17·2. Calc. for $C_8H_6N_2O_2$: C, 59·3; H, 3·7; N, 17·2%). Sodium dithionite in acetic acid reduced it to 2-hydroxyquinoxaline, m. p. 272° (from acetic acid) (Found: C, 65·6; H, 4·1. Calc. for $C_8H_6N_2O$: C, 65·8; H, 4·1%), identical (mixed m. p. and infrared spectrum) with a synthetic sample.[8] When shaken with dimethyl sulphate and alkali for 5 hr. at room temperature the *N*-oxide (II; R = H) yielded the *N*-methyl derivative (VI; R = H), m. p. 216° (buff needles from methanol), $\nu_{max.}$ 1650, 1580, and 1525 cm.$^{-1}$ (Found: C, 61·0; H, 4·5; N, 15·6. Calc. for $C_9H_8N_2O_2$: C, 61·3; H, 4·5; N, 15·9%), reduced by sodium dithionite in acetic acid to 1,2-dihydro-1-methyl-2-oxoquinoxaline, m. p. 110° (from methanol), identical (mixed m. p. and infrared spectrum) with an authentic sample.[7]

α-Acetyl-*o*-nitroacetanilide, warmed for 1 hr. as above with 20% aqueous potassium hydroxide, gave the *N*-oxide (II; R = H) (70%), m. p. and mixed m. p. 276°.

2,3-Dihydroxyquinoxaline 1-Oxide (II; R = OH).—When oxidised with 30% hydrogen peroxide in acetic acid as described by Landquist,[6] the *N*-oxide (II; R = H) gave 2,3-dihydroxyquinoxaline 1-oxide (72%), m. p. 292° (white needles from acetic acid), giving a blood-red colour with ferric chloride in ethanol, $\nu_{max.}$ *ca.* 2500 (broad) and 1680 cm.$^{-1}$ (Found: C, 53·9; H, 3·4; N, 15·5. Calc. for $C_8H_6N_2O_3$: C, 53·9; H, 3·4; N, 15·7%). Warming it with acetic anhydride formed the *1-acetoxy-derivative*, m. p. 204° (from acetic acid), $\nu_{max.}$ 1800 cm.$^{-1}$ (Found: C, 54·4; H, 3·7; N, 12·6. $C_{10}H_8N_2O_4$ requires C, 54·5; H, 3·6; N, 12·7%). This derivative was hydrogenated in ethanol over palladium–charcoal, affording 2,3-dihydroxyquinoxaline, m. p. >360° (from acetic acid), identical (infrared and ultraviolet spectra) with an authentic sample.[10]

2-Benzoyl-3-hydroxyquinoxaline 1-Oxide (II; R = Bz).—The anilide (I; R = Bz) (11·4 g.) was refluxed for 0·5 hr. with N-sodium hydroxide (80 ml.), and the mixture worked up as for 2-hydroxyquinoxaline 4-oxide; this gave the oxide (8·0 g.) (II; R = Bz), m. p. 274° (from acetic acid), $\nu_{max.}$ 2700 (broad), 1700, and 1660 cm.$^{-1}$ (Found: C, 67·4; H, 3·8; N, 10·5. $C_{15}H_{10}N_2O_3$ requires C, 67·7; H, 3·8; N, 10·5%). The oxide was warmed with 20% aqueous potassium hydroxide for 0·5 hr., affording 2-hydroxyquinoxaline 4-oxide (90%), m. p. 276° (from acetic acid), identical (mixed m. p. and infrared spectrum) with a sample prepared as above. With dimethyl sulphate and alkali it yielded the N-*methyl derivative* (VI; R = Bz) (95%), m. p. 193° (from acetic acid), $\nu_{max.}$ 1680, 1650, 1580, and 1525 cm.$^{-1}$ (Found: C, 68·7; H, 4·5; N, 9·7. $C_{16}H_{12}N_2O_3$ requires C, 68·6; H, 4·3; N, 10·0%), which was reduced by sodium dithionite in acetic acid to the deoxy-compound (VII; R = Bz), m. p. 159° alone or mixed with a synthetic sample (cf. below). The infrared spectra of the two samples were identical.

2-Benzoyl-3-hydroxyquinoxaline (V; R = Bz).—The oxide (II; R = Bz) (0·4 g.) in glacial acetic acid (50 ml.) was refluxed with sodium dithionite (0·4 g.) for an hour, then with more dithionite (0·4 g.) for a further hour. Concentration of the filtered mixture gave the *quinoxaline* (0·3 g.), m. p. 275° (pale yellow needles from acetic acid), $\nu_{max.}$ 2700 (broad), 1700, and 1670 cm.$^{-1}$ (Found: C, 71·5; H, 4·1; N, 11·4. $C_{15}H_{10}N_2O_2$ requires C, 72·0; H, 4·0; N, 11·2%). After

being refluxed for 5 hr. with 20% aqueous potassium hydroxide or 20% w/v aqueous sulphuric acid in acetic acid this product was recovered (90%) unchanged (m. p. and mixed m. p. 275°). The quinoxaline (V; R = Bz), when oxidised with 30% hydrogen peroxide in acetic acid, afforded 2,3-dihydroxyquinoxaline, m. p. >360° (identified spectroscopically (i.r., u.v) with an authentic sample [10]), and with dimethyl sulphate and alkali gave the *N*-methyl derivative (VII; R = Bz), m. p. and mixed m. p. 159° (identical infrared spectrum; cf. below). This methyl derivative with 30% hydrogen peroxide in acetic acid gave the compound (VII; R = OH), m. p. 299°, identical (mixed m. p. and infrared spectrum) with a synthetic sample.[6]

2-*Benzoyl*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline* (VII; R = Bz).—The benzyl derivative [17] (VII; R = CH_2Ph) (0·25 g.) in 70% v/v aqueous acetic acid (10 ml.) was treated with chromium trioxide (0·5 g.) in portions at 100°, and the mixture warmed for 0·5 hr. at this temperature, then concentrated and diluted with water, giving the *quinoxaline* (0·12 g.), m. p. 159° (from methanol), $\nu_{max.}$ 1680, 1650, 1580, and 1550 cm.$^{-1}$ (Found: C, 72·8; H, 4·8; N, 10·5. $C_{16}H_{12}N_2O_2$ requires C, 72·7; H, 4·6; N, 10·6%).

2-*Acetyl*-3-*hydroxyquinoxaline* 1-*Oxide* (II; R = Ac).—The anilide (I; R = Ac) (24·0 g.) in N-sodium hydroxide (130 ml.) was heated to the b. p. A vigorous reaction set in and a yellow solid separated from the boiling mixture, which was warmed for 5 min., then cooled; the precipitate was collected, washed with dilute sodium hydroxide solution and water, and dried *in vacuo* (6·0 g.; product X). Non-acidic material was removed from the combined filtrate and washings by extraction with chloroform. Acidification with dilute sulphuric acid of the aqueous layer gave a buff precipitate which was collected next morning, washed with aqueous sodium hydrogen carbonate and water, and combined with material recovered from the filtrate by extraction with chloroform and evaporation of the dried (Na_2SO_4) extract. The crude product, treated with N-sodium hydroxide (100 ml.), left a red solid (1·8 g.; product Y). Recovery from the alkaline filtrate by acidification and extraction with chloroform as before afforded material that was separated by repeated extraction with boiling methanol into an insoluble fraction (2·0 g.; product Z) and the N-*oxide* (7·5 g.) (II; R = Ac) (obtained on concentrating the methanol extract), m. p. 188° (from methanol), $\nu_{max.}$ 2700 (broad), 1715, and 1660 cm.$^{-1}$ (Found: C, 58·5; H, 3·9; N, 13·8. $C_{10}H_8N_2O_3$ requires C, 58·8; H, 3·9; N, 13·7%). Warming this oxide for 0·5 hr. with N-sodium hydroxide or 20% aqueous potassium hydroxide afforded a violet solid, m. p. >360°, which was not further characterised.

2-*Acetyl*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline* 1-*Oxide* (VI; R = Ac).—The oxide (II; R = Ac) (0·55 g.) in acetone (30 ml.) was refluxed for 3 hr. with anhydrous potassium carbonate (0·6 g.) and methyl iodide (0·25 ml.). Concentration of the filtered mixture and crystallisation (charcoal) of the residual solid gave the N-*methyl derivative* (0·4 g.), m. p. 157° (from water), $\nu_{max.}$ 1715, 1650, 1580, and 1525 cm.$^{-1}$ (Found: C, 60·3; H, 4·6; N, 12·9. $C_{11}H_{10}N_2O_3$ requires C, 60·6; H, 4·6; N, 12·8%). Sodium dithionite in acetic acid reduced it to the compound (VII; R = Ac), m. p. 130°, alone or mixed with a sample prepared as below. The infrared spectra of the two samples were identical.

2-*Acetyl*-3-*hydroxyquinoxaline* (V; R = Ac).—Reduction of the oxide (II; R = Ac) (1·0 g.) in glacial acetic acid (10 ml.) with sodium dithionite (2·0 g.) as above, filtration, evaporation, and extraction with hot water gave yellow needles of the *quinoxaline* (0·6 g.), m. p. 188° (from water), $\nu_{max.}$ 2700 (broad), 1715, and 1650 cm.$^{-1}$ (Found: C, 64·1; H, 4·1; N, 15·0. $C_{10}H_8N_2O_2$ requires C, 63·8; H, 4·3; N, 14·9%). Warming this product for 0·5 hr. with N-sodium hydroxide or 20% w/v aqueous sulphuric acid in acetic acid afforded amorphous products. With 30% hydrogen peroxide in acetic acid it formed 2,3-dihydroxyquinoxaline (93%), m. p. >360° (from acetic acid), identified by comparison with a synthetic sample.[10]

2-*Acetyl*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline* (VII; R = Ac).—The quinoxaline (V; R = Ac) (0·5 g.) in acetone (30 ml.) with anhydrous potassium carbonate (0·6 g.) and methyl iodide (0·25 ml.) at 100° for 3 hr. gave, after working up as above and purification, orange needles of the N-*methyl derivative* (0·2 g.), m. p. 130° (from water), $\nu_{max.}$ 1715, 1650, 1580, and 1525 cm.$^{-1}$ (Found: C, 65·5; H, 4·8; N, 13·7. $C_{11}H_{10}N_2O_2$ requires C, 65·3; H, 5·0; N, 13·9%). With hydrogen peroxide in acetic acid, the *N*-methyl derivative afforded compound (VII; R = OH), m. p. and mixed m. p. with a synthetic sample [6] 299° (from acetic acid).

2,3-*Dihydroxyquinoxaline and its* N-*Methyl Derivative*.—Solutions of the oxides (II; R = H, Ac, or Bz) or their *N*-methyl derivatives (VI) (0·002 mole) in acetic acid (10 ml.) and 20% w/v

[17] Cook and Perry, *J.*, **1943**, 394.

aqueous sulphuric acid (4 ml.) were refluxed for 3 hr., concentrated, and diluted with water, affording 2,3-dihydroxyquinoxaline (quantitative), m. p. >360° (from acetic acid) (Found: C, 59·4; H, 3·8. Calc. for $C_8H_6N_2O_2$: C, 59·2; H, 3·7%), or its *N*-methyl derivative (78%), m. p. 299° (from acetic acid) (Found: C, 61·4; H, 4·6; N, 15·7. Calc. for $C_9H_8N_2O_2$: C, 61·4; H, 4·5; N, 15·9%). Both compounds were further identified by comparison with authentic samples.[10,6]

α-Chloro-o-nitroacetanilide (I; R = Cl).—Solutions of chloroacetyl chloride (3 mol.; 171 ml.) in acetone (200 ml.) and 10% sodium hydroxide (750 ml.) were added, dropwise with stirring to *o*-nitroaniline (90·0 g.) in acetone (200 ml.) at 0°, at such a rate as to keep the mixture alkaline. After 2 hours' stirring at room temperature the mixture was neutralised with sulphuric acid, and the crystalline precipitate was collected, washed with water, and dried *in vacuo* (140 g.). The chloroanilide formed pale yellow needles, m. p. 90° (123 g.), from ethanol (Found: C, 44·7; H, 3·2; N, 12·7. Calc. for $C_8H_7ClN_2O_3$: C, 44·8; H, 3·3; N, 13·0%).

1-(o-*Nitrophenylcarbamoylmethyl*)*pyridinium Chloride* (III).—α-Chloro-*o*-nitroacetanilide (40·0 g.) was warmed with pyridine (40 ml.) at 100° for 0·5 hr. The excess of pyridine was removed *in vacuo* and the residual solid recrystallised, giving the *salt*, m. p. 241° (53·0 g.) (from aqueous ethanol) (Found: C, 53·3; H, 4·2; N, 13·9. $C_{13}H_{12}ClN_3O_3$ requires C, 53·2; H, 4·1; N, 14·3%).

2-*Amino*-3-*hydroxyquinoxaline* 1-*Oxide* (II; R = NH_2).—The salt (III) (10 g.) in methanol (20 ml.) was refluxed for 3 hr. with piperidine (20 ml.). Concentration of the mixture and trituration of the residual red gum with chloroform afforded the product as a pale yellow powder. Crystallised (twice) from acetic acid (charcoal), the *amine* (2·5 g.) formed white needles, m. p. 320°, $\nu_{max.}$ 3400, 3200, 2500 (broad), 1680, and 1650 cm.$^{-1}$ (Found: C, 54·5; H, 4·3; N, 23·8. $C_8H_7N_3O_2$ requires C, 54·2; H, 4·0; N, 23·7%), giving a deep blue colour with ferric chloride in ethanol, and with ethanolic picric acid *a picrate*, m. p. 262° (from ethanol (Found: C, 41·2; H, 2·7; N, 20·7. $C_{14}H_{10}N_6O_9$ requires C, 41·4; H, 2·5; N, 20·7%). Treatment of the amine with nitrous acid by the procedure of Sharp and Spring [13] gave starting material (80% recovery), m. p. and mixed m. p. 320°. With dimethyl sulphate and 5% aqueous sodium hydroxide at 0° it afforded an N-*methyl derivative* (45%), m. p. 310° (from aqueous acetic acid), $\nu_{max.}$ 3400, 3200, 1660, and 1626 cm.$^{-1}$ (Found: C, 56·4; H, 4·9; N, 21·8. $C_9H_9N_3O_2$ requires C, 56·5; H, 4·7; N, 21·9%). Reduction of this derivative with sodium dithionite in acetic acid afforded the compound (VII; R = NH_2), m. p. 275° alone or mixed with a synthetic sample.[7]

2-*Amino*-3-*hydroxyquinoxaline* (V; R = NH_2).—The oxide (II; R = NH_2) (0·3 g.), when reduced in acetic acid (7·5 ml.) with sodium dithionite (0·6 g.) as above, gave the deoxy-compound on concentration of the reaction mixture. Purified by extraction with N-hydrochloric acid and neutralisation of the filtered extract, the amine formed cream-coloured needles (0·2 g.), m. p. >360° (from acetic acid) (Found: C, 59·7; H, 4·5; N, 26·0. Calc. for $C_8H_7N_3O$: C, 59·6; H, 4·3; N, 26·0%), identified by conversion with nitrous acid [16] into 2,3-dihydroxyquinoxaline and by comparison of its infrared and ultraviolet spectra with those of a synthetic sample.[15] With dimethyl sulphate and alkali, it afforded the *N*-methyl derivative (VII; R = NH_2), m. p. 276° (from aqueous acetic acid) alone or mixed with an authentic sample [7] (Found: N, 23·7. Calc. for $C_9H_9N_3O$: N, 24·0%).

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