Quinoxaline Derivatives. X.[1a] A Novel Rearrangement of Certain Quinoxaline N-Oxides to 2-Benzimidazolinones[1b]

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Quinoxaline 1-oxides, bearing a substituent at C-2, a carbonyl at C-3, and a free hydrogen at N-4, when heated with acetic anhydride, are transformed into 1-acetyl-3-acyl-2-benzimidazolinones or 1,3-diacetyl-2-benzimidazolinones. A mechanism for this novel rearrangement has been proposed and discussed. In the absence of a carbonyl at C-3, the quinoxaline 1-oxides fail to rearrange. On the other hand, if the hydrogen at N-4 is replaced by a methyl, a different type of rearrangement[1a,3,4] takes place and an acetoxy group is introduced at C-6 in the quinoxaline molecule with simultaneous loss of the N-oxide function.

Derivatives of 3-hydroxyquinoxaline 1-oxide[5] bearing a substituent at position 2 possess some special structural features. As in such simple and mild reactions as heating with acetyl chloride or ethanolic hydrogen chloride, these compounds undergo chlorination at C-6 of the molecule. In earlier studies[1a,3,4] it has been shown that this chlorination takes place through the attack of the reagent on the oxygen function at C-3 and the N-oxide, whereby C-6 becomes electron deficient and hence prone to the attack by the chloride anions. The oxygen function at C-3 seems to be essential for this nucleophilic chlorine substitution at C-6, as in its absence no reaction takes place.

In the present study it was considered of interest to replace acetyl chloride with acetic anhydride and to see if by the same analogy an acetoxy group could be introduced at C-6. When 3-hydroxy-2-phenylquinoxaline 1-oxide (Ia) was heated under reflux with acetic anhydride for 4 hr, a compound was obtained in good yield, which corresponded in composition to $C_{16}H_{12}N_2O_3$ of 6-acetoxy-3-hydroxy-2-phenylquinoxaline (IX, H for Me). However, after hydrolysis with alkali, the deacetylated compound proved to be quite different from the expected 3,6-dihydroxy-2-phenylquinoxaline (X, H for Me). It finally proved to be identical with 2-benzimidazolinone (VIa), an authentic sample of which was obtained by the condensation of *o*-phenylenediamine and urea. The formation of VIa suggested that the product obtained by the action of acetic anhydride on Ia was 1-acetyl-3-benzoyl-2-benzimidazolinone (IIIa), which was isomeric with IX (H for Me) and which on hydrolysis lost both acetyl and benzoyl groups. Benzoic acid was also isolated.

Similarly 7-ethoxy-3-hydroxy-2-phenylquinoxaline 1-oxide (Ib) and 3-hydroxy-7-methyl-2-phenylquinoxaline 1-oxide (Id) on being heated with acetic anhydride under reflux for 4 hr yielded 5-ethoxy- and 5-methyl-1-acetyl-3-benzoyl-2-benzimidazolinone (IIIb and IIId), respectively, which on hydrolysis with aqueous alkali lost their acetyl and benzoyl groups and yielded 5-ethoxy- and 5-methyl-2-benzimidazolinones (VIb and VId) (Scheme I).

7-Methoxy- and 6-methoxy-3-hydroxy-2-phenylquinoxaline 1-oxide (Ic and XIII) when heated with acetic anhydride for 4 hr gave the same compound 1,3-diacetyl-5-methoxy-2-benzimidazolinone (IVc). When the time of heating was reduced in order to trap the expected intermediates, 5-methoxy- and 6-methoxy-1-acetyl-3-benzoyl-2-benzimidazolinones IIIc and III (R = H; R′ = MeO), respectively, only a mixture of the starting material and IVc was obtained in each case. It appears that the expected intermediate benzoyl derivatives in these cases undergo a facile transacylation with acetic anhydride under the conditions of the reaction and exchange their benzoyl group with the acetyl group. Benzoic acid was isolated as the other product of reaction in each case. Similarly 7-chloro- and 6,7-dichloro-3-hydroxy-2-phenylquinoxaline 1-oxide (Ie and If) when heated with acetic anhydride gave 5-chloro- and 5,6-dichloro-1,3-diacetyl-2-benzimidazolinone (IVe and IVf), respectively. The expected intermediates 1-acetyl-3-benzoyl-2-benzimidazolinones (IIIe and IIIf) again could not be isolated in these cases. Compounds Ie and If needed longer hours for complete conversion into benzimidazolinone derivatives. If the time of heating was reduced in order to trap the expected intermediates IIIe and IIIf, only a mixture of the starting material and the corresponding diacetylbenzimidazolinone was obtained in each case. When the time of heating was increased from 4 hr to 10 hr in the case of quinoxaline 1-oxide derivatives Ia, Ib, and Id (see above), the rearrangement products, here too, were entirely the diacetyl derivatives IVa, IVb, and IVd, obtained through a facile transacylation of the 1-acetyl-3-benzoyl-2-benzimidazolinones IIIa, IIIb, and IIId formed earlier. Benzoic acid was isolated as the other product of reaction in each case. That rearrangement products IVa–f (and by inference their precursors IIIa–f) were in fact benzimidazolinones was established by (i) their hydrolysis with aqueous alkali to 2-benzimidazolinones VIa–f which were identical with the authentic samples synthesized, for comparison, by the condensation of respective *o*-phenylenediamines (VIIa–f) with urea and (ii) their identity with the diacetyl derivatives obtained by the acetylation of authentic 2-benzimidazolinones VIa–f with acetic anhydride.

2-(*p*-Chlorophenyl)-3-hydroxyquinoxaline 1-oxide (Ih) on being heated under reflux with acetic anhydride also afforded 1,3-diacetyl-2-benzimidazolinone (IVa), and *p*-chlorobenzoic acid could also be obtained from the reaction products. It clearly established that the

(1) (a) Part IX: Y. Ahmad, M. S. Habib, Ziauddin, and B. Bakhtiari, *J. Org. Chem.*, **31**, 2613 (1966). (b) Presented at the First International Congress of Heterocyclic Chemistry, Albuquerque, N. M., June 12–15, 1967.

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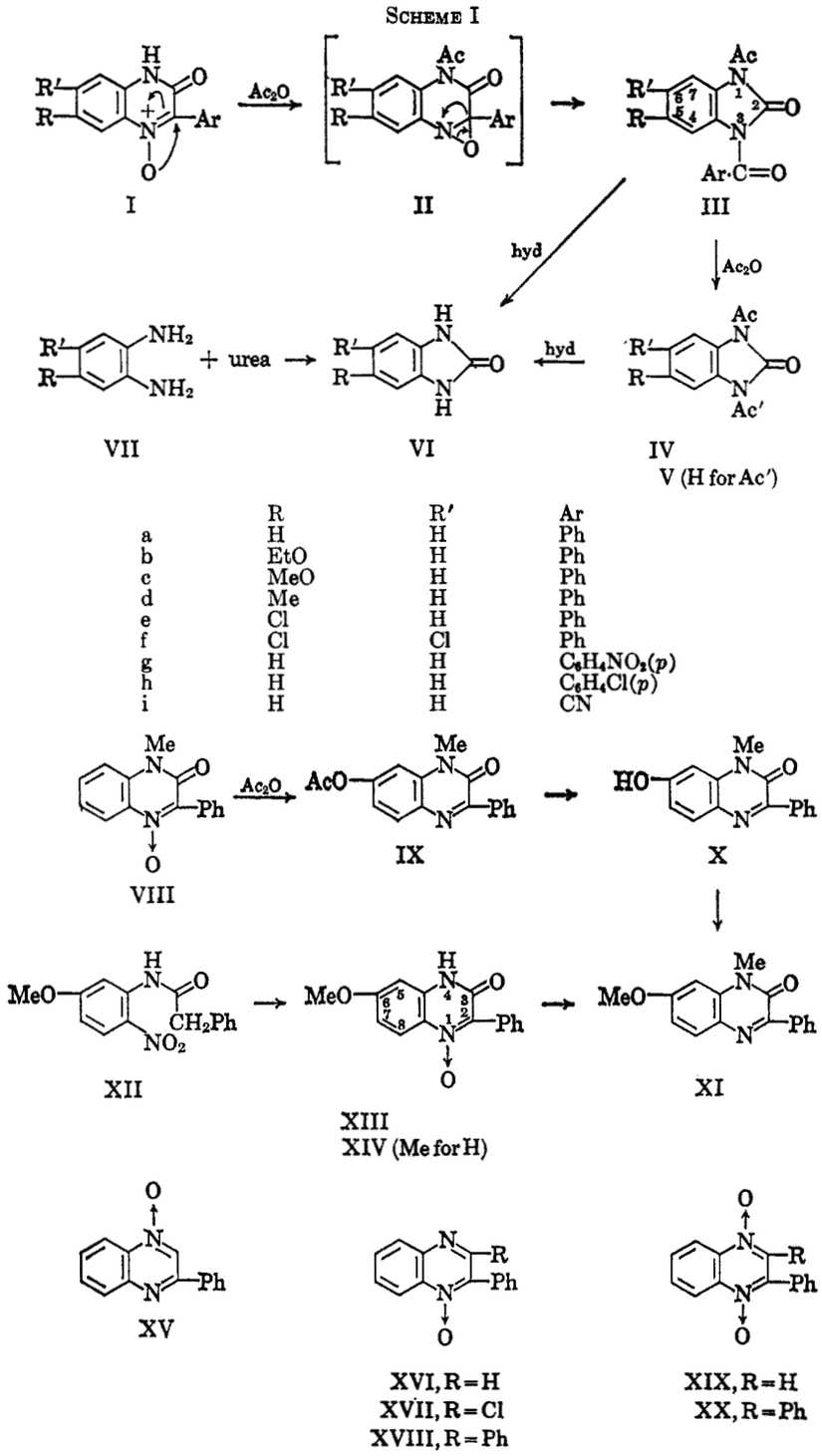
(3) Y. Ahmad, M. S. Habib, Ziauddin, and N. Bashir, *Bull. Chem. Soc. Japan*, **38**, 1654 (1965).

(4) Y. Ahmad, M. S. Habib, M. Iqbal, M. I. Qureshi, and Ziauddin, *ibid.*, **38**, 1659 (1965).

(5) 2- or 3-hydroxyquinoxalines and their derivatives exist predominantly in the amide form and should be named accordingly. However, as in earlier papers of this series, these compounds have been named in this paper as hydroxyquinoxalines for the sake of brevity and simplicity.

SCHEME I



rearrangement in this case was confined to the heterocyclic ring of the quinoxaline molecule.

3-Hydroxy-2-(*p*-nitrophenyl)quinoxaline 1-oxide (Ig) remained unchanged even on prolonged heating under reflux with acetic anhydride. However, when the two reactants were heated together in a sealed tube at 180° for 12 hr, the products of the reaction were 1,3-diacetyl- and 1-acetyl-2(3H)-benzimidazolinones (IVa and Va), along with *p*-nitrobenzoic acid. Similarly, 2-cyano-3-hydroxyquinoxaline 1-oxide (Ii) failed to react with acetic anhydride under ordinary conditions of reflux. However in a sealed tube at 180°, it also gave 1,3-diacetyl-2-benzimidazolinone (IVa).

3-Phenylquinoxaline 1-oxide (XV), which has an unsubstituted position adjacent to the N-oxide, when heated under reflux with acetic anhydride, underwent the well-known rearrangement[6] [—CH=N(O)— to —C(O)NH—] of the oxides of the N-heterocycles and gave exclusively 3-hydroxy-2-phenylquinoxaline (XI, H for Me and MeO). 2-Phenylquinoxaline 1,4-dioxide (XIX), on the other hand, under the same conditions gave 1-acetyl-3-benzoyl-2-benzimidazolinone (IIIa). As a first step XIX must have undergone the rearrangement similar to that of XV to give 3-hydroxy-2-phenylquinoxaline 1-oxide (Ia), which has been shown above to yield IIIa under the conditions of the reaction.

(6) E. Hayashi and C. Iijima, *Yakugaku Zasshi*, **82**, 1093 (1962); E. Ochiai and T. Okamoto, *J. Pharm. Soc. Japan*, **68**, 88 (1948); E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953); S. Oae and S. Kozuka, *Tetrahedron*, **20**, 2691 (1964).

2-Phenylquinoxaline 1-oxide (XVI), 3-chloro-2-phenylquinoxaline 1-oxide (XVII), 2,3-diphenylquinoxaline 1-oxide (XVIII), and 2,3-diphenylquinoxaline 1,4-dioxide (XX) were recovered unchanged even when heated with acetic anhydride in a sealed tube at 180°. On a very prolonged heating under these conditions XVIII and XX were deoxygenated and yielded 2,3-diphenylquinoxaline.

It was rather peculiar to note that Ia, which with acetic anhydride smoothly underwent the rearrangement to IIIa, failed to do so when the free hydrogen at N-4 was replaced with a methyl group and instead took a different course (similar to the nucleophilic chlorination at C-6 of the molecule with simultaneous loss of the N-oxide function, during the interaction of Ia with acetyl chloride as reported in part VI[3]) and yielded 6-acetoxy-3,4-dihydro-4-methyl-3-oxo-2-phenylquinoxaline (IX) instead. No trace of a benzimidazolinone derivative was obtained in this case. For establishing the constitution of IX, 5-methoxy-2-nitro-α-phenylacetanilide (XII) was cyclized[7] with alkali to 3-hydroxy-6-methoxy-2-phenylquinoxaline 1-oxide (XIII), which on methylation[7] and then deoxygenation[7] gave an authentic sample of 3,4-dihydro-6-methoxy-4-methyl-3-oxo-2-phenylquinoxaline (XI). The latter was identical with the compound obtained by deacetylation of IX with alkali, followed by methylation of the free hydroxyl group so generated in the resulting molecule.

It may be pertinent here to point out that derivatives of Ia, whether bearing a free hydrogen or a methyl group at N-4, when treated with acetyl chloride have been reported[3,4] to undergo nucleophilic chlorination exclusively at C-6 of the molecule with simultaneous loss of N-oxide function.

From the above study it can be inferred that this novel rearrangement and consequent ring contraction of quinoxalines to benzimidazoles (from a six-membered to a five-membered ring) during this reaction is a general one, provided the starting quinoxaline derivative has the following structural features: (i) an oxide function at N-1, (ii) a substituent at C-2, (iii) a carbonyl at C-3, and (iv) a free hydrogen at N-4. In the absence of either an oxide at N-1 or a carbonyl at C-3, no reaction takes place. If the position adjacent to the N-oxide is unoccupied, the rearrangement[6] —N(O)=CH— to —NHC(O)— takes over and results in the formation of a 2-hydroxyquinoxaline derivative. In case the free hydrogen at N-4 is replaced with a methyl group, the rearrangement similar to the one reported in part VI[3] of this series takes place and the corresponding deoxygenated 6-acetoxyquinoxaline is formed.

As one of the most plausible mechanisms of this rearrangement, it can be envisaged that the quinoxaline derivatives which fulfill the above requirements undergo acetylation at N-4 as the first step, then the nucleophilic oxygen at N-1 seeks a bond with the electron-deficient C-2, whereby a three-membered N–O–C oxaziridine ring is formed as depicted in structures I → II. An immediate shift of electrons and consequent realignment of the bonds as shown in II should give the rearranged 1-acetyl-3-acyl-2-benzimidazolinone. The oxaziridine species of the type II which have been invoked to explain the formation of benzimidazolinones III–V have not been isolated in this thermal rearrangement. However, in a somewhat analogous photolytic rearrangement of heterocyclic N-oxides the intermediate oxaziridines have been actually isolated by Kaneko, *et al.*[8] Recently the same workers[9] have explained the formation of 1-benzoyl-2-phenylbenzimidazole from 2,3-diphenylquinoxaline 1-oxide (XVIII) through the intermediate formation of an oxaziridine by a photolytic rearrangement, although in a later paper[10] they have shown that the intermediate in this rearrangement instead of being an oxaziridine is an oxadiazepine. Haddadin and Issidorides[11] have also explained the formation of 1,3-dibenzoyl-2-benzimidazolinone (IIIa, Bz for Ac) from 2-benzoyl-3-phenylquinoxaline 1-oxide by a photolytic rearrangement through the intermediate formation of an oxaziridine.

(7) *Cf.* Y. Ahmad, M. S. Habib, Ziauddin, and N. Bashir, *Tetrahedron*, **21**, 861 (1965).

Experimental Section[12]

Materials.—2-Phenylquinoxaline 1-oxide[13] (XVI), 3-chloro-2-phenylquinoxaline 1-oxide[13] (XVII), 2,3-diphenylquinoxaline 1-oxide[14] (XVIII), and 2,3-diphenylquinoxaline 1,4-dioxide[14] (XX) were prepared according to the published methods. 2-Nitro-α-phenylacetanilide and its 7-chloro, 6,7-dichloro, 7-ethoxy, 7-methoxy, and 7-methyl derivatives, α-(*p*-chlorophenyl)-2-nitroacetanilide, and 2-nitro-α-(*p*-nitrophenyl)acetanilide were prepared by a modification (described below under the preparation of XII) of the earlier methods.[7,15,16] All these anilides were cyclized to their corresponding 2-substituted 3-hydroxyquinoxaline 1-oxides, as described in part IV[7] of this series.

***p*-Chlorophenylacetic Acid.**[17a]—*p*-Chlorobenzyl chloride (50 g), alcohol (150 ml), and potassium cyanide (30 g) dissolved in 90 ml of water were heated under reflux for 8 hr. After removal of excess of alcohol, 20% aqueous sodium hydroxide (100 ml) was added and heating continued for another 8 hr. The solution was cooled and extracted with ether. The ether-free aqueous layer on acidification gave a precipitate (50 g), which on crystallization from hot water gave colorless needles of *p*-chlorophenylacetic acid, mp 103–104° (lit.[17b] mp 103.5–104°).

5-Methoxy-2-nitro-α-phenylacetanilide (XII).—5-Methoxy-2-nitroaniline[18] (5.6 g) and phenylacetic acid (5.1 g) were dissolved in dry benzene (90 ml). Thionyl chloride (7 ml) was added slowly and a yellow precipitate which separated out dissolved when the mixture was heated under reflux. Heating was continued until no more gases were evolved (4 hr). Removal of excess benzene gave a solid, which on crystallization from benzene and petroleum ether (bp 60–80°) gave yellow needles of XII (63% yield), mp 119–121°.

Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.9; H, 4.9; N, 9.8. Found: C, 62.95; H, 4.9; N, 9.5.

3-Hydroxy-6-methoxy-2-phenylquinoxaline 1-Oxide (XIII).[7,15,16]—A mixture of XII (5 g), pyridine (25 ml), and 20% aqueous potassium hydroxide (25 ml) was vigorously stirred and heated

(8) M. Ishikawa, S. Yamada, and C. Kaneko, *Chem. Pharm. Bull.* (Tokyo), **13**, 747 (1965); C. Kaneko and S. Yamada, *ibid.*, **14**, 555 (1966); M. Ishikawa, S. Yamada, H. Hotta, and C. Kaneko, *ibid.*, **14**, 1102 (1966); C. Kaneko and S. Yamada, *Shikya Zairyo Kenkyusho Hokoku*, **2**, 804 (1966).

(9) C. Kaneko, I. Yokoe, S. Yamada, and M. Ishikawa, *Chem. Pharm. Bull.* (Tokyo), **14**, 1316 (1966).

(10) C. Kaneko, I. Yokoe, S. Yamada, and M. Ishikawa, *Tetrahedron Letters*, 1873 (1967).

(11) M. J. Haddadin and C. H. Issidorides, *ibid.*, 753 (1967).

(12) All melting points are uncorrected and were determined on Gallenkamp MF 370 melting points apparatus. Infrared spectra were measured in Nujol mull using a Perkin-Elmer Model 137 B. Unless otherwise specified the solvent used for the final crystallization of the compounds was ethanol.

(13) E. Hayashi, C. Iijima, and Y. Nagasawa, *Yakugaku Zasshi*, **84**, 163 (1964).

(14) J. K. Landquist and G. J. Stacey, *J. Chem. Soc.*, 2822 (1953).

(15) Y. Ahmad, M. S. Habib, and Ziauddin, *Tetrahedron*, **20**, 1107 (1964).

(16) R. Fusco and S. Rossi, *Gazz. Chim. Ital.*, **94**, 1 (1964).

(17) (a) M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 1512 (1929); (b) R. v. Walther and A. Wetzlich, *J. Prakt. Chem.*, **61**, 169 (1900).

(18) F. Reverdin and K. Widmer, *Ber.*, **46**, 4066 (1913).

on a water bath for 1 hr. The red solution was diluted with water, cooled, and acidified with hydrochloric acid. The solid (4 g) which separated was filtered and washed with water. Crystallization from dilute ethanol gave pale yellow needles of XIII, mp 275–277°.

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.2; H, 4.5; N, 10.5. Found: C, 66.8; H, 4.4; N, 10.5.

With weaker alkali the anilide (XII) remained unchanged even on prolonged heating. With much stronger alkali instead of undergoing cyclization it underwent hydrolysis and yielded 5-methoxy-2-nitroaniline.

3,4-Dihydro-6-methoxy-4-methyl-3-oxo-2-phenylquinoxaline 1-Oxide (XIV).—The N-oxide (XIII) (2 g) was dissolved in 2 *N* aqueous sodium hydroxide (20 ml). Dimethyl sulfate (5 ml) was added dropwise with vigorous shaking, always keeping the solution alkaline. The mixture was heated on a water bath for 15 min. The solid (1 g) which separated out on cooling was filtered; crystallization from ethanol gave yellow needles of XIV, mp 147–148°, in almost quantitative yield.

Anal. Calcd for $C_{16}H_{14}N_2O_3$: C, 68.1; H, 5.0; N, 9.9. Found: C, 67.8; H, 5.25; N, 9.8.

3,4-Dihyro-6-methoxy-4-methyl-3-oxo-2-phenylquinoxaline (XI).—Compound XIV (1 g), 50% aqueous ethanol (150 ml), and sodium dithionite (4 g) were heated together under reflux on a water bath for 2 hr. The volume of the solution was reduced to 50 ml by distillation under vacuum. The solid which separated on cooling was filtered and on crystallization from ethanol gave yellow needles (0.5 g) of XI, mp 94–96°.

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.2; H, 5.3; N, 10.5. Found: C, 72.4; H, 5.3; N, 10.7.

Reactions with Acetic Anhydride. Reaction with 3-Hydroxy-2-phenylquinoxaline 1-Oxide[7] (Ia). General Procedure A.—Compound Ia (2.0 g) and acetic anhydride (40 ml) were heated under reflux for 4 hr. Acetic anhydride was removed under vacuum in a rotary film evaporator. The residue was triturated with cold dilute aqueous sodium bicarbonate, filtered, and washed with ice-cold water. Crystallization of the solid (1.8 g) from ethanol gave pale yellow needles of a compound the constitution of which was proved (see below) to be **1-acetyl-3-benzoyl-2-benzimidazolinone** (IIIa), mp 164–165°.

Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.6; H, 4.3; N, 10.0. Found: C, 69.5; H, 4.7; N, 10.1.

When the time of heating in the above procedure was increased from 4 to 10 hr or the product IIIa was heated with an excess of acetic anhydride for 10 hr, in each case the product isolated was 1,3-diacetyl-2-benzimidazolinone (IVa, *i.e.*, the acyl part in IIIa had further been displaced by another acetyl group), mp 153–154° (lit.[19] mp 153–154°), identical[20] with an authentic sample obtained by heating (the appropriate) 2-benzimidazolinone with an excess of acetic anhydride.

General Procedure B (Hydrolysis).—The solid obtained above (0.5 g) was hydrolyzed by heating it with 10% aqueous sodium hydroxide (20 ml) on a water bath for 2 hr. The solution so obtained was cooled and acidified with 25% HCl. The precipitate was triturated with cold dilute aqueous sodium bicarbonate, filtered, and washed with cold water. The solid (0.23 g) on crystallization from ethanol afforded white shining plates of 2-benzimidazolinone (VIa), mp 306–308°, identical[20] with an authentic sample.

The aqueous sodium bicarbonate filtrates from A and B were combined, evaporated to a small bulk, cooled, and acidified with HCl. The precipitate was taken up in ether. The ether layer was dried (Na_2SO_4) and on evaporation yielded an aromatic acid identical[20] with a pure sample of benzoic acid, mp 121°, in the present case.

General Procedure C. Preparation of Authentic 2-Benzimidazolinones.—Appropriate *o*-phenylenediamine VII (in the above case VIIa) and urea (each 0.05 mole) were heated together at 150° until the melt resolidified. The residue was extracted with warm dilute sodium hydroxide. Clear alkaline extract on acidification precipitated the corresponding 2-benzimidazolinone in 80–90% yield. On crystallization from ethanol white shining needles of 2-benzimidazolinone (VIa, in the above case), mp 306–308°, were obtained (lit.[21] mp 308°).

Unless otherwise stated, the same quantities of the reactants and the general procedures A, B, and C as exemplified above were used for the reactions of the quinoxaline N-oxides reported below.

Reaction with 7-Ethoxy-3-hydroxy-2-phenylquinoxaline 1-Oxide (Ib).—Compound Ib yielded[22] **1-acetyl-3-benzoyl-5-ethoxy-2-benzimidazolinone** (IIIb, 1.8 g) as pale yellow silky needles, mp 135–136°.

Anal. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.7; H, 4.9; N, 8.6. Found: C, 66.4; H, 5.0; N, 8.6.

When the time of heating was increased to 10 hr, instead of IIIb, **1,3-diacetyl-5-ethoxy-2-benzimidazolinone** (IVb, 1.2 g) was obtained as white needles, mp 162° (lit.[23] mp 163°), which was identical[20] with the product obtained by acetylation of an authentic sample[24] of VIb.

Hydrolysis[25] of IIIb or IVb with aqueous alkali yielded 5-ethoxy-2-benzimidazolinone (VIb), mp 260–262° (lit.[26] mp 262–264°), identical[20] with an authentic sample.[24] Benzoic acid was obtained as the other product of hydrolysis in case of IIIb.

Reaction with 3-Hydroxy-7-methyl-2-phenylquinoxaline 1-Oxide (Id).—Compound Id gave[22] **1-acetyl-3-benzoyl-5-methyl-2-benzimidazolinone** (IIId, 1.85 g) as colorless needles, mp 190–191°.

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.4; H, 4.8; N, 9.5. Found: C, 69.6; H, 4.9; N, 9.7.

When the time of heating was increased to 10 hr, instead of IIId, **1,3-diacetyl-5-methyl-2-benzimidazolinone** (IVd, 1.4 g) was obtained as white needles, mp 174–175° (lit.[27] mp 174–175°), which was identical[20] with the product obtained by acetylation of an authentic sample[24] of VId.

Hydrolysis[25] of IIId or IVd with aqueous alkali gave **5-methyl-2-benzimidazolinone** (VId), mp 288–290° (lit.[21] mp 292°), which was identical[20] with an authentic sample.[24] Benzoic acid was obtained as the other product of hydrolysis in the case of IIId.

Reaction with 3-Hydroxy-7-methoxy-2-phenylquinoxaline 1-Oxide (Ic).—Compound Ic when heated with acetic anhydride for 4 hr yielded[22] 1,3-diacetyl-5-methoxy-2-benzimidazolinone (IVc, 1.2 g) as colorless needles, mp 169–170°.

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.1; H, 4.8; N, 11.3. Found: C, 58.4; H, 4.9; N, 11.3.

Benzoic acid was obtained as the other product from aqueous $NaHCO_3$ washings.

When the time of heating was reduced, a mixture of the starting material and IVc was obtained. The expected intermediate IIIc could not be isolated.

Hydrolysis[25] of IVc afforded **5-methoxy-2-benzimidazolinone** (VIc), mp 256–257° (lit.[28] mp 256–257°), identical[20] with an authentic sample.[24]

3-Hydroxy-6-methoxy-2-phenylquinoxaline 1-oxide (XIII) with acetic anhydride behaved similarly as Ic and gave the same products IVc and benzoic acid. Here again when the time of heating was reduced, a mixture of the starting material XIII and IVc was obtained and again the expected intermediate, 1-acetyl-3-benzoyl-6-methoxybenzimidazolinone, could not be isolated.

Reaction with 7-Chloro-3-hydroxy-2-phenylquinoxaline 1-Oxide (Ie).—Compound Ie gave[22] 1,3-diacetyl-5-chloro-2-benzimidazolinone (IVe, 1.1 g), mp 175–176° (lit.[28] mp 172–173°).

Anal. Calcd for $C_{11}H_9ClN_2O_3$: C, 52.3; H, 3.6; N, 11.1. Found: C, 52.8; H, 3.5; N, 11.0.

However, 10-hr heating was necessary for completion of the reaction and as usual benzoic acid was obtained as the other product. When the time of heating was reduced a mixture of the starting material and the diacetyl IVe was obtained.

Compound IVe on hydrolysis[25] yielded 5-chloro-2-benzimidazolinone (VIe), mp 306–307° (lit.[29] mp >270°), which was identical[20] with the authentic sample.[24]

Reaction with 6,7-Dichloro-3-hydroxy-2-phenylquinoxaline 1-Oxide (If).—Compound If after 10 hr of heating afforded[22]

(19) S. Takahashi and H. Kano, *Chem. Pharm. Bull.* (Tokyo), **12**, 282 (1964).

(20) Same infrared spectra and undepressed mixture melting point.

(21) L. S. Efros, B. A. Porai-Koshits, and S. G. Farbenshtein, *Zh. Obshch. Khim.*, **23**, 1691 (1953); *Chem. Abstr.*, **48**, 13886*f* (1954).

(22) See general procedure A under the reaction of Ia with Ac_2O.

(23) K. Elbs, *J. Prakt. Chem.*, **83**, 1 (1911).

(24) See general procedure C under the reaction of Ia with Ac_2O.

(25) See general procedure B under the reaction of Ia with Ac_2O.

(26) L. Spirer, *Roczniki Chem.*, **28**, 455 (1954).

(27) D. Harrison, J. T. Ralph, and A. C. B. Smith, *J. Chem. Soc.*, 2930 (1963).

(28) R. L. Clark and A. A. Pessolano, *J. Am. Chem. Soc.*, **80**, 1657 (1958).

(29) O. Fischer and F. Limmer, *J. Prakt. Chem.*, **74**, 57 (1906).

1,3-diacetyl-5,6-dichloro-2-benzimidazolinone (IVf, 1.1 g) as colorless needles, mp 218–219° (lit.[28] mp 218–219°).

Anal. Calcd for $C_{11}H_8Cl_2N_2O_3$: C, 46.0; H, 2.8; N, 9.7. Found: C, 46.0; H, 2.8; N, 8.9.

Benzoic acid was the other product of reaction.

Compound IVf on hydrolysis with aqueous alkali gave 5,6-dichloro-2-benzimidazolinone (VIf), mp 343–345° (lit.[28] mp 345°), which was identical[20] with the authentic sample.[24]

Reaction with 2-(*p*-Chlorophenyl)-3-hydroxyquinoxaline 1-Oxide (Ih).—In this case also a 10-hr heating was necessary for completion of the reaction. Compound Ih yielded[22] 1,3-diacetyl-2-benzimidazolinone (IVa, 1.3 g) as white needles, mp 151–152° (lit.[19] mp 153–154°).

Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.5; H, 4.6; N, 12.8. Found: C, 60.9; H, 4.7; N, 12.7.

p-Chlorobenzoic acid (mp 238–240°) was recovered as the other product from the aqueous $NaHCO_3$ extract.

Reaction with 3-Hydroxy-2-(*p*-nitrophenyl)quinoxaline 1-Oxide (Ig).—Compound Ig remained unchanged even on prolonged heating with acetic anhydride. However, when Ig (1.0 g) was heated with acetic anhydride (25 ml) in a sealed tube at 180° for 12 hr, it gave a mixture of compounds, which could be separated with the help of petroleum ether in which **1,3-diacetyl-2-benzimidazolinone** (IVa, 0.6 g), mp 153–154°, was soluble and **1-acetyl-2(3H)-benzimidazolinone** (Va, 0.18 g), mp 213–214° (lit.[19] mp 212–214°), remained insoluble. *p*-Nitrobenzoic acid was recovered from the aqueous $NaHCO_3$ extract. Compounds IVa and Va both on hydrolysis with aqueous alkali gave 2-benzimidazolinone (VIa).

Reaction with 2-Cyano-3-hydroxyquinoxaline 1-Oxide[15] (Ii).—Here again it was necessary to heat the reactants in a sealed tube at 180°. Even after 8 hr of heating under such drastic conditions it afforded a mixture of Ii (1.3 g) and 1,3-diacetyl-2-benzimidazolinone (IVa, 0.3 g). Compound IVa, mp 153–154°, was extracted with petroleum ether leaving behind the unreacted Ii.

Reaction with 3-Phenylquinoxaline 1-oxide[14] (XV) gave[22] 3-hydroxy-2-phenylquinoxaline (1.8 g) as pale yellow microneedles, mp 258–260 (lit.[7] mp 258–260°), which was identical[20] with the authentic sample.[7]

Reaction with 2-Phenylquinoxaline 1,4-Dioxide[14] (XIX).—Compound XIX afforded[22] **1-acetyl-3-benzoyl-2-benzimidazolinone** (IIIa, 1.8 g) as pale yellow needles, mp 164–165°.

Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.6; H, 4.3; N, 10.0. Found: C, 68.5; H, 4.7; N, 10.1.

It was identical[20] with the product obtained by the reaction of Ia with acetic anhydride (see above) and similarly on hydrolysis[25] gave 2-benzimidazolinone (VIa), mp 308°, and benzoic acid.

Reaction with 3,4-Dihydro-4-methyl-3-oxo-2-phenylquinoxaline 1-Oxide[7] (VIII).—Compound VIII (1 g) when heated under reflux with acetic anhydride (25 ml) for 4 hr gave[22] **6-acetoxy-3,4-dihydro-4-methyl-3-oxo-2-phenylquinoxaline** (IX, 0.8 g) as yellow plates, mp 132–134°.

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.4; H, 4.8; N, 9.5. Found: C, 69.3; H, 4.8; N, 9.5.

Hydrolysis[25] of IX (0.5 g) with aqueous alkali yielded **3,4-dihydro-6-hydroxy-4-methyl-3-oxo-2-phenylquinoxaline** (X, 0.3 g) as light yellow needles, mp 298–300°.

Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.4; H, 4.8; N, 11.1. Found: C, 71.5; H, 4.8; N, 11.3.

Methylation of X gave 3,4-dihydro-6-methoxy-4-methyl-3-oxo-2-phenylquinoxaline (XI), identical[20] with an authentic sample obtained through an unambiguous route (see XII → XIII → XIV → XI).

To a mixture of X (0.5 g), dry acetone (50 ml), and anhydrous sodium carbonate (2 g) being heated under reflux, dimethyl sulfate (1 ml) was added slowly dropwise. After 4 hr of heating acetone was removed and cold water added. The solid so obtained was filtered and crystallized from dilute ethanol to give XI (0.4 g).

2,3-Diphenylquinoxaline 1-oxide (XVIII), 1,4-dioxide (XX), 2-phenylquinoxaline 1-oxide (XVI), and 3-chloro-2-phenylquinoxaline 1-oxide (XVII) remained unchanged even on prolonged heating with acetic anhydride. Compounds XVI and XVII were recovered unchanged even when heated with acetic anhydride in a sealed tube at 180° for 12 hr. However XVIII and XX under these conditions were deoxygenated and both gave the same product, 2,3-diphenylquinoxaline.

Registry No.—IIIa, 14596-42-0; IIIb, 14661-49-5; IIId, 14661-50-8; IVa, 2735-73-1; IVc, 14661-52-0; IX, 14661-53-1; X, 14661-54-2; XI, 14661-55-3; XII, 14661-56-4; XIII, 14661-57-5; XIV, 14661-58-6.

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