Quinoxaline Derivatives. VII.[1] The Mechanism of the Formation of 6-Chloro-1, 2, 3, 4, 2′, 3′-hexahydro-4, 1′-dimethyl-3, 2′-dioxoquinoxaline-2-spiro-3′-indole from a Quinoxaline *N*-Oxide Derivative by Nucleophilic Chlorination

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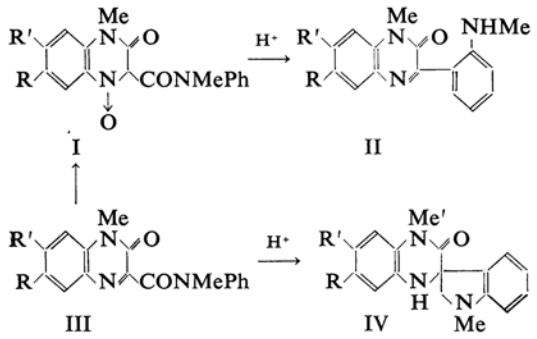
Usherwood and Whiteley[2] found that 3, 4-dihydro-4-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-3-oxoquinoxaline 1-oxide (Ia), on reaction with ethanolic hydrogen chloride, was converted to the compound $C_{17}H_{16}ClN_3O_2$, whereas with acetyl chloride it gave the compound $C_{19}H_{18}ClN_3O_3$. The latter compound apparently was the acetyl derivative of the former, and in both the compounds chlorine was inactive. However, no structures were proposed for these products. Clark-Lewis and Katekar[3] in 1959 re-examined the problem and revised the molecular formula of these compounds to $C_{17}H_{14}ClN_3O_2$ and $C_{19}H_{16}ClN_3O_3$ respectively; on the basis of spectroscopic data, the study of the degradation products and the synthesis of 6-chloro-3, 4-dihydro-4-methyl-2-(*o*-methylaminophenyl)-3-oxoquinoxaline (IIb, the major product of the degradation of $C_{19}H_{16}ClN_3O_3$), they deduced the structure of the compound $C_{17}H_{14}ClN_3O_2$ to be 6-chloro-1, 2, 3, 4, 2′, 3′-hexahydro-4, 1′-dimethyl-3, 2′-dioxoquinoxaline-2-spiro-3′-indole (IVb), the acetylation of which with acetyl chloride gave a product which was identical with the other compound, $C_{19}H_{16}ClN_3O_3$. However, no synthesis of the compound, which would have confirmed the proposed structure of the spiro-indole (IVb) had previously been reported. It has now been accomplished and is reported below.



(a) R=R′=H (b) R=H; R′=Cl
(c) R=Cl; R′=H

Clark-Lewis and Katekar[3] discounted the electrophilic chlorination of the molcule in this interaction of the *N*-oxide (Ia) with acetyl chloride (or ethanolic hydrogen chloride) on the grounds that the "formation of such chlorinating species would consume the *N*-oxide function, and subsequent cyclisation would then be difficult to understand." According to them, for this chlorination, the protonation of the *N*-oxide (Ia) to the conjugate acid (V) is the first step; the powerful inductive effect of the hydroxylammonium ion then promotes the intramolecular electrophilic substitution at the ortho-position of the methylanilide moiety by the quinoxaline 2-C-atom, giving the *N*-hydoxy-compound (VI). The known nucleophilic substitution by chloride ions (i. e., *N*-phenylhydroxylamine with hydrochloric acid → *p*-chloro-aniline[4]) with the intermediate (VI) then leads to the formation of the 6-chloro-spiro-indole (IVb). If this order

1) Part VI: Y. Ahmad, M. S. Habib, Ziauddin and N. Bashir. This Bulletin, **38**, (1965).

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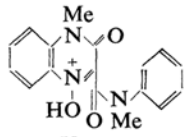
2) E. H. Usherwood and M. A. Whiteley, *J. Chem Soc* **1923**, 1069.

3) J. W. Clark-Lewis and G. F. Katekar, ibid., **1959**, 2825.

4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London (1953), p. 621; H. E. Heller, E. D. Hughes and C. K. Ingold, *Nature*, **168**, 909 (1951).

of the two steps for this nucleophilic chlorination is accepted, then the analogy drawn by



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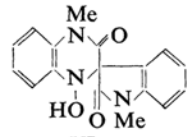
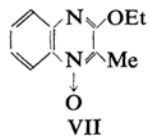
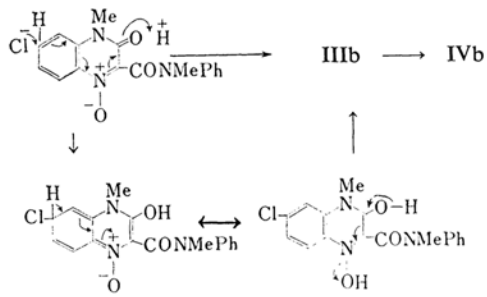


VI



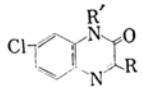
VII

the same authors between this substitution by chlorine in the 6-position of this quinoxaline spiro-indole (IVb) and the reported[5] conversion of 3-ethoxy-2-methyl-quinoxaline 1-oxide (VII) into 6-chloro-3-hydroxy-2-methylquinoxaline (VIIIa; R=Me) cannot be explained, as the cyclisation step to convert VII into an *N*-hydroxy intermediate analogous to VI is not possible in the latter case. The mechanism proposed in Part VI[1] for this type of nucleophilic chlorination of quinoxaline *N*-oxides satisfactorily accounts for both the cases, as, according to it, this nucleophilic chlorination takes place as a result of the combined action of the protonation of oxygen functions at $C_{(3)}$ and $N_{(1)}$ of the quinoxaline molecule, whereby $C_{(6)}$ becomes prone to the attack of the nucleophile (chloride anion), irrespective of the substituent at position 2.

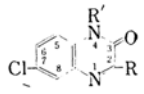


Accordingly, the *N*-oxide (Ia) first gives the chloroquinoxalineanilide (IIIb), which then immediately undergoes the known[6,12] acid-catalysed rearrangement to the isomeric 6-chloro-spiro-indole (IVb).

It is now well established, on the basis of the studies made in earlier papers,[6,12] that 3, 4-dihydro-4-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-3-oxoquinoxaline (IIIa), when treated with concentrated sulphuric acid or ethanolic hydrogen chloride, isomerises to 1, 2, 3, 4, 2', 3'-hexahydro-4, 1'-dimethyl-3, 2'-dioxoquinoxaline-2-spiro-3'-indole (IVa). Substituted derivatives of IIIa behave similarly and give the corresponding spiro-indoles.[12] On the other hand, the *N*-oxides of IIIa and its substituted derivatives, with concentrated sulphuric acid, undergo rearrangement,[13] accompanied by dehydration and decarboxylation, to give the corresponding amines (IIa and its substituted derivatives).



VIII



IX

	R	R'		R	R'
(a)	H	H	(f)	$CONH_2$	H
(b)	CO_2Et	H	(g)	$CONH_2$	Me
(c)	CO_2Et	Me	(h)	CONHPh	H
(d)	CO_2H	H	(i)	CONMePh	H
(e)	CO_2H	Me	(j)	CN	H 1-oxide

For the synthesis of spiro-indole IVb, 6-chloro-3, 4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxylic acid (VIIIe, see below) was converted to its methylanilide (IIIb) by the usual methods.[12,13] IIIb, when heated with ethanolic hydrogen chloride, rearranged intramolecularly to the isomeric spiro-indole (IVb), which was identical (infrared spectrum and mixed melting point) with the product obtained by the action of ethanolic hydrogen chloride on the chlorine free *N*-oxide (Ia), as described by Clark-Lewis and Katekar.[3] The position of the entering chlorine atom in the molecule in the latter reaction is thereby fully established.

7-Chloro-3-hydroxyquinoxaline-2-carboxylic acid (IXd) was converted to its methylanilide (IXi), and then this was further methylated to IIIc. IXi and IIIc, on being heated with ethanolic hydrogen chloride, rearranged, as expected,[6,12] to their corresponding 7-chloro-spiro-indoles IVc (H for Me') and IVc. IIIb and IIIc both were smoothly converted to their *N*-oxides (Ib and Ic) with hydrogen peroxide and acetic acid. Both of these *N*-oxides (Ib and Ic) underwent intramolecular rearrangement, accompanied by dehydration and decarboxylation, in concentrated sulphuric acid, yielding 6-chloro-3, 4-dihydro-4-methyl-2-(*o*-methylaminophenyl)-3-oxoquinoxaline (IIb) and the 7-chloro-isomer (IIc) respectively, which were identical (infrared spectrum and mixed melting point) with the synthetic samples provided by Professor J. W. Clark-Lewis.

As expected,[14] the methylanilide IXi, on reaction with hydrogen peroxide in hot acetic acid, yielded 6-chloro-2, 3-dihydroxyquinoxaline (IXa; R=OH) instead of giving its *N*-oxide.

During the preparation of the intermediates needed for this investigation, it was observed

5) W. Dawson, G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, **1949**, 2579.
6) M. S. Habib and C. W. Rees, ibid., **1962**, 123.

that if a large excess of ethyl mesoxalate was not used in its condensation with 4-chloro-*o*-phenylenediamine or 4-chloro-2-methylaminoaniline, instead of the expected quinoxaline-2-carboxylic esters, products of a very high melting point were formed; these probably resulted from the further condensation of the ethoxycarbonyl moiety of the esters formed with another molecule of the *o*-phenylenediamines, as these products[7] were sparingly soluble in, and stable to, acids and alkalies. 4-Chloro-2-methylaminoaniline, on being heated with an excess of ethyl mesoxalate in ethanol (or dry benzene), gave, in a good yield, the ester VIIIc, which, on being shaken with aqueous potassium hydroxide, hydrolysed to the acid VIIIe. The ester which was separated in a good yield by the reaction of 4-chloro-*o*-phenylenediamine with ethyl mesoxalate under similar conditions was the 7-chloro isomer (IXb); its hydrolysis with aqueous alkali gave the corresponding acid (IXd), which, on decarboxylation, gave 6-chloro-2-hydroxyquinoxaline (IXa), identical with a sample[8] which had previously been obtained by an unambiguous route. The 6-chloro isomeric ester (VIIIb), which was the second expected product of the reaction, was formed to a much lesser extent and remained in the mother liquor; on hydrolysis in situ with aqueous alkali it gave 6-chloro-3-hydroxyquinoxaline-2-carboxylic acid (VIIId), which, on decarboxylation, in turn gave the known 6-chloro-3-hydroxyquinoxaline (VIIIa). The structure of this acid (VIIId) was further confirmed by methylation, with methyl sulphate in acetone in the presence of anhydrous potassium carbonate, to lead to a product identical (infrared spectrum and mixed melting point) with the 6-chloro-3,4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxylic acid (VIIIe) described above.

Experimental

The infrared spectra were measured in Nujol mulls with a Perkin-Elmer spectrophotometer model 137. The light petroleum used had a boiling range of 60—80°C.

The Condensation of 4-Chloro-*o*-phenylenediamine with Ethyl Mesoxalate.—4-Chloro-*o*-phenylenediamine (8.4 g.), obtained by the reduction of 4-chloro-2-nitroaniline[9] (10 g.) with stannous chloride and hydrogen chloride (by adopting the procedure of Dawson et al.[5]), was taken up in dry benzene (150 ml.), and then the solution was added portion-by-portion to ethyl mesoxalate (35 ml.). After the mixture had been heated under reflux for 1 hr., about half of the solvent of the mixture was removed under reduced pressure. On cooling, a yellow solid separated (10.5 g.); this was collected and crystallised from ethanol as yellow needles of ethyl 7-chloro-3-hydroxyquinoxaline-2-carboxylate (IXb), m. p. 206—207°C.

Found: Cl, 13.9; N, 11.3. Calcd. for $C_{10}H_9ClN_2O_3$: Cl, 14.05; N, 11.1%.

This compound, which separated as the major product of the condensation, gave, on hydrolysis, an acid the decarboxylation of which afforded the known 6-chloro-2-hydroxyquinoxaline (IXa, see below); this established its structure as a 7-chloro-ester (IXb).

The 6-chloro-ester (VIIIb), the other expected product of the condensation, remained in the mother liquor and was hydrolysed in situ by heating it with 3 N aqueous potassium hydroxide (50 ml.) on a steam bath for 2 hr. The dark red mixture was filtered, and the filtrate, on acidification with concentrated hydrochloric acid, gave a precipitate (purified by dissolution in aqueous potassium hydrogen carbonate and reprecipitation with acid) of 6-chloro-3-hydroxyquinoxaline-2-carboxylic acid (VIIId), m. p. 194—196°C (decomp.).

Found: Cl, 15.2; N, 11.6. Calcd. for $C_9H_5ClN_2O_3 \cdot H_2O$: Cl, 14.7; N, 11.55%.

This acid (VIIId), on being heated to its melting point, gave 6-chloro-3-hydroxyquinoxaline (VIIIa), m. p. 251—252°C, for which Crowther et al.[10] have recorded a m. p. of 270°C (decomp.). VIIId, on methylation, gave the methylated acid (VIIIe), which was identical with the product of the hydrolysis of the authentic ester (VIIIc, see below).

Ethyl 6-Chloro-3,4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxylate (VIIIc).—4-Chloro-2-methylaminoaniline (6.2 g.), obtained from 5-chloro-*N*-methyl-2-nitroaniline (7.5 g.) according to the method of Dawson et al.[5]; was taken up in dry benzene (125 ml.) and then the solution was added to ethyl mesoxalate (28 ml.). After the mixture had been heated under reflux on a water bath for 1.5 hr., the excess solvent was removed under reduced pressure. The solid which separated (in a 60% yield) on cooling was crystallised from ethanol as light yellow needles of the 6-chloro-*N*-methyl ester (VIIIc), m. p. 134—135°C.

Found: Cl, 12.8; N, 9.9. Calcd. for $C_{12}H_{11}ClN_2O_3$: Cl, 13.3; N, 10.5%.

The mother liquor contained more of the ester, as the residue obtained on its evaporation to dryness, on hydrolysis with aqueous alkali, gave an additional amount of the 6-chloro-4-methyl acid (VIIIe, see below).

In the preparation of the esters VIIIc and IXb above, if a large excess of ethyl methoxalate was not used, products with very high melting points were formed; these probably resulted from the further condensation of the ethoxycarbonyl moiety of these esters with another molecule of the *o*-phenylenediamines. These products[7] were stable and sparingly soluble in, acids and alkalies.

7) Cf. H. Ohle and W. Gross, *Ber.*, **68**, 2262 (1935).
8) Y. Ahmad, M. S. Habib and Ziauddin, *Tetrahedron*, **20**, 1107 (1964).
9) M. K. Bose, *J. Indian Chem. Soc.*, **22**, 169 (1945).
10) A. F. Crowther, F. H. S. Curd, D. G. Davy and G. J. Stacey, *J. Chem. Soc.*, **1949**, 1260.
11) F. Kehrmann and H. Muller, *Ber.*, **34**, 1095 (1901).
12) Y. Ahmad, M. S. Habib, M. Iqbal and M. I. Qureshi, *J. Chem. Soc.*, **1964**, 4053.
13) M. S. Habib and C. W. Rees, ibid., **1960**, 3371.
14) M. S. Habib and C. W. Rees, ibid., **1960**, 3386.

6-Chloro-3, 4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxylic Acid (VIIIe).—a) 6-Chloro-*N*-methyl ester (VIIIc; 5 g.) was shaken with 20% aqueous potassium hydroxide (100 ml.) at room temperature for 2 hr., during which period it dissolved. On acidification with 25% sulphuric acid with cooling, a light brown precipitate was obtained; this crystallised from ethanol as cream-coloured needles of the 6-chloro-4-methyl acid (VIIIe), m. p. 186—187°C (decomp.). Yield 3.9 g.

Found: Cl, 14.3; N, 11.4. Calcd. for $C_{10}H_7ClN_2O_3$: Cl, 14.8; N, 11.7%.

b) The acid VIIId (1 g.), methyl sulphate (0.5 ml.) and anhydrous potassium carbonate (2 g.) were heated together under reflux in an acetone suspension (100 ml.) for 3 hr. The mixture was then evaported to dryness and acidified with dilute hydrochloric acid. The solid which separated was collected and crystallised from ethanol as cream-coloured needles, m. p. 188—189°C (decomp.), identical (infrared spectrum and mixed melting point) with the 6-chloro-4-methyl acid (VIIIe) described under a).

7-Chloro-3-hydroxyquinoxaline-2-carboxylic Acid (IXd).—The ester (IXb) and 3 N aqueous potassium hydroxide were heated on a steam bath for 1 hr. The reaction mixture was then filtered, and the filtrate, on acidification with concentrated hydrochloric acid, gave the 7-chloro acid (IXd) in quantitative yield, m. p. 308—310°C (decomp.).

Found: Cl, 15.5; N, 12.8. Calcd. for $C_9H_5ClN_2O_3$: Cl, 15.8; H, 12.5%.

This could, when heated at 310°C, be decarboxylated to 6-chloro-2-hydroxyquinoxaline (IXa), m. p. 320—321°C, identical with that of a sample[8] (m. p. 320—321°C) obtained by the reduction of 7-chloro-2-cyano-3-hydroxyquinoxaline 1-oxide (IXj) with sodium dithionite in boiling 50% aqueous ethanol.

7-Chloro-3, 4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxylic Acid (IXe).—The ester (IXb) in acetone was methylated with methyl sulphate in the presence of anhydrous potassium carbonate to give the 7-chloro-4-methyl ester (IXc) (crystallised from ethanol as yellow needles) in a good yield, m. p. 125—126°C.

Found: Cl, 10.4; N, 12.8. Calcd. for $C_{12}H_{11}ClN_2O_3$: Cl, 10.5; N, 13.3%.

This ester, on hydrolysis with 3 N aqueous potassium hydroxide, gave yellow cubes (from ethanol) of the 7-chloro-4-methyl acid (IXe) (yield 80%), m. p. 198—199°C (decomp.).

Found: Cl, 13.9; N, 11.9. Calcd. for $C_{10}H_7ClN_2O_3$: Cl, 14.8; N, 11.7%.

7-Chloro-3-hydroxyquinoxaline-2-carboxyamide (IXf).—The ester (IXb), on being heated with concentrated ammonia on a steam bath for 2 hr., afforded a solid which crystallised from ethanol as yellow micro-crystals of the amide (IXf) in a quantitative yield, m. p. 310—311°C.

Found: Cl, 15.2; N, 18.4. Calcd. for $C_9H_6ClN_3O_2$: Cl, 15.8; N, 18.8%.

7-Chloro-3,4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxyamide (IXg).—Similarly, the ester (IXc) with concentrated ammonia gave yellow needles (from ethanol) of the 4-methyl amide (IXg) in a good yield, m. p. 325—326°C (decomp.).

Found: Cl, 13.7; N, 16.6. Calcd. for $C_{10}H_8ClN_3O_2 \cdot H_2O$: Cl, 13.9; N, 16.4%.

6-Chloro-3, 4-dihydro-4-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-3-oxoquinoxaline (IIIb).—The acid (VIIIe) (1 g.) and thionyl chloride (20 ml.) were heated under reflux for 1 hr. The solid obtained after the removal of thionyl chloride was taken up in a small amount of dry benzene and added portion-by-portion to a solution of *N*-methylaniline (8 ml.) in dry benzene (10 ml.). The reaction mixture was then heated on a steam bath for 10 min. and washed with 2 N hydrochloric acid. The solid which separated was crystallised from ethanol as light yellow cubes of the 4-methyl-*N*-methylanilide (IIIb); yield 80%; m. p. 192—193°C.

Found: C, 62.7; H, 4.6; Cl, 10.6. Calcd. for $C_{17}H_{14}ClN_3O_2$: C, 62.3; H, 4.3; Cl, 10.8%.

This general procedure was also used for the preparation of the other anilides described below.

7-Chloro-3-hydroxy-2-(*N*-phenylcarbamoyl)-quinoxaline (IXh).—The acid chloride from the acid (IXd), on reaction as above, gave with aniline yellow needles (from glacial acetic acid) of the anilide (IXh); yield 90%, m. p. >340°C.

Found: Cl, 11.45. Calcd. for $C_{15}H_{10}ClN_3O_2$: Cl, 11.85%.

7-Chloro-3, 4-dihydro-4-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-3-oxoquinoxaline (IIIc).—Similarly, the acid chloride from the acid (IXd) with *methylaniline* gave yellow needles (from ethanol) of 7-chloro-3-hydroxy-2-(*N*-methyl-*N*-phenylcarbamoyl)-quinoxaline (IXi); yield 70%; m. p. 285°C.

Found: Cl, 10.9; N, 13.7. Calcd. for $C_{16}H_{12}ClN_3O_2$: Cl, 11.3; N, 13.4%.

The methylation of this anilide with methyl sulphate and anhydrous potassium carbonate in acetone gave cream-coloured cubes (from benzene-light petroleum) of 4-methyl-*N*-methylanilide (IIIc) in a good yield, m. p. 164—166°C.

Found: Cl, 10.7. Calcd. for $C_{17}H_{14}ClN_3O_2$: Cl, 10.8%.

6-Chloro-1, 2, 3, 4, 2′, 3′-hexahydro-4, 1′-dimethyl-3, 2′-dioxoquinoxaline-2-spiro-3′-indole (IVb).—The anilide (IIIb) (0.5 g.) was boiled under reflux for 2 hr. with saturated ethanolic hydrogen chloride (25 ml.), and then the mixture was evaporated under reduced pressure to dryness. The residue crystallised from ethanol as colourless needles of the spiro-indole (IVb), m. p. 239—240°C, in a good yield. The spiro-indole was identical (infrared spectrum and mixed melting point) with a sample[2] obtained by the action of ethanolic hydrogen chloride on 3,4-dihydro-4-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-3-oxoquinoxaline 1-oxide (Ia). The above procedure was used for the preparation of the following spiro-indoles.

7-Chloro-1, 2, 3, 4, 2′, 3′-hexahydro-1′-methyl-3, 2′-dioxoquinoxaline-2-spiro-3′-indole (IVc; H for Me′).—The anilide (IXi), on being treated with ethanolic hydrogen chloride as above, gave white needles (from acetic acid) of the spiro-indole (IVc; H for Me′); yield 70%; m. p. 320°C (decomp.).

Found: C, 61.6; H, 4.5; Cl, 11.7. Calcd. for $C_{16}H_{12}ClN_3O_2$: C, 61.2; H, 3.8; Cl, 11.3%.

7-Chloro-1, 2, 3, 4, 2′, 3′-hexahydro-4, 1′-dimethyl-3,2′-dioxoquinoxaline-2-spiro-3′-indole (IVc).—Similarly, the anilide (IIIc) gave light yellow needles (from ethanol) of the 4-methyl spiro-indole (IVc); yield 80%; m. p. 260—262°C (decomp.).

Found: Cl, 61.8; H, 4.1. Calcd. for $C_{17}H_{14}ClN_3O_2$: C, 62.3; H, 4.3%.

6-Chloro-3, 4-dihydro-4-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-3-oxoquinoxaline 1-Oxide (Ib).—The anilide (IIIb) (1.0 g.), acetic acid (10 ml.), and 30% hydrogen peroxide (1 ml.) were heated at 55—60°C for 72 hr.; the acetic acid was removed under reduced pressure, and the residue was crystallised from benzene-light petroleum as yellow crystals of the 1-oxide (Ib); yield 25%; m. p. 160—162°C.

Found: C, 57.9; H, 3.8; N, 12.0. Calcd. for $C_{17}H_{14}ClN_3O_3 \cdot 1/2H_2O$: C, 57.9; H, 4.0; N, 11.9%.

7-Chloro-3, 4-dihydro-4-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-3-oxoquinoxaline 1-Oxide (Ic).—Similarly, the anilide (IIIc) gave yellow crystals (from benzene-light petroleum) of the 1-oxide (Ic); yield 40%; m. p. 180—182°C.

Found: N, 12.5. Calcd. for $C_{17}H_{14}ClN_3O_3$: N, 12.2%.

6-Chloro-2, 3-dihydroxyquinoxaline (IXa; R=OH).—The anilide (IXi), on being treated with a mixture of hydrogen peroxide and glacial acetic acid at 60°C, gave colourless flakes (from glacial acetic acid) of the dihydroxyquinoxaline (IXa; R=OH); yield 50%; m. p. >350°C, identical (infrared spectrum) with an authentic sample.[10]

6-Chloro-3, 4-dihydro-4-methyl-2-(*o*-methylaminophenyl)-3-oxoquinoxaline (IIb).—The *N*-oxide (Ib) (0.5 g.) was stirred gradually into concentrated sulphuric acid (2 ml.) at room temperature. After the evolution of carbon dioxide had ceased, the solution was poured on ice and filtered. The basification of the filtrate gave a precipitate which crystallised from ethanol as orange needles of the 6-chloro-amine (IIb) (yield 40%); m. p. 186—188°C; identical (infrared spectrum and mixed melting point) with the synthetic sample[3] supplied by Professor J. W. Clarke-Lewis.

7-Chloro-3, 4-dihydro-4-methyl-2-(*o*-methylaminophenyl)-3-oxoquinoxaline (IIc).—The *N*-oxide (Ic) (0.5 g.) obtained by the above method yielded the 7-chloroamine (IIc); yield 50%; m. p. 163—164°C; indentical (infrared spectra and mixed melting point) with a synthetic sample[3] supplied by Professor J. W. Clark-Lewis.

Summary

The compound IVb named in the title has been obtained by an unambiguous route. It has been shown to be identical with the product of the reaction of the *N*-oxide (Ia) with ethanolic hydrogen chloride. Clark-Lewis and Katekar's mechanism[3] for the nucleophilic chlorination in the latter case has been discussed, and a modified mechanism proposed.

Isomeric 7-chloro-spiro-indole (IVc) has also been obtained by the rearrangement of the anilide IIIc. Similarly, the anilide IXi gives spiro-indole (IVc; H for Me′).

The anilides IIIb and IIIc give normal *N*-oxides Ib and Ic, which, with concentrated sulphuric acid, decompose and afford the amines IIb and IIc. IXi, instead of giving its *N*-oxide, yields 6-chloro-2, 3-dihydroxyquinoxaline.

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