The Synthesis of Some Quinoxaline Ring Systems

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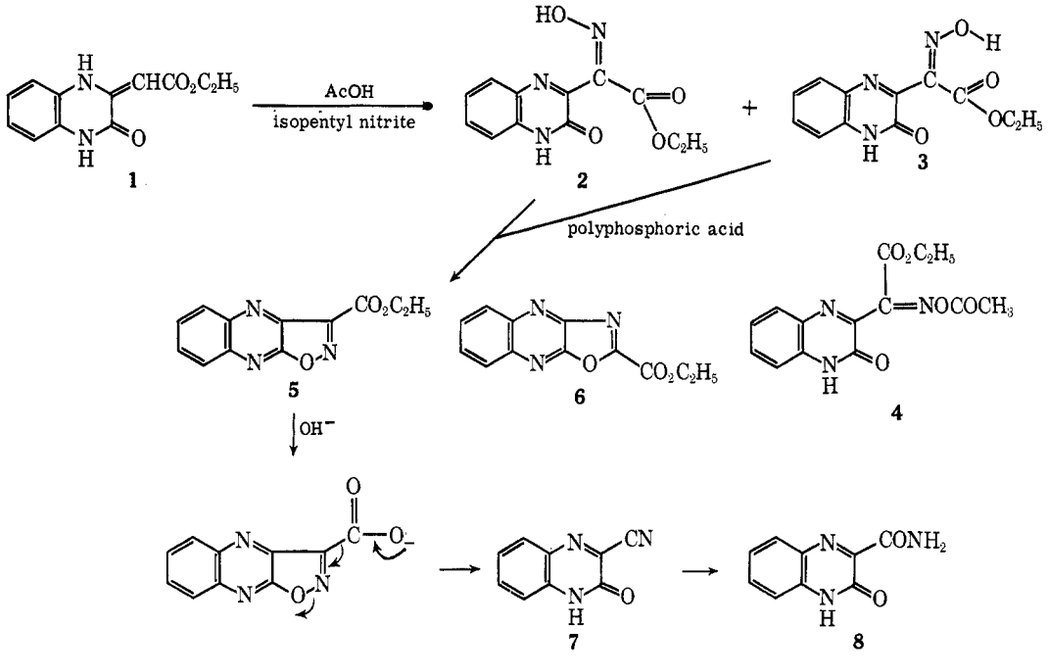
2-Ethoxycarbonylmethylene-1,2,3,4-tetrahydroquinoxalin-3-one was used as an intermediate to prepare both the isoxazolo[4,5-*b*]- and *v*-triazolo[1,5-*a*]quinoxaline ring systems. Some furo[2,3-*b*]- and pyrrolo[2,3-*b*]quinoxalin-2-one derivatives were synthesized and their behavior on alkylation is described. The tautomerism of some quinoxaline acetic acid derivatives is discussed.

We have reported previously on the tautomerism of product **1** obtained by the interaction of ethyl ethoxalylacetate with *o*-phenylenediamine[1] and now describe the use of this readily available starting material to prepare some fused quinoxaline ring systems.

The nitrosation of **1** by isopentyl nitrite according to the procedure described by Biekert and Kössel[2] yielded a mixture of isomeric products. One (A) precipitated from the reaction mixture and the other (B) was isolated by concentration of the mother liquor. These isomers are thought to be the two hydroxyimino derivatives, one in which the hydroxyl group is syn to the quinoxaline ring **2** and the other in which it is anti



1 **2** **3** **4** **5** **6** **7** **8**

(**3**). It was not possible to study these isomers rigorously by spectroscopic means owing to their lack of solubility in suitable solvents; however, a tentative assignment of structure can be made. Isomer A can be converted into isomer B by prolonged boiling in ethanol or by treatment with methanolic HCl. Isomer B appears to have a more strongly hydrogen bonded structure than A, as evidenced by the appearance of a peak at δ 14 in its nmr spectrum (DMSO) which is absent from that of A.

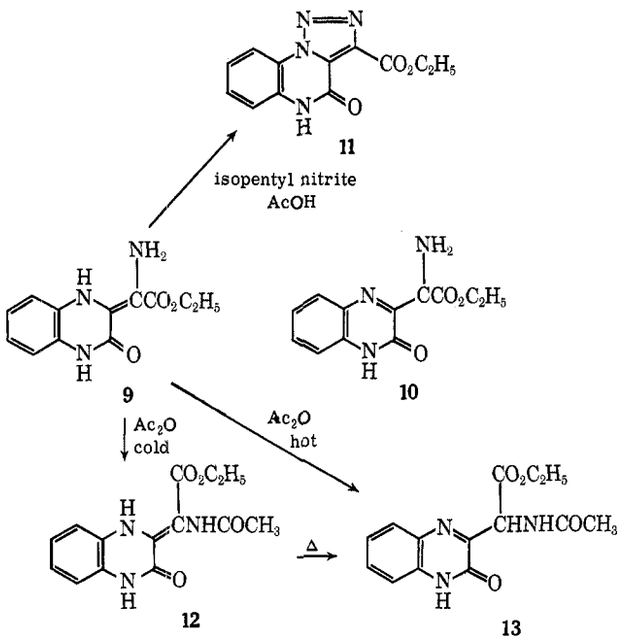
The ester carbonyl frequency in B is lower than that in A, 1730 *vs.* 1740 cm^{-1}, suggesting hydrogen bonding to the carbonyl. Assuming the correctness of this suggestion, isomer A would have structure **2** and isomer B would have structure **3**.

Both A and B on acetylation with acetic anhydride and pyridine gave the same acetoxyimino compound **4**. The stereochemistry of this acetate could not be established.

Ring closure between the hydroxyimino and quinoxalone functions to form an isoxazole ring could be accomplished for both isomers by heating with polyphosphoric acid. The new isoxazolo[4,5-*b*]quinoxaline ring system was thereby formed in good yield. In view of the acidic conditions used for this cyclization, the possibility of a Beckmann rearrangement prior to ring closure could not be overlooked. This would lead to the isomeric oxazoloquinoxaline **6**. However, treatment of the product with cold 5% sodium hydroxide solution showed that structure **5** was correct. After hydrolysis of the ester, decarboxylation with ring opening occurred, forming the nitrile **7**. Prolonged base treatment gave the amide **8**, whereas, if the oxazoloquinoxaline structure had been correct, 2-amino-3,4-dihydroquinoxalin-3-one would have been produced. A small amount of the amide **8** was also found as a by-product in large-scale cyclizations of **2** and **3**. This series of reactions provides convenient syntheses for both the nitrile **7** and the amide **8**.

The hydroxyimino compounds could also be used as a means to enter the *v*-triazolo[1,5-*a*]quinoxaline series. This was accomplished by catalytic reduction to the amino compound **9**, which was cyclized with isopentyl nitrite in acetic acid solution to give ethyl 4,5-dihydro-4-oxo-*v*-triazolo[1,5-*a*]quinoxaline-3-carboxylate (**11**) in

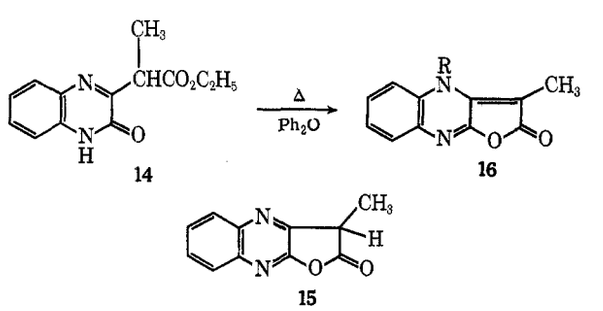
(1) D. D. Chapman, *J. Chem. Soc.*, 806 (1966).
(2) E. Biekert and H. Kössel, *Justus Liebigs Ann. Chem.*, **662**, 83 (1963).



reasonable yield. In an earlier synthesis of this ring system, the quinoxaline ring is closed as the final step.[3]

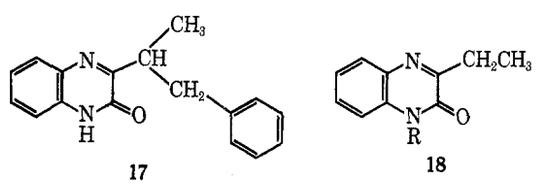
Although **9** could not be purified by recrystallization owing to decomposition, its structure was apparent from its spectral properties and an examination of its acetylation products. Its molecular weight was established as 247 from its mass spectrum; and, as its ir spectrum did not show a peak above 1700 cm^{-1}, this ruled out an alternative structure **10** which would be expected to have a carbonyl absorption in the 1730–1750-cm^{-1} range. With acetic anhydride in the cold a yellow monoacetate was formed, whereas in the hot a colorless isomeric product was isolated. The yellow product was formulated as **12** because again the ir spectrum lacked a peak in the saturated ester range. The colorless product had ir and nmr spectra which were consistent with structure **13**. In particular, the ester carbonyl appeared at 1755 cm^{-1} and the methine proton was a doublet at δ 5.98 owing to coupling with the adjacent NH. This doublet collapsed to a singlet on addition of D_2O to the solution. Attempts to run the nmr spectrum of **12** in DMSO solution were unsuccessful, as rapid rearrangement to the more stable form **13** took place.

In connection with the problems of tautomerism in quinoxaline acetic acid derivatives, it is of interest to recall that a methyl group may have a large effect. Whereas compound **1** exists in the solid as the exocyclic tautomer and in solution as a mixture of the exo- and endocyclic tautomers, **14** is completely in the endocyclic form both in the solid phase and in solution.[1] However, as will become apparent shortly, if the ester function is part of a ring, the equilibrium shifts toward the tautomer with the double bond exocyclic to the quinoxaline ring.



L'Italien and Banks[4] first obtained ester **14** from *o*-phenylenediamine and ethyl ethoxalylpropionate; they also reported that heating **14** in diphenyl ether caused it to cyclize to the furoquinoxalone **15**. However, repetition of this latter reaction and spectral examination of the product showed that structure **15** was incorrect. The ir spectrum in KBr showed bands at 3200 cm^{-1} attributable to an NH stretch and at 1745 cm^{-1} for the carbonyl group. The nmr spectrum had a three-proton peak at δ 1.75 assigned to a methyl group. This latter piece of evidence is sufficient to rule out the presence of structure **15** in solution, and with the ir evidence indicates that structure **16**, R = H, is correct. Methylation with methyl iodide and potassium carbonate gave the *N*-methyl compound **16**, R = CH_3. The nmr spectrum of this latter compound showed two peaks of equal intensity at δ 2.12 and 3.84 for the two methyl groups. Additional evidence for the assignment of structure **16**, R = H, was obtained by a comparison of its ultraviolet spectrum with that of **16**, R = CH_3. The two spectra were very similar, both in the position of the peaks and in intensity. Thus, a consideration of all the evidence leads to the conclusion that the product arising from the cyclization of **14** has structure **16**, R = H, both in the solid phase and in solution.

The *N*-octyl derivative was prepared similarly by reaction of **16**, R = H, with octyl bromide. However, when benzyl bromide was employed, the reaction took a different course and the major product isolated was **17**, identified by its elemental analysis and nmr spectrum, which showed a methyl doublet at δ 1.34 (J = 5 Hz), a nonequivalent methylene at δ 3.15 split by an adjacent proton, and a methine proton as a complex multiplet centered at δ 4.04. This product must have arisen by C-alkylation at position 3 prior to ring opening and decarboxylation because the reaction of **18**, R = H, under the same conditions gave only the *N*-benzyl derivative **18**, R = CH_2Ph, and no product resulting from C-alkylation.

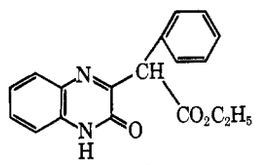


The 3-phenyl analog of **16**, R = H, was prepared in a similar manner. Ethyl phenyloxalacetate was condensed with *o*-phenylenediamine to yield the ester **19**, which was cyclized to a furoquinoxalone whose nmr spectrum in DMSO was in agreement with structure **20**; no peak corresponding to a methine proton was seen. Compound **20** could also be prepared from **21** by reaction with diethyl carbonate in the presence of sodium hydride.

The nature of the substituent on the α carbon of quinoxaline acetic acid derivatives has therefore been shown to have a profound effect on the position of the

(3) J. C. Kaver, U. S. Patent 3,262,943 (1966).

(4) Y. J. L'Italien and C. K. Banks, *J. Amer. Chem. Soc.*, **73**, 3246 (1951).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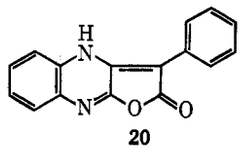
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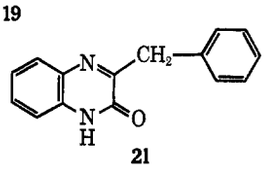
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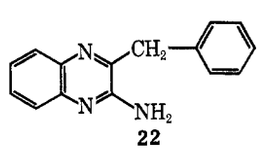
tautomeric equilibrium in these systems. In the case of an acetamido substituent, both tautomers can be isolated, although the exocyclic form is less stable and is readily converted to the endocyclic form. When the substituent is methyl or phenyl, the endocyclic form is the only one observed; and, when there is no substituent, a mixture of the two tautomers is present in solution. Also, if the ester function is part of a ring, the tautomeric stability is reversed in the methyl and phenyl cases as the tautomer with the double bond exocyclic to the quinoxaline ring is the stable one.

It was also of interest to compare the alkylation of the furoquinoxalones with that of the corresponding pyrroloquinoxalones.

A suitable intermediate for the synthesis of the pyrroloquinoxalone **23** appeared to be the amino compound **22**, which should react with diethyl carbonate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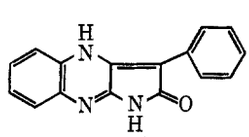
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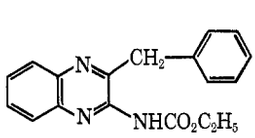
and sodium hydride to give **23**. Accordingly, the benzylquinoxalone **21** was converted to **22** *via* the chloro compound.

Unfortunately, the cyclization of the amino compound **22** with diethyl carbonate gave a mixture of four products. Two of these were identified as the desired compound **23** and the urethane **24**. The third product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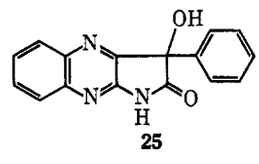
contained one oxygen atom more than **23** and structure **25** is proposed. This is by analogy with the reaction of 3-phenyloxindoles with oxygen in alkaline solution.[5a] The basic hydrolysis of **25** gave 2-amino-3-benzoylquinoxaline, generated by decarboxylation followed by aerial oxidation.

The fourth product, isolated in very low yield, surprisingly contained an ethyl group attached to a tertiary carbon atom, with the methyl appearing at δ 0.88 and the methylene at δ 2.55, and showed an infrared band at 1740 cm^{-1}. When the empirical formula is taken into consideration, the structure most favored is **26**, which could arise from alkylation of **27** by diethyl

(5) (a) P. Aeberli and W. J. Houlihan, *J. Org. Chem.*, **33**, 1640 (1968). (b) D. D. Chapman and J. W. Gates, Jr., U. S. Patent 883,018 (1970); U. S. Defensive Publication T883018.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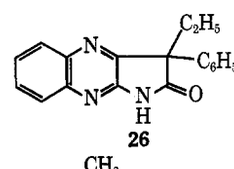
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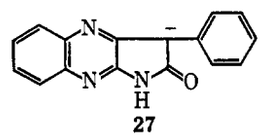
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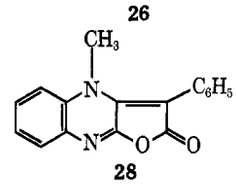
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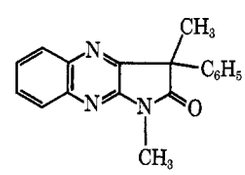
carbonate. Accordingly, **23** was heated with diethyl carbonate and sodium hydride and the alkylated product was obtained in 50% yield.

The pyrroloquinoxalone **23** differs from its oxygen analog **20** in its behavior on alkylation. Compound **23** undergoes methylation at position 3 and at position 1 to give only the C-alkylated product **29**, whereas under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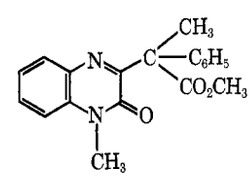
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the same conditions **20** gives mainly the N-4 methylated product **28**. However, the mass spectrum of the crude product from the latter reaction shows a peak that corresponds to a structure such as **30**, which could result from C-3 methylation followed by ring opening and further methylation. In this case the anion derived from **20** is behaving as an ambident nucleophile. Thus, a replacement of an oxygen atom by a nitrogen on going from the furoquinoxalone **20** to the pyrroloquinoxalone **23** is sufficient to change the position of methylation from mainly N- to completely C-methylation.

Many of the quinoxalin-2-one compounds described in this paper are highly fluorescent and have been considered as optical brighteners.[5b] However, the furo[2,3-*b*]quinoxalin-2-one **20** and the corresponding pyrrolo compound **23**, although fluorescent, had their emission at too long a wavelength to be useful for this purpose.

Experimental Section

All melting points are uncorrected. Nmr spectra were recorded in deuteriochloroform solutions except where noted otherwise. Infrared spectra were run as potassium bromide disks.

2-Ethoxycarbonylmethylene-1,2,3,4-tetrahydroquinoxalin-3-one (1) was prepared as described previously.[4]

Reaction of 1 with Isopentyl Nitrite.—The ester (23.2 g) was suspended in glacial acetic acid (500 ml) containing trichloroacetic acid (3 g). After the addition of isopentyl nitrite (15 g), the mixture was stirred and all the solid dissolved. A white solid precipitated and after 1 hr the solution was filtered, yielding 9.5 g of ethyl 2-(3,4-dihydro-3-oxo-2-quinoxalinyl)-2-hydroxyiminoacetate (A), mp 227–229° after recrystallization from ethanol, ir 1740 and 3300 cm^{-1}.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.2; H, 4.2; N, 16.1. Found: C, 55.0; H, 4.5; N, 16.1.

The acetic acid mother liquor was evaporated to dryness at 55° under vacuum and the residue was triturated with ethyl acetate. The isomeric ethyl 2-(3,4-dihydro-3-oxo-2-quinoxalinyl)-2-hydroxyiminoacetate (B, 14 g) was obtained as a powder,

which was recrystallized from ethanol, mp 218–219°, ir 1730 cm^{-1}.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.2; H, 4.2; N, 16.1. Found: C, 55.2; H, 4.3; N, 16.1.

Ethyl 2-(3,4-dihydro-3-oxo-2-quinoxalinyl)-2-acetoxyiminoacetate.—Ethyl 2-(3,4-dihydro-3-oxo-2-quinoxalinyl)-2-hydroxyiminoacetate (A, 1 g) was suspended in acetic anhydride (5 ml) and sufficient pyridine was added to give solution. After 15 min a pale yellow product (0.8 g) precipitated. After recrystallization from ethanol the acetate melted at 161–163°, ir 1790 and 1735 cm^{-1}, mass spectrum *m/e* 303.

Anal. Calcd for $C_{14}H_{13}N_3O_5$: C, 55.4; H, 4.3; N, 13.9. Found: C, 55.5; H, 4.4; N, 14.1.

The same acetate was obtained from the hydroxyimino isomer B in similar yield. On hydrolysis by cold methanolic HCl, isomer B was regenerated.

3-Ethoxycarbonylisoxazolo[4,5-*b*]quinoxaline (5).—A mixture of A and B (10 g) was added to polyphosphoric acid (200 g) and the mixture was heated on the steam bath with intermittent stirring for 4 hr. The solution was cooled and diluted with water, and the product was filtered off. The ester **5** (7 g) melted at 139–140° after recrystallization from ethanol, ir 1730 cm^{-1}.

Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.3; H, 3.7; N, 17.3. Found: C, 59.0; H, 4.0; N, 17.3.

In some larger scale runs, some of the amide **8** was also formed. This was separated by taking advantage of its insolubility in chloroform.

3-Cyano-1,2-dihydroquinoxalin-2-one (7).—The ester **5** (2 g) was added to 5% sodium hydroxide solution with stirring. After 2 hr the solution was filtered and the filtrate was acidified with hydrochloric acid, giving the nitrile **7** (1.3 g), mp 290° after recrystallization from ethanol (lit.[6] mp 288°), mass spectrum *m/e* 171.

Anal. Calcd for $C_9H_5N_3O$: C, 63.2; H, 2.9; N, 24.6. Found: C, 63.5; H, 3.1; N, 24.8.

3-Carbamoyl-1,2-dihydroquinoxalin-2-one (8).—The previous experiment was repeated with the reaction time increased to 24 hr. Acidification gave the amide **8**, mp 307–308°. The infrared spectrum of the product was identical with that of an authentic sample.[7]

Hydrogenation of Ethyl 2-(3,4-Dihydro-3-oxo-2-quinoxalinyl)-2-hydroxyiminoacetate.—The hydroxyiminoacetate (9.7 g) was dissolved in tetrahydrofuran and hydrogenated at atmospheric pressure over platinum until the uptake of hydrogen ceased. The catalyst was removed by filtration and washed with ethanol and the filtrate was evaporated under vacuum at 25°. The orange-yellow product **9** separated when nearly all the solvent had been removed, and was filtered off. Attempts to recrystallize this product were unsuccessful (6.3 g), mp 159–161°, mass spectrum *m/e* 247.

Anal. Calcd for $C_{12}H_{13}N_3O_3$: C, 58.2; H, 5.3; N, 17.0. Found: C, 57.4; H, 5.7; N, 16.8.

Acetylation of the Reduction Product 9. A.—The amine **10** (2.3 g) was dissolved in acetic anhydride (15 ml) and the yellow acetyl derivative **12** was filtered off, yield 2.2 g, mp 227–229°, with change from yellow to colorless at *ca.* 180°. Recrystallization from ethanol did not change the melting point.

Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.1; H, 5.2; N, 14.5. Found: C, 57.9; H, 5.4; N, 14.5.

B.—The amine **10** (1 g) was heated on the steam bath with acetic anhydride (20 ml) for 45 min. After being cooled, the reaction mixture was filtered and the product *N*-acetyl-3,4-dihydro-3-oxo-2-quinoxalinylglycine ethyl ester (**13**, 0.9 g) was recrystallized from ethanol, mp 230–231°.

Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.1; H, 5.2; N, 14.5. Found: C, 57.8; H, 5.2; N, 14.4.

2,4-Dihydro-3-methylfuro[2,3-*b*]quinoxalin-2-one (16, R = H) was prepared as described by L'Italien and Banks:[4] mp 310° (lit. mp 310°); ir 1745 and 3200 cm^{-1}; nmr (DMSO) δ 1.75; uv (ethanol) 268 nm (ϵ 1.69 × 10^4), and 380 (1.71 × 10^4).

2,4-Dihydro-3,4-dimethylfuro[2,3-*b*]quinoxalin-2-one (16, R = CH_3).—The furoquinoxalone **16**, R = H (9 g), was dissolved in dry acetone (250 ml) and refluxed with methyl iodide (20 ml) in the presence of anhydrous potassium carbonate (9 g) for 36 hr. The solution was filtered and the filtrate was evaporated to dryness. Recrystallization from ethanol gave the 4-methyl derivative (7 g): mp 220–222°; ir 1755 cm^{-1}; nmr (DMSO) two peaks of equal intensity at δ 3.84 and 2.12; uv 270 nm (ϵ 1.74 × 10^4), 384 (1.81 × 10^4).

Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.3; H, 4.7; N, 13.1. Found: C, 67.0; H, 5.1; N, 13.2.

The 4-octyl derivative **16**, R = *n*-octyl, was prepared by refluxing **16**, R = H, with a slight excess of *n*-octyl bromide and potassium carbonate in acetone solution: yield 42% after recrystallization from ethanol; mp 125–126°; ir 1750 cm^{-1}.

Anal. Calcd for $C_{19}H_{24}N_2O_2$: C, 73.0; H, 7.7; N, 9.0. Found: C, 72.9; H, 7.7; N, 8.7.

The Alkylation of 16, R = H, with Benzyl Bromide.—The furoquinoxalone **16**, R = H (4.0 g), benzyl bromide (3.4 g), and potassium carbonate (8 g) were refluxed in acetone for 48 hr. The solution was filtered and the filtrate was evaporated to dryness. Trituration of the residue with ethyl acetate gave a trace of a yellow product (50 mg) that was presumably the 4-benzyl derivative. The ethyl acetate filtrate was evaporated to dryness and the residue was recrystallized from aqueous ethanol to give 3,4-dihydro-3-oxo-2-(1-phenyl-2-propyl)quinoxaline (**17**, 5.1 g), mp 174–175°.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.2; H, 6.1; N, 10.6. Found: C, 76.9; H, 6.2; N, 10.6.

1-Benzyl-1,2-dihydro-3-ethylquinoxalin-2-one (18, R = CH_2Ph) was prepared from 1,2-dihydro-2-oxo-3-ethylquinoxaline[4] by alkylation with benzyl bromide under conditions similar to those of the previous reaction. After recrystallization from ethanol it melted at 98–99°, yield 60%.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.2; H, 6.1; N, 10.6. Found: C, 77.2; H, 6.3; N, 10.6.

Ethyl (3,4-Dihydro-3-oxo-2-quinoxalinyl)phenylacetate (19).—The sodium salt of ethylphenyloxalacetate (5.8 g) was dissolved in water and a solution of *o*-phenylenediamine (2 g) in acetic acid (10 ml) was added. After being heated on the steam bath for 1 hr, the reaction mixture was cooled and filtered to give **19** as a colorless solid, mp 190–191°. Recrystallization from ethanol raised the melting point to 191–192°.

Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.1; H, 5.2; N, 9.1. Found: C, 70.1; H, 5.5; N, 9.2.

2,4-Dihydro-3-phenylfuro[2,3-*b*]quinoxalin-2-one (20).—The ester **19** (5 g) was dissolved in refluxing diphenyl ether (100 ml) and, after the ethanol had boiled off, the solution was cooled and diluted with petroleum ether (bp 30–60°). Filtration yielded 2,4-dihydro-3-phenylfuro[2,3-*b*]quinoxalin-2-one as a bright yellow powder (3 g), mp 271–272°, unchanged on recrystallization from ethanol.

Anal. Calcd for $C_{16}H_{10}N_2O_2$: C, 73.3; H, 3.8; N, 10.7. Found: C, 73.0; H, 3.8; N, 11.0.

Methylation as for the 3-methyl analog gave 2,4-dihydro-4-methyl-3-phenylfuro[2,3-*b*]quinoxalin-2-one (**28**) as yellow prisms from ethanol: mp 229–230°; yield 45%; ir 1745 cm^{-1}; nmr δ 3.40.

Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.9; H, 4.4; N, 10.1. Found: C, 73.9; H, 4.4; N, 10.0.

The mass spectrum of the crude product showed peaks at *m/e* 276 and 322.

2-Benzyl-3,4-dihydroquinoxalin-3-one (21).—Crude hydroxyiminophenylpyruvic acid[8] (115 g) was added to a solution of *o*-phenylenediamine (90 g) in water (1:1) and concentrated hydrochloric acid (200 ml). The reaction mixture was stirred and heated on a steam bath for 3 hr. After being cooled, the product (98 g) was filtered off and recrystallized from ethanol, mp 197–198° (lit.[9] mp 197°).

The above product (1.7 g) was heated in toluene with diethyl carbonate (10 ml) and sodium hydride (0.79 g, 53% oil dispersion) for 18 hr. The reaction mixture was evaporated to dryness. The residue was dissolved in water and the solution was acidified with acetic acid. The product (1.3 g) was recrystallized from ethanol and had an infrared spectrum identical with that of **20**.

2-Benzyl-3-chloroquinoxaline.—The quinoxaline **21** (34 g) was added to phosphoryl chloride (200 ml), refluxed for 5 hr, and poured onto ice. The pH was adjusted to 6 (ammonia), the mixture was allowed to stand overnight, and the product was filtered off, yield 31 g, mp 86–87° after recrystallization from ethyl acetate–ligroin (lit.[10] mp 86–87°).

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2-Amino-3-benzylquinoxaline (22).—2-Benzyl-3-chloroquinoxaline (10 g) was added to ethanol (400 ml) that had been saturated with ammonia gas at 0° and the solution was heated at 170° for 8 hr. The reaction mixture was concentrated, filtered to remove ammonium chloride, and evaporated to dryness. Recrystallization from ethanol gave the aminoquinoxaline (4 g), mp 155–157°.

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.1; H, 5.6; N, 17.9. Found: C, 76.1; H, 5.3; N, 17.8.

Interaction of 2-Amino-3-benzylquinoxaline with Diethyl Carbonate.—The amino compound (5 g) was dissolved in toluene (250 ml) containing sodium hydride (2.1 g of 53% mineral oil dispersion). The apparatus was arranged such that any ethanol formed could be removed after condensation. Diethyl carbonate (25 ml) was added dropwise over 30 min to the boiling reaction mixture and refluxing was continued for 4.5 hr. The solution was then evaporated to dryness and acidified with dilute acetic acid. The solid was filtered off, dissolved in chloroform, and extracted with 2 *N* potassium hydroxide. The dried chloroform solution was passed through an alumina column and the major fraction was recrystallized from ethanol to give the urethane **24** (2 g): mp 132°; nmr δ 4.43 ($C_6H_5CH_2$), 4.22 (q), 1.26 (t, C_2H_5O).

Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.3; H, 5.6; N, 13.7. Found: C, 70.2; H, 5.5; N, 13.7.

The alkaline extract was acidified with hydrochloric acid and the yellow solid was filtered off and dried. After three recrystallizations from isopropyl alcohol, the yellow pyrroloquinoxalone **23** (0.6 g), mp 296–300°, was obtained: mass spectrum *m/e* 261; ir 3360, 3200, 1660 cm^{-1}.

Anal. Calcd for $C_{16}H_{11}N_3O$: C, 73.6; H, 4.2; N, 16.1. Found: C, 73.3; H, 4.0; N, 16.0.

The mother liquors were evaporated and the residue was recrystallized successively from acetic acid and isopropyl alcohol (Norit) to give colorless crystals (1.2 g) of **25**: mp 297–298°; ir 3350 and 1745 cm^{-1}; mass spectrum *m/e* 277.

Anal. Calcd for $C_{16}H_{11}N_3O_2$: C, 69.3; H, 4.0; N, 15.2. Found: C, 69.0; H, 4.4; N, 15.1.

The mother liquors were again evaporated and the residue was extracted with chloroform. The extract gave a solid (120 mg) which, when recrystallized from ethanol, yielded 2,3-dihydro-3-ethyl-3-phenyl-1*H*-pyrrolo[2,3-*b*]quinoxalin-2-one (**26**): mp 217–218°; ir 1740 cm^{-1}; mass spectrum *m/e* 289.

Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.7; H, 5.2; N, 14.5. Found: C, 74.4; H, 5.3; N, 14.4.

Reaction of 22 with Diethyl Carbonate and Sodium Hydride.—The pyrroloquinoxalone **22** (320 mg), diethyl carbonate (7 ml), and sodium hydride (0.15 g, 53% oil dispersion) were refluxed in toluene (100 ml) for 36 hr. The solution was evaporated to dryness and acidified with dilute acetic acid. The product was dissolved in chloroform and the solution was extracted with 1 *N* potassium hydroxide. Acidification of the alkaline extract gave **26** (180 mg) having an infrared spectrum identical with that obtained previously.

Hydrolysis of 2,3-Dihydro-3-hydroxy-3-phenyl-1*H*-pyrrolo[2,3-*b*]quinoxalin-2-one.—Compound **25** (0.6 g) was dissolved in 2 *N* potassium hydroxide solution (15 ml) and heated on the steam bath overnight. The precipitated material was collected, dissolved in chloroform, chromatographed on silica gel, and recrystallized from ethanol to give 2-amino-3-benzoylquinoxaline (0.12 g), mp 168–169°, mass spectrum *m/e* 249.

Anal. Calcd for $C_{15}H_{11}N_3O$: C, 72.3; H, 4.5; N, 16.9. Found: C, 71.9; H, 4.2; N, 16.9.

Methylation of 2,4-Dihydro-3-phenyl-1*H*-pyrrolo[2,3-*b*]quinoxalin-2-one (22).—The pyrroloquinoxalone (0.33 g) was dissolved in acetone (75 ml) and, after the addition of methyl iodide (3 ml) and anhydrous potassium carbonate (1.5 g), the mixture was refluxed overnight. The product was worked up in the usual manner and chromatographed on neutral alumina in chloroform. 1,3-Dimethyl-2,3-dihydro-3-phenylpyrrolo[2,3-*b*]quinoxalin-2-one (**29**) (0.25 g) was eluted and recrystallized from aqueous ethanol to give colorless crystals: mp 129–130°; nmr δ 3.47 (NCH_3) and 1.95 (CCH_3); ir 1740 cm^{-1}.

Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.7; H, 5.2; N, 14.5. Found: C, 74.4; H, 5.2; N, 14.8.

Registry No.—**2**, 34731-45-8; **3**, 34712-59-9; **4**, 34712-60-2; **5**, 34731-46-9; **7**, 34731-47-0; **9**, 34731-48-1; **12**, 34731-49-2; **13**, 34712-61-3; **16** (R = CH_3), 34731-50-5; **16** (R = *n*-octyl), 32444-98-7; **17**, 34731-52-7; **18** (R = CH_2Ph), 34731-53-8; **19**, 30747-72-9; **20**, 32444-97-6; **22**, 34731-56-1; **23**, 34731-57-2; **24**, 34712-62-4; **25**, 34731-58-3; **26**, 34731-59-4; **28**, 33904-61-9; **29**, 34731-61-8; 2-amino-3-benzylquinoxaline, 34731-62-9.

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Notes

Reactions of Arylcyclopropanes with *N*-Bromosuccinimide in Hydroxylic Solvents[1]

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Earlier we observed that the reactivity of bromine with arylcyclopropanes in hydrocarbon and halogenated hydrocarbon solvents is very sensitive to light, temperature, and solvent. These reactions resulted in the formation of aryldibromopropanes and products of aromatic ring substitution.[2] It was also of interest to explore the action of electropositive bromine on arylcyclopropanes in more polar, hydroxylic solvents. Therefore phenylcyclopropane (**1a**), *p*-bromophenylcyclopropane (**2a**), and *cis*- (**3a**) and *trans*-1,2-diphenylcyclopropane (**4a**) were treated with *N*-bromosuccinimide (NBS) in methanol solution. In addition, the diphenylcyclopropanes were treated with NBS in 1,2-dimethoxyethane–water. The distributions of product components were determined in most cases by glc analyses and are summarized in Table I. The principal products were isolated and the structures were determined by spectral and elemental analyses

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