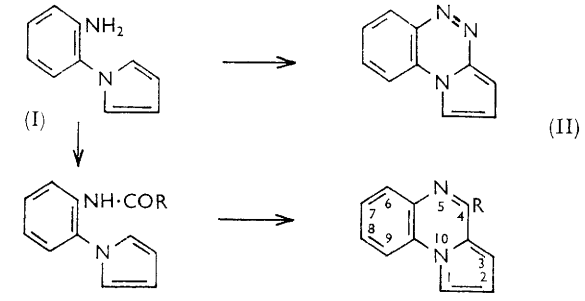
The Synthesis of Pyrrolo[1,2-*a*]quinoxalines from *N*-(2-Acylaminophenyl)-pyrroles *

By G. W. H. Cheeseman and B. Tuck

N-(2-Acylaminophenyl)pyrroles undergo ready cyclisation to pyrrolo[1,2-*a*]quinoxalines. The parent heterocycle is quaternised at the 5-nitrogen with methyl iodide, and on treatment with potassium amide yields 4-amino-pyrrolo[1,2-*a*]quinoxaline.

In a previous Paper [1] we discussed three main methods for the preparation of pyrrolo[1,2-*a*]quinoxalines from quinoxaline intermediates. We now report an alternative and more convenient synthesis of the ring system, which involves the cyclisation of an acyl derivative of *N*-(2-aminophenyl)pyrrole. Gross and his co-workers described the preparation of *N*-(2-aminophenyl)pyrrole (I) from *o*-phenylenediamine and tetrahydro-2,5-dipropoxyfuran,[2] and also the conversion of compound (I) into pyrrolo[2,1-*c*]-[1,2,4]-benzotriazine (II) by treatment with aqueous nitrous acid.[3] This facile intramolecular cyclisation is a reflection of the general ease with which pyrroles undergo electrophilic substitution, and the ready cyclisation of *N*-(2-acylaminophenyl)-pyrroles is a further example of the intramolecular electrophilic substitution of a pyrrole ring.

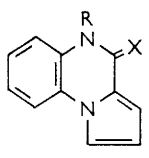


(IIIa : R = H)
(IIIb : R = Me)
(IIIc : R = Ph)
(IIId : R = OEt)

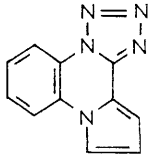
(IVa : R = H)
(IVb : R = Me)
(IVc : R = Ph)

In our work we prepared *N*-(2-aminophenyl)pyrrole from *o*-phenylenediamine and either 2,5-dimethoxy- or 2,5-diethoxy-tetrahydrofuran; the latter compound was available commercially. Pyrrolo[1,2-*a*]quinoxaline (IVa) was prepared in excellent yield by refluxing *N*-(2-aminophenyl)pyrrole with 90% aqueous formic acid. In this case the intermediate, presumably the *N*-formyl derivative (IIIa), cyclised under the conditions of the reaction. Treatment of compound (I) with acetic anhydride, benzoyl chloride, and ethyl chloroformate under standard conditions gave the *N*-acyl derivatives (IIIb), (IIIc), and (IIId), respectively. Compounds (IIIb) and (IIIc) were cyclised to the pyrrolo[1,2-*a*]-quinoxalines (IVb) and (IVc) by treatment with boiling phosphoryl chloride. Compound (IIId) failed to cyclise under these conditions but was converted into the 4-oxo-compound (Va) with zinc chloride in boiling *o*-dichlorobenzene. Analogous ring-closure reactions of 2-acylaminobiphenyls give phenanthridines, but more vigorous conditions are necessary for synthesis of phenanthridines than the corresponding pyrrolo[1,2-*a*]-quinoxalines.[4] This is indicative of the greater difficulty of affecting electrophilic substitution in a benzene compared to a pyrrole ring.

The compound (Va) was readily converted into 4-chloropyrrolo[1,2-*a*]quinoxaline by treatment with phosphoryl chloride. The 4-chlorine had the expected mobility to nucleophilic reagents [5] and reaction with methanolic sodium methoxide and methanolic ammonia furnished 4-methoxy- and 4-amino-pyrrolo[1,2-*a*]-quinoxaline, respectively. Displacement of the 4-chlorine with sodium azide gave the tetrazole compound (VI), and treatment with thiourea gave the 4-thioxo-compound (Vc). Methylation of compound (Vc) gave 4-(methylthio)pyrrolo[1,2-*a*-]quinoxaline, and methylation of (Va) gave the *N*-methyl derivative (Vb). The structure of compound (Vb) was indicated by its closely similar ultraviolet absorption to that of the parent lactam (Va), by its strong carbonyl absorption at 1650 cm.$^{-1}$, and by its p.m.r. spectrum.



(Va : R = H, X = O)
(Vb : R = Me, X = O)
(Vc : R = H, X = S)



(VI)

In an earlier Paper,[1] we presented spectroscopic evidence that the basic centre in pyrrolo[1,2-*a*]quinoxalines is the 5-nitrogen. We now find that the parent heterocycle (IVa) is quaternised readily with methanolic methyl iodide at room temperature. Confirmation that quaternisation had taken place at the 5-nitrogen was obtained by conversion of the methiodide into compound (Vb) on treatment with aqueous sodium carbonate. As expected, the ultraviolet absorption of the methiodide was closely similar to that of the cation of pyrrolo-

* A preliminary account of some of this work appeared in *Chem. and Ind.*, 1965, 1382.

[1] G. W. H. Cheeseman and B. Tuck, *J. Chem. Soc.*, 1965, 3678.

[2] H. Gross, *Chem. Ber.*, 1962, **95**, 2270.

[3] H. Gross and J. Gloede, *Angew. Chem., Internat. Edn.*, 1963, **2**, 262.

[4] N. Campbell, in "Chemistry of Carbon Compounds," ed. E. H. Rodd, Elsevier, Amsterdam, 1957, vol. IVA, p. 691.

[5] R. G. Shepherd and J. L. Fedrick, *Adv. Heterocyclic Chem.*, 1965, **4**, 146.

[1,2-*a*]quinoxaline. The 4-methyl derivative (IVb) formed a quaternary salt with methyl iodide very much more slowly than the parent base. As the respective basic strengths of compounds (IVa) and (IVb) in 50% ethanol are 3·94 and 4·89,[1] the relative rates of quaternisation indicate a considerable degree of steric hindrance in 4-methylpyrrolo[1,2-*a*]quinoxaline.

Analogy with phenanthridine chemistry[6] suggested that pyrrolo[1,2-*a*]quinoxaline (IVa) would react with nucleophilic reagents such as metal amides, and this expectation was realised by the formation of 4-aminopyrrolo[1,2-*a*]quinoxaline on treatment of compound (IVa) with potassium amide. Further reactions of pyrrolo[1,2-*a*]quinoxalines with both nucleophilic and electrophilic reagents are being investigated.

EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer model 137 instrument in Nujol mulls, ultraviolet spectra on a Unicam S.P. 700 recording spectrophotometer, and p.m.r. spectra in carbon tetrachloride on an instrument operating at 60 Mc./sec.; chemical shifts are quoted in p.p.m. relative to tetramethylsilane as an internal standard; assignments are in accord with the integrated intensities of the absorption bands.

N-(2-*Aminophenyl*)*pyrrole* (I).—A mixture of 2,5-dimethoxytetrahydrofuran (26·4 g., 0·2 mole) and *o*-phenylenediamine (43·2 g., 0·4 mole) in acetic acid (25 ml.) was heated under reflux for 15 min., then distilled in steam until about 3½ l. of distillate had been collected (the first 150 ml. were rejected). The distillate was cooled on ice, and the crystalline precipitate of *N*-(2-aminophenyl)pyrrole (12·2 g., 38%) collected, washed with cold water, and dried, m. p. 94—96° (lit.,[2] 97—99°); it was sufficiently pure for use as an intermediate.

Pyrrolo[1,2-a]*quinoxaline* (IVa).—A mixture of *N*-(2-aminophenyl)pyrrole (5·0 g.) and formic acid (90%; 25 ml.) was heated under reflux for 10 min., then cooled on ice. Water and ice were added, followed by a solution of sodium hydroxide (25 g.) in water (100 ml.) so that the temperature did not exceed 60°. The precipitate of the *product* (5·22 g., 98%), m. p. 131—132°, was collected, washed well with water, and dried. Crystallisation from light petroleum (b. p. 80—100°) (20 parts) followed by sublimation in a vacuum gave pale yellow needles, m. p. 133—134° (Found: C, 78·4; H, 4·9; N, 16·6. $C_{11}H_8N_2$ requires C, 78·55; H, 4·8; N, 16·7%), pK_a (in 50% ethanol) 3·94 ± 0·03, $\lambda_{max.}$ (at pH 6·9) 224, 247, and 334 mμ (log ε 4·44, 4·39, and 3·93), $\lambda_{max.}$ (at pH 1·0,) 225, 240, and 352 mμ (log ε 4·52, 4·44, and 4·07).

N-(2-*Acetamidophenyl*)*pyrrole* (IIIb).—A solution of *N*-(2-aminophenyl)pyrrole (4·0 g.) in a mixture of acetic acid (25 ml.) and acetic anhydride (3 ml.) was left at room temperature for 1 hr. Water (100 ml.) was added, and the mixture cooled on ice. The resulting crystalline precipitate of the *product* (3·2 g., 63%), m. p. 72—73°, was washed with water and dried. Crystallisation from light petroleum (b. p. 40—60°) gave colourless needles, m. p. 73·5—74·5° (Found: C, 71·6; H, 6·0; N, 14·4. $C_{12}H_{12}N_2O$ requires C, 72·0; H, 6·05; N, 14·0%). The p.m.r. spectrum showed singlet absorption at 1·98 p.p.m. due to the methyl group. Triplet absorptions centred at 6·37 and 6·77 p.p.m. are assigned to the 3- and 4-, and 2- and 5-protons of the pyrrole ring, respectively. The protons of the benzene ring gave rise to a multiplet in the range 6·9—7·5 p.p.m. and the N–H absorption appeared as a quartet centred at 8·28 p.p.m. (cf. spectrum of pyrrole [7]).

4-*Methylpyrrolo*[1,2-a]*quinoxaline* (IVb).—A mixture of *N*-(2-acetamidophenyl)pyrrole (3·02 g.) and freshly redistilled phosphoryl chloride (25 ml.) was heated under reflux for 15 min., then evaporated in a vacuum. Ice–water was added to the residue, and the crystalline precipitate of 4-methylpyrrolo[1,2-*a*]quinoxaline hydrochloride collected by filtration. The hydrochloride was dissolved in warm water (*ca.* 100 ml.) and solid sodium hydrogen carbonate added in excess. The resulting precipitate of 4-methylpyrrolo[1,2-*a*]quinoxaline (2·44 g., 89%), m. p. 135·5—138°, was washed with water and dried. This material was identical (i.r., u.v., mixed m. p.) with a sample prepared previously.[1] The *methiodide* was prepared similarly to the methiodide of the parent heterocycle, except that the reaction mixture was left for 3 weeks at room temperature. It crystallised from water in yellow needles, m. p. 258—260° (decomp.) (23% yield) (Found: C, 48·5; H, 4·1; N, 8·4. $C_{13}H_{13}IN_2$ requires C, 48·2; H, 4·0; N, 8·6%).

N-(2-*Benzamidophenyl*)*pyrrole* (IIIc).—*N*-(2-Aminophenyl)pyrrole (3·96 g.) was carefully added to an ice cold mixture of benzoyl chloride (2·9 ml.) and pyridine (10 ml.), and the mixture warmed at 60° for 1 hr. The pyridine was evaporated in a vacuum and water and ether added to the residue. The ethereal layer was separated, washed with 2N-hydrochloric acid (3 × 50 ml.), and dried (Na_2SO_4). Evaporation of the ether and crystallisation of the residue from light petroleum (b. p. 40—60°) (20 parts) gave the *product* (4·20 g., 64%), m. p. 72·5—74°. Crystallisation from light petroleum (b. p. 40—60°) gave colourless needles, m. p. 73—74·5° (Found: C, 77·75; H, 5·5; N, 11·2. $C_{17}H_{14}N_2O$ requires C, 77·8; H, 5·4; N, 10·7%). The p.m.r. spectrum showed triplet absorptions centred at 6·44 and 6·83 p.p.m. assigned to the 3- and 4-, and 2- and 5-protons of the pyrrole ring, respectively. The protons attached to the two benzene rings gave rise to a multiplet in the range 6·9—8·0 p.p.m., and the N–H absorption appeared as a quartet centred at 8·64 p.p.m.

4-*Phenylpyrrolo*[1,2-a]*quinoxaline* (IVc).—A mixture of *N*-(2-benzamidophenyl)pyrrole (4·2 g.) and freshly redistilled phosphoryl chloride (25 ml.) was heated under reflux for 20 min., and then evaporated in a vacuum. Chloroform (100 ml.) was added to the residue, followed by ice–water and an excess of saturated sodium hydrogen carbonate solution. The chloroform layer was separated, washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue was extracted with light petroleum (b. p. 60—80°) (200 ml.), treated with charcoal, and filtered. Concentration of the solution to *ca.* 100 ml., removal of some precipitated material by filtration, and cooling on ice gave the *product* (2·26 g., 58%), m. p. 97·5—99°. An analytical sample, m. p. 98—100°, was prepared by sublimation in a vacuum (Found: C, 84·0; H, 4·9; N, 11·4. $C_{17}H_{12}N_2$ requires C, 83·6; H, 4·95; N, 11·4%), $\lambda_{max.}$ (in 96% ethanol) 229, 247, 271, 339, and 351 mμ (log ε 4·37, 4·47, 4·37, 3·87, and 3·87).

N-(2-*Ethoxycarbonylaminophenyl*)*pyrrole* (IIId).—Ethyl chloroformate (6 ml.) was added dropwise during 30 min.

[6] G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 1932, 2225.
[7] Varian N.M.R. Spectra Catalogue, vol. 1, spectrum No. 55.

to a cooled stirred solution of *N*-(2-aminophenyl)pyrrole (5·0 g.) in pyridine (100 ml.). When the addition was complete, the mixture was stirred for 30 min. at 0°, for 1 hr. at room temperature, then for 1 hr. at 45°. The pyridine was evaporated in a vacuum, ether and water were added to the residue, and the aqueous layer was made acid with 2N-hydrochloric acid. The ethereal layer was separated, washed with 2N-hydrochloric acid and water, dried (Na_2SO_4), and evaporated. Low-temperature crystallisation from light petroleum (b. p. 30—40°) (30 ml.) gave the *product* (5·8 g., 80%), m. p. 39—43°. An analytical sample prepared by crystallisation from light petroleum (b. p. 30—40°) (10 parts), followed by distillation on to a cold finger, had m. p. 41—43·5° (Found: C, 67·9; H, 6·25; N, 12·4. $C_{13}H_{14}N_2O_2$ requires C, 67·8; H, 6·1; N, 12·2%). The p.m.r. spectrum showed a triplet centred at 1·23 p.p.m. (J = 14 c./sec.) and a quartet centred at 4·08 p.p.m. (J = 14 c./sec.) due to the ethyl group. Triplets centred at 6·26 and 6·66 p.p.m. are assigned to the 3- and 4-, and 2- and 5-protons of the pyrrole ring, respectively. The protons of the benzene ring gave rise to a multiplet in the range 6·8—7·5 p.p.m., and the N–H group to a quartet centred at 8·21 p.p.m.

4,5-*Dihydro*-4-*oxopyrrolo*[1,2-a]*quinoxaline* (Va).—A mixture of *N*-(2-ethoxycarbonylaminophenyl)pyrrole (14·6 g.), anhydrous zinc chloride (30 g.), and *o*-dichlorobenzene (50 ml.) was heated under reflux for 1 hr., then distilled in steam until the distillate contained no *o*-dichlorobenzene. The mixture was cooled and the suspended solid collected and dried. Sublimation of this solid at 230° in a vacuum gave the *product* (6·6 g., 56%). An analytical sample, prepared as colourless needles by crystallisation from methanol (60 parts), had m. p. 268—269° (decomp.) (Found: C, 71·4; H, 4·2; N, 15·6. $C_{11}H_8N_2O$ requires C, 71·7; H, 4·4; N, 15·6%), $\lambda_{max.}$ (in 96% ethanol) 227, 251, 260, 312, and 325 mμ (log ε 4·45, 4·16, 4·08, 4·07, and 4·00), ν 1660 cm.$^{-1}$ (C=O).

4-*Chloropyrrolo*[1,2-a]*quinoxaline*.—A mixture of 4,5-dihydro-4-oxopyrrolo[1,2-*a*]quinoxaline (0·70 g.) and freshly redistilled phosphoryl chloride (25 ml.) was heated under reflux for 1 hr., then evaporated in a vacuum. The residue was dissolved in chloroform (100 ml.) and ice–water, and an excess of sodium hydrogen carbonate added. The organic layer was separated, washed with sodium hydrogen carbonate solution and water, and dried (Na_2SO_4). Evaporation of the chloroform gave the *product* (0·69 g., 89%), m. p. 168—171°. An analytical sample obtained by crystallisation from light petroleum (b. p. 80—100°) (140 parts), followed by sublimation in a vacuum, had m. p. 171—172° (Found: C, 65·6; H, 3·5; N, 13·5. $C_{11}H_7ClN_2$ requires C, 65·2; H, 3·5; N, 13·8%)

4-*Methoxypyrrolo*[1,2-a]*quinoxaline*.— 4-Chloropyrrolo-[1,2-*a*]quinoxaline (0·32 g.) was dissolved in a methanolic solution of sodium methoxide (from 0·9 g. of sodium and 25 ml. of methanol). The mixture was heated under reflux for 1 hr. and then evaporated in a vacuum. Water (50 ml.) was added to the residue, and the precipitate of the *product* (0·29 g., 93%), m. p. 82—86°, filtered off, washed with water, and dried. Crystallisation from light petroleum (b. p. 40—60°) (30 parts) followed by distillation on to a cold finger gave colourless needles, m. p. 87—89° (Found: C, 72·65; H, 5·2; N, 13·8. $C_{12}H_{10}N_2O$ requires C, 72·7; H, 5·1; N, 14·1%).

4-*Aminopyrrolo*[1,2-a]*quinoxaline*.— (*a*) A mixture of 4-chloropyrrolo[1,2-*a*]quinoxaline (1·0 g.) and methanolic ammonia (prepared by saturating 10 ml. of methanol with ammonia gas at 0°) was heated at 140° for 24 hr. and then cooled. The crystalline precipitate of the *product* (0·75 g., 84%), m. p. 195—196° (decomp.), was filtered off, washed with a little methanol, and dried. Crystallisation from 50% ethanol (60 parts) followed by sublimation in a vacuum gave an analytical sample of m. p. 213—215° (decomp.) (Found: C, 71·8; H, 5·2; N, 23·0. $C_{11}H_9N_3$ requires C, 72·1; H, 4·95; N, 22·9%).

(*b*) A solution of pyrrolo[1,2-*a*]quinoxaline (1·68 g.) in xylene (100 ml.) was added dropwise with stirring to a suspension of potassium amide (prepared from 1·56 g. of potassium and 100 ml. of liquid ammonia). The mixture was warmed gently to evaporate the ammonia, then heated under reflux for 2 hr. After cooling, ammonium chloride (4 g.) was added with vigorous stirring, followed by a little ethanol, and then water (50 ml.). Solvents were evaporated in a vacuum, water (100 ml.) was added to the residue, and the mixture extracted with chloroform (3 × 100 ml.). The combined organic extracts were dried (Na_2SO_4), then evaporated in a vacuum. Crystallisation of the residue from ethanol–water (1 : 2) (100 ml.) gave 4-aminopyrrolo[1,2-*a*]quinoxaline (1·02 g., 56%), m. p. 210—213° (decomp.). Sublimation in a vacuum at 175° gave pale yellow needles (0·93 g.) of unchanged m. p., identical (i.r. and mixed m. p.) with a sample prepared as described above.

The 4-amino-compound was isolated (23%) from an experiment in which potassium amide was allowed to react at room temperature with an ether solution of pyrrolo-[1,2-*a*]quinoxaline for 3½ days. Unreacted starting material was also isolated from this experiment.

Pyrrolo[1,2-a]*tetrazolo*[c]*quinoxaline* (VI).— 2N-Hydrochloric acid (2·5 ml.) was added to a mixture of 4-chloropyrrolo[1,2-*a*]quinoxaline (0·50 g.) and sodium azide (0·65 g.) suspended in 90% aqueous ethanol (40 ml.). The mixture was heated under reflux for 3½ hr. and then cooled. The precipitated fine white needles of the *product* (0·45 g., 87%), m. p. 215—217° (decomp.), were collected, washed with 90% ethanol and water, and dried in a vacuum. An analytical sample of m. p. 217—218° (decomp.) was prepared by crystallisation from 96% ethanol (125 parts) (Found: C, 63·1; H, 3·4; N, 33·75. $C_{11}H_7N_5$ requires C, 63·15; H, 3·4; N, 33·5%). The i.r. spectrum showed no azido bands.

4,5-*Dihydro*-4-*thioxopyrrolo*[1,2-a]*quinoxaline* (Vc).— A mixture of 4-chloropyrrolo[1,2-*a*]quinoxaline (0·50 g.) and thiourea (0·25 g.) in methanol (30 ml.) was heated under reflux for 30 min. during which time pale yellow needles of the *product* were precipitated. The mixture was cooled, and the product (0·34 g., 74%) collected by filtration, washed with methanol (10 ml.), and dried. Crystallisation from 96% ethanol (200 parts) gave pale yellow needles, m. p. *ca.* 265° (decomp.) (Found: C, 65·8; H, 3·9; N, 13·8. $C_{11}H_8N_2S$ requires C, 66·0; H, 4·0; N, 14·0%).

4-*Methylthiopyrrolo*[1,2-a]*quinoxaline*.—4,5-Dihydro-4-thioxopyrrolo[1,2-*a*]quinoxaline (0·34 g.) and methyl iodide (5 ml.) were added to methanolic sodium methoxide (from 0·5 g. of sodium and 50 ml. of methanol), and the mixture left at room temperature for 1 hr., then evaporated in a vacuum. Water (25 ml.) was added to the residue, the mixture extracted with methylene chloride (3 × 15 ml.), and the combined extracts were dried (Na_2SO_4). Evaporation of the methylene chloride, followed by crystallisation of the residue from light petroleum (b. p. 30—40°) (25 ml.),

gave the *product* (0·26 g., 68%). An analytical sample, prepared by distillation on to a cold finger at 95°/0·2 mm., had m. p. 62—64° (Found: C, 66·9; H, 4·6; N, 13·3. $C_{12}H_{10}N_2S$ requires C, 67·3; H, 4·7; N, 13·1%).

Pyrrolo[1,2-a]*quinoxaline Methiodide*.—Methyl iodide (5 ml.) was added to a solution of pyrrolo[1,2-*a*]quinoxaline (1·22 g.) in methanol (5 ml.), and the mixture left at room temperature for 3 days. The precipitated yellow crystals of the *methiodide* (1·83 g., 84%), m. p. 244—245° (decomp.), were washed with a little methanol and dried. Crystallisation from methanol gave an analytical sample of m. p. 245° (decomp.) (Found: C, 44·9; H, 3·8; N, 9·2. $C_{12}H_{11}IN_2$ requires C, 46·5; H, 3·6; N, 9·0%), $\lambda_{max.}$ (in water with compensation for iodide absorption) 227, 244, and 355 mμ (log ε 4·41, 4·32, and 4·02.)

4,5-*Dihydro*-5-*methyl*-4-*oxopyrrolo*[1,2-a]*quinoxaline* (Vb). —(*a*) Freshly distilled dimethyl sulphate (5 ml.) was added dropwise to a solution of 4,5-dihydro-4-oxopyrrolo[1,2-*a*]-quinoxaline (0·55 g.) in methanolic sodium methoxide (from 0·5 g. of sodium and 25 ml. of methanol). The mixture was heated under reflux for 4 hr. and then evaporated in a vacuum. Water was added to the residue, and the mixture extracted with chloroform (75 ml.). The chloroform solution was dried (Na_2SO_4), filtered through an alumina column, and elution continued with chloroform. Evaporation of the first 300 ml. of eluant gave the *product* (0·45 g., 76%), m. p. 120—132°. Crystallisation from cyclohexane (130 parts) gave colourless needles, m. p. 132—134°, identical (i.r., m. p., mixed m. p.) with material obtained from pyrrolo[1,2-*a*]quinoxaline as described below.

(*b*) 2N-Sodium carbonate (25 ml.) was added to a solution of pyrrolo[1,2-*a*]quinoxaline methiodide (0·35 g.) in warm water (50 ml.) at 60°, and the mixture shaken well, left for 5 min., then extracted with chloroform. The combined organic extracts were dried (Na_2SO_4), and then evaporated to give an oil which partially crystallised. Crystallisation from cyclohexane (20 ml.) gave 4,5-dihydro-5-methyl-4-oxopyrrolo[1,2-*a*]quinoxaline (0·07 g., 31%), m. p. 133—134°. Recrystallisation from cyclohexane gave colourless needles, m. p. 134—135° (Found: C, 72·8; H, 4·7; N, 14·2. $C_{12}H_{10}N_2O$ requires C, 72·7; H, 5·1; N, 14·1%) $\lambda_{max.}$ (in 96% EtOH) 228, 260, 314, and 327 mμ (log ε 4·44, 4·11, 4·09, and 3·99), ν 1650 cm.$^{-1}$ (C=O). The p.m.r. spectrum showed singlet absorption at 3·78 p.p.m. due to the methyl group. A quartet centred at 6·89 p.p.m. is assigned to the 2-proton. Protons 1, 3, 7, and 8 give rise to a multiplet in the range 7·4—7·6 p.p.m., and protons 6 and 9 to a multiplet in the range 7·8—8·0 p.p.m.

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