Preparation and Reactions of Pyrrolo[1,2-*a*]quinoxalinesulphonic Acids

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The major product of sulphonation of pyrrolo[1,2-*a*]quinoxaline at 130° is the 2-sulphonic acid. The nitro-group of the 1-nitro-3-sulphonic acid is very readily displaced by a chlorine atom by treatment either with concentrated hydrochloric acid or with lithium chloride in dimethylformamide. The corresponding reactions with hydrobromic acid and lithium bromide are more complex; for example, in hydrobromic acid, a mixture of 2,3-dibromo- and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxalines is formed.

We have reported the very ready sulphonation of pyrrolo[1,2-*a*]quinoxaline, and of its 1-methyl-, 2,4-dimethyl-, and 1-chloro-derivatives.[1] These reactions were carried out with concentrated sulphuric acid at room temperature and in each case 3-sulphonic acids were obtained in excellent yield. We now report that sulphonation of the parent base in concentrated sulphuric acid at 130° gives the isomeric and less soluble 2-sulphonic acid in *ca.* 49% yield. When the 3-sulphonic acid is heated in concentrated sulphuric acid, rearrangement to the 2-acid occurs. These observations parallel the well-known α-sulphonation of naphthalene at moderate temperatures and the rearrangement of the α-sulphonic acid to the thermodynamically more stable β-sulphonic acid, on heating in sulphuric acid to higher temperatures.[2]

Assignment of structure to pyrrolo[1,2-*a*]quinoxaline-2-sulphonic acid is based on elemental analysis and its ready conversion into a 1-chloro-derivative. Like that of the isomeric 1-chloro-3-sulphonic acid, the ^{1}H n.m.r. spectrum of the 1-chloro-2-sulphonic acid shows a characteristic low-field quartet in the region δ 8·5—9·1.

We were also able to sulphonate 3-aminopyrrolo-[1,2-*a*]quinoxaline in the 2-position, but were unable to carry out a similar sulphonation of the 3-nitro-compound.

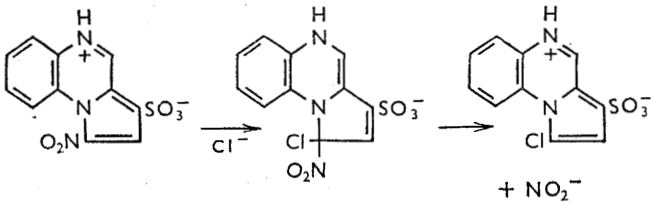
Pyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid was hydrolysed to the parent base when heated under reflux with 50% aqueous sulphuric acid, and in view of the ready availability of the 3-sulphonic acids in this series, we investigated the usefulness of a 3-sulphonic acid substituent as a protective grouping. For example, hydrolysis of the readily available 1-nitro-3-sulphonic acid, appeared to offer a more convenient preparative route to the 1-nitro-compound than direct nitration of the parent base, which yields a mixture of 1- and 3-nitro-compounds containing the lower melting, more soluble 1-nitro-compound only to the extent of about 33%. We were able to hydrolyse the 1-nitro-3-sulphonic acid to 1-nitropyrrolo[1,2-*a*]quinoxaline with 50% aqueous sulphuric acid and also to carry out the corresponding

[1] G. W. H. Cheeseman and B. Tuck, *J. Chem. Soc.* (*C*), 1967, 1164.

[2] L. F. Feiser and M. Feiser, 'Advanced Organic Chemistry,' Reinhold, New York, 1961, p. 884.

hydrolysis of the 1-amino-3-sulphonic acid to the 1-amino-compound. These reactions were, however, carried out on a relatively small scale and we were not able to develop convenient procedures for larger scale preparations.

When 1-nitropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid was boiled with concentrated hydrochloric acid, the sulphonic acid grouping survived but displacement of the nitro-group occurred and 1-chloropyrrolo[1,2-*a*]-quinoxaline-3-sulphonic acid was formed in excellent yield. This appears to be an example of nucleophilic displacement of the nitro-group: an excellent yield of the 1-chloro-3-sulphonic acid could also be obtained by treating the nitrosulphonic acid with lithium chloride in boiling dimethylformamide. In these reactions the nitrosulphonic acid is presumably reacting as the zwitterion and it is significant that the sodium salt of the acid did not react with lithium chloride in dimethylformamide.

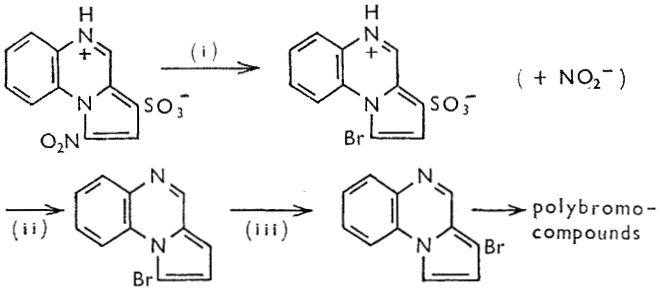


Literature precedents for the replacement of a nitro-group by a chlorine atom include the conversion of the 1-nitronaphthalene-2-diazonium ion into the 1-chloro-naphthalene-2-diazonium ion in hydrochloric acid[3] and the conversion of 4-nitropyridine 1-oxide into 4-chloropyridine 1-oxide with hydrochloric acid,[4] or, more conveniently, acetyl chloride.[5]

1-Nitropyrrolo[1,2-*a*]quinoxaline was slowly converted into the 1-chloro-compound in boiling concentrated hydrochloric acid but no similar displacement could be effected with lithium chloride in boiling dimethylformamide. This observation is analogous to the well established acid catalysis of the nucleophilic displacement reactions of 2- and 4-halogenopyridines and related halogenoheterocycles.[6] In our case, activation of the 1-nitro-group to nucleophilic substitution can be attributed to protonation at N-5.

We also considered the possibility that replacement of a nitro-group by a chlorine atom in hydrochloric acid could occur by initial electrophilic displacement of the nitro-group as NO_2^+, followed by chlorination. This does not appear to be the case because displacement of the nitro-group from the 1-nitro-compound occurs less readily than from the 1-nitro-3-sulphonic acid; the latter compound would be expected to be *less* activated to electrophilic attack. Furthermore, when the 1-nitro-3-sulphonic acid was treated with 50% sulphuric acid no parent base or 3-sulphonic acid was isolated, but, as mentioned before, electrophilic removal of the 3-sulphonic acid group occurred and 1-nitro-pyrrolo[1,2-*a*]quinoxaline was formed.

When 1-nitropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid was treated with boiling concentrated hydrobromic acid, a mixture of 2,3-dibromo- and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxalines was formed. Probable intermediates in this reaction are the 1-bromo-3-sulphonic acid and the 1-bromo-compound. Further bromination is the result of the generation of a brominating species, probably bromine, by the oxidation of hydrobromic acid by the nitrite ion released in the initial nucleophilic displacement.

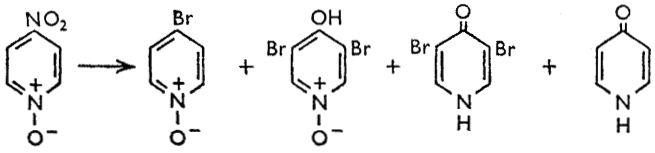


Our postulate of nucleophilic displacement of nitrite ion by bromide ion [stage (i)] is supported by the observation that this displacement can be carried out on the free acid, but not on its sodium salt, by lithium bromide in boiling dimethylformamide; also by the parallel behaviour of the acid with concentrated hydrochloric acid and lithium chloride. Stage (ii) of the illustrated reaction sequence appears reasonable because, in a separate experiment, treatment of pyrrolo-[1,2-*a*]quinoxaline-3-sulphonic acid with concentrated hydrobromic acid gives mainly parent base together with a little (4%) of the 3-bromo-compound. In an experiment to simulate the formation of polybrominated products, we heated an equimolar mixture of 1-bromo-pyrrolo[1,2-*a*]quinoxaline and sodium nitrite in concentrated hydrobromic acid under reflux and obtained the expected mixture of 2,3-dibromo- and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxalines. These products may arise as the result of further bromination of either the 1- or the 3-bromo-compound, because we have shown[7] that the 1-bromo-compound rearranges to the 3-bromo-compound in boiling hydrobromic acid [stage (iii)].

A similar mixture of di- and tri-bromo-compounds was formed when 1-nitropyrrolo[1,2-*a*]quinoxaline was heated under reflux with hydrobromic acid. We again envisage a reaction sequence leading *via* the 1-bromo-compound to polybrominated products. The alternative route involving the parent base as an intermediate and release of the nitro-group as nitronium ion appears less probable. However such a route would lead to the observed products, because reaction of an equimolecular mixture of parent base and potassium nitrate in boiling

[3] N. N. Vorozhtsov, V. V. Kozlov, and I. S. Travkin, *Zhur. obschei Khim.*, 1939, **9**, 522 (*Chem. Abs.*, 1940, **34**, 410).
[4] H. J. den Hertog and W. P. Combé, *Rec. Trav. chim.*, 1951, **70**, 581.
[5] E. Ochiai, *J. Org. Chem.*, 1953, **18**, 534.
[6] C. K. Banks, *J. Amer. Chem. Soc.*, 1944, **66**, 1127.
[7] G. W. H. Cheeseman and P. D. Roy, *J. Chem. Soc.* (*C*), 1968, 2848.

hydrobromic acid gave both 2,3-dibromo- and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxaline. In all experiments in which mixtures of these compounds were produced, prolonged reaction times led to a decreased percentage of tribromo-derivative. This is in accord with our previous observation that bromine can be electrophilically removed from position 1 by strong acids. 1-Nitropyrrolo[1,2-*a*]quinoxaline did not react with lithium bromide in boiling dimethylformamide; this was further demonstration that the nitro-group in the unprotonated molecule was less susceptible to displacement. Our observations find some parallel in the reactions of 4-nitropyridine 1-oxide with hydrobromic acid. When the *N*-oxide is heated with the concentrated aqueous acid, displacement of the nitro-group occurs; products of hydrolysis and bromination are also formed.[8]



Although 1-bromopyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid can be isolated from the reaction of the 1-nitro-3-sulphonic acid with lithium bromide in boiling dimethylformamide, the bromo-acid does not survive long under these conditions and is transformed into the 3-bromo-compound. This probably arises from a similar sequence of reactions to the one already discussed [stages (i)—(iii)]. In independent experiments, it was found that the 1-bromo-compound rearranged to the 3-bromo-compound when treated with lithium bromide in boiling dimethylformamide. Similar treatment of the 1,3-dibromo-compound also gave the 3-bromo-compound, which could not however be obtained by direct nucleophilic displacement of the sulphonic acid group of the 3-sulphonic acid with bromide ion. The removal of bromine from position 1 in the 1-bromo- and 1,3-dibromo-compounds was inhibited by the addition of sodium hydrogen carbonate to the reaction medium of lithium bromide and dimethylformamide. This observation indicates firstly that thermal removal of bromide from position 1 is not occurring under the conditions of our experiments,[9] and secondly that this rearrangement is probably acid-catalysed. The 1-bromo-compound did not rearrange in boiling dimethylformamide alone but only when lithium bromide was present; we suggest that the small amounts of acid present in commercial samples of lithium bromide are sufficient to catalyse the rearrangement.

Reaction of 1-chloropyrrolo[1,2-*a*]quinoxaline with potassium hydroxide in aqueous dimethyl sulphoxide gave pyrrolo[1,2-*a*]quinoxalin-1(5*H*)-one. Identical material was produced from the polyphosphoric acid-promoted cyclisation of β-quinoxalin-2-ylpropionic acid, though in much better yield. This result confirms previous observations regarding the comparatively inert nature of chlorine in position 1.[10]

EXPERIMENTAL

I.r. spectra were measured with a Perkin-Elmer model 237 instrument for Nujol mulls and ^{1}H n.m.r. spectra with a Perkin-Elmer R10 at 60 MHz. The identity of samples was established by comparison of i.r. spectra and where possible by mixed m.p. determination. Microanalyses were performed by Mr. G. Crouch at the Microanalytical Laboratory of the School of Pharmacy, London W.C.1.

High-temperature Sulphonation of Pyrrolo[1,2-a]*quinoxaline.*—The parent base (2·00 g.) was added slowly to conc. sulphuric acid (20 ml.) preheated to *ca.* 130°, and the resulting solution was kept at this temperature for 2 hr. The mixture was then cooled and poured into ice–water, and the precipitate was filtered off. A solution of the product in hot dilute sodium hydroxide solution was acidified with an excess of 2N-sulphuric acid to give pale yellow crystals of *pyrrolo*[1,2-a]-*quinoxaline-2-sulphonic acid* (1·44 g., 49%), m.p. >360°. The analytical specimen was further purified *via* its sodium salt, and dried at 110°/0·4 mm. for 5 hr. (Found: C, 53·2; H, 3·3; N, 11·4. $C_{11}H_8N_2O_3S$ requires C, 53·2; H, 3·3; N, 11·3%).

Rearrangement of Pyrrolo[1,2-a]*quinoxaline-3-sulphonic Acid.*—A solution of the 3-sulphonic acid monohydrate (2·0 g.) in conc. sulphuric acid (20 ml.) was heated at 160° for 2 hr. The cooled solution was poured into ice–water and the precipitate was filtered off then redissolved in hot dilute sodium hydroxide solution. Acidification with an excess of 2N-sulphuric acid gave pyrrolo[1,2-*a*]quinoxaline-2-sulphonic acid (0·82 g., 44%), readily distinguishable from the isomeric 3-acid by its higher mobility on t.l.c. (silica gel; elution with 2N-sulphuric acid).

3-*Aminopyrrolo*[1,2-a]*quinoxaline-2-sulphonic Acid.*—The high-temperature sulphonation of the 3-amino-compound was carried out in a similar manner to that of the parent base and gave 3-*aminopyrrolo*[1,2-a]*quinoxaline-2-sulphonic acid monohydrate* (35%), purified *via* its sodium salt and dried *in vacuo* at room temperature. It decomposed when heated above 350° (Found: C, 46·8; H, 3·8; N, 14·6. $C_{11}H_9N_3O_3S,H_2O$ requires C, 47·0; H, 3·9; N, 14·9%). Unchanged starting material (20%) was recovered from the diluted reaction mixture by neutralisation with ammonia. The hydrate did not lose water when heated at 110°/0·1 mm. for several hr.

1-*Chloropyrrolo*[1,2-a]*quinoxaline-2-sulphonic Acid.*—*N*-Chlorosuccinimide (0·35 g.) was added to a stirred solution of pyrrolo[1,2-*a*]quinoxaline-2-sulphonic acid (0·68 g.) in aqueous sulphuric acid (50% v/v; 25 ml.) and the solution was left at room temperature overnight. The mixture was then poured into ice–water and the precipitate was filtered off. After dissolution in hot dilute sodium hydroxide solution, followed by acidification with an excess of 2N-sulphuric acid, yellow needles of the 1-*chloro-2-sulphonic acid* (0·65 g., 84%), m.p. >350°, were obtained (Found: C, 46·4; H, 2·7; N, 9·6. $C_{11}H_7ClN_2O_3S$ requires C, 46·7; H, 2·5; N, 9·9%).

Hydrolysis of Pyrrolo[1,2-a]*quinoxaline-3-sulphonic Acids.*

[8] E. Ochiai in 'Aromatic Amine Oxides,' Elsevier, Amsterdam, 1967, p. 373.

[9] *Cf.* V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 624.

[10] E. C. Taylor and G. W. H. Cheeseman, *J. Amer. Chem. Soc.*, 1964, **86**, 1830.

—(a) *Pyrrolo*[1,2-a]*quinoxaline-3-sulphonic acid.* A solution of the monohydrate (1·00 g.) in aqueous sulphuric acid (50% v/v, 12 ml.) was heated under reflux for 2 hr., then cooled, and poured into ice–water. The diluted mixture was filtered, the filtrate was made alkaline with an excess of conc. ammonia solution, and the product (0·53 g., 84%) was filtered off. Crystallisation from light petroleum (b.p. 80—100°) gave colourless needles of the parent base, m.p. 133—134°.

(b) 1-*Nitropyrrolo*[1,2-a]*quinoxaline-3-sulphonic acid.* The nitro-sulphonic acid, hydrolysed essentially as in (a), gave a product which gave 1-nitropyrrolo[1,2-*a*]quinoxaline (23%), m.p. 132—139° [from light petroleum (b.p. 80—100°)]. Unchanged nitro-sulphonic acid (30%) was recovered from the diluted reaction mixture.

(c) 1-*Aminopyrrolo*[1,2-a]*quinoxaline-3-sulphonic acid.* The amino-sulphonic acid was hydrolysed essentially as in (a), except that the reaction mixture was heated under reflux for 1·25 hr. The product yielded 1-aminopyrrolo-[1,2-*a*]quinoxaline (29%), m.p. *ca.* 140° (decomp.) (from 50% aqueous ethanol).

Reaction of 1-*Nitropyrrolo*[1,2-a]*quinoxaline-3-sulphonic Acid with Concentrated Hydrochloric Acid.*—A solution of 1-nitropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid monohydrate (1·00 g.) in conc. hydrochloric acid (70 ml.) was heated under reflux for 6 hr., cooled, then poured on ice. The precipitate was filtered off and dissolved in hot dilute sodium hydroxide solution. Acidification with an excess of 2N-sulphuric acid gave pale yellow needles of 1-chloropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid monohydrate (0·87 g., 90%).

Reaction of 1-*Nitropyrrolo*[1,2-a]*quinoxaline-3-sulphonic Acid with Lithium Chloride in Dimethylformamide.*—1-Nitropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid monohydrate (1·00 g.) was added to a hot solution of lithium chloride (*ca.* 3 g.) in dimethylformamide (15 ml.), and the mixture was heated under reflux for 1 hr. The precipitate obtained by dilution with water and acidification with 2N-hydrochloric acid was filtered off and redissolved in hot dilute sodium hydroxide. Acidification with an excess of 2N-hydrochloric acid gave 1-chloropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid monohydrate (0·85 g., 88%).

Reaction of 1-*Nitropyrrolo*[1,2-a]*quinoxaline with Concentrated Hydrochloric Acid.*—A solution of 1-nitropyrrolo-[1,2-*a*]quinoxaline (1·00 g.) in conc. hydrochloric acid (25 ml.) was heated under reflux for 6 hr., cooled, then poured on ice. An excess of conc. ammonia solution was cautiously added, and the precipitate of 1-chloro- and unchanged 1-nitro-pyrrolo[1,2-*a*]quinoxaline was extracted into chloroform. The residue obtained by evaporation of the dried (Na_2SO_4) extracts was dissolved in conc. sulphuric acid (10 ml.), and the solution was set aside at room temperature overnight, then poured on ice. The resulting precipitate was dissolved in hot dilute sodium hydroxide; acidification with an excess of 2N-hydrochloric acid gave pale yellow crystals of 1-chloropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid monohydrate (0·32 g., 33%).

The acidic mother liquor from the sulphonation was made alkaline with conc. ammonia solution to give a precipitate which on crystallisation from light petroleum (b.p. 80—100°) yielded 1-nitropyrrolo[1,2-*a*]quinoxaline (0·32 g.).

Reaction of 1-*Nitropyrrolo*[1,2-a]*quinoxaline-3-sulphonic Acid with Concentrated Hydrobromic Acid.*—A solution of 1-nitropyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid monohydrate (2·66 g.) in conc. hydrobromic acid (70 ml.) was heated under reflux for 6 hr., cooled, and poured on ice. An excess of conc. ammonia solution was added cautiously and the resulting precipitate (2·76 g.) was filtered off. I.r. analysis [7] indicated it to contain 2,3-dibromo- (44%) and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxaline (56%).

Reaction of 1-*Nitropyrrolo*[1,2-a]*quinoxaline-3-sulphonic Acid with Lithium Bromide in Dimethylformamide.*—The sulphonic acid monohydrate (2·00 g.) was added to a hot solution of lithium bromide (*ca.* 5 g.) in dimethylformamide (25 ml.), and the mixture was heated under reflux for 1 hr. The precipitate obtained after cooling, dilution with water, and addition of an excess of ammonia, gave 3-bromo-pyrrolo[1,2-*a*]quinoxaline (0·57 g., 36%), m.p. 184—185° [from light petroleum (b.p. 100—120°; 20 ml.)].

In a similar experiment in which the reaction time was 10 min., 1-bromopyrrolo[1,2-*a*]quinoxaline-3-sulphonic acid was isolated (34%).

Reaction of Pyrrolo[1,2-a]*quinoxaline-3-sulphonic Acid with Concentrated Hydrobromic Acid.*—A solution of the monohydrate (1·00 g.) in conc. hydrobromic acid (12 ml.) was heated under reflux for 6 hr., cooled, and poured on ice. A slight excess of conc. ammonia solution was added and the product was extracted into chloroform. Evaporation of the dried (Na_2SO_4) extracts left a residue which was dissolved in benzene and chromatographed on a silica gel column. Elution with benzene–ethyl acetate (33 : 1) gave a fraction which yielded 3-bromopyrrolo[1,2-*a*]quinoxaline (0·035 g., 4%), m.p. 186—187° [from light petroleum (b.p. 100—120°)]. Further elution with benzene–ethyl acetate (5 : 1) gave a fraction which yielded pyrrolo[1,2-*a*]quinoxaline (0·26 g., 41%), m.p. 134—136° [from light petroleum (b.p. 80—100°)].

Reaction of 1-*Bromopyrrolo*[1,2-a]*quinoxaline with Sodium Nitrite and Concentrated Hydrobromic Acid.*—The 1-bromo-compound (0·35 g., 0·0014 mole) was added to a solution of sodium nitrite (0·097 g., 0·0014 mole) in conc. hydrobromic acid (10 ml.). The mixture was heated under reflux for 2 hr. and the product was isolated as described in the preceding experiment. Crystallisation from light petroleum (b.p. 100—120°) gave a mixture (0·25 g.) shown by i.r. analysis [7] to contain 2,3-dibromo- (13%) and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxaline (87%).

Reaction of 1-*Nitropyrrolo*[1,2-a]*quinoxaline with Concentrated Hydrobromic Acid.*—A solution of the 1-nitro-compound (0·30 g.) in conc. hydrobromic acid (10 ml.) was heated under reflux for 2 hr., cooled, and poured on ice. It was then made alkaline with conc. ammonia and the product was extracted into chloroform. Evaporation of the dried (Na_2SO_4) extracts left a residue which [from light petroleum (b.p. 100—120°)] gave a mixture (0·23 g.) found by i.r. analysis [7] to contain 2,3-dibromo- (5%) and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxaline (95%).

Reaction of Pyrrolo[1,2-a]*quinoxaline with Potassium Nitrate and Concentrated Hydrobromic Acid.*—The parent base (1·68 g., 0·01 mole) was added to potassium nitrate (1·01 g., 0·01 mole) in conc. hydrobromic acid (50 ml.). The mixture was heated under reflux for 4 hr., then cooled, and poured on ice. A slight excess of conc. ammonia was added and the product was extracted into chloroform. Evaporation of the dried (Na_2SO_4) extracts gave a residue which [from light petroleum (b.p. 100—120°)] gave a mixture (2·05 g.) found by i.r. analysis [7] to contain 2,3-dibromo- (33·5%) and 1,2,3-tribromo-pyrrolo[1,2-*a*]quinoxaline (66·5%).

Reaction of 1-*Bromopyrrolo*[1,2-a]*quinoxaline*-3-*sulphonic Acid with Lithium Bromide in Dimethylformamide*.—The sulphonic acid monohydrate (2·00 g.) was added to a hot solution of lithium bromide (*ca.* 5 g.) in dimethylformamide (25 ml.) and the mixture was heated under reflux for 20 min. The precipitate obtained after cooling, dilution with water, and addition of an excess of 2N-sodium hydroxide gave 3-bromopyrrolo[1,2-*a*]quinoxaline (0·28 g., 20%), m.p. 180—181° [from light petroleum (b.p. 100—120°; 15 ml.)].

Rearrangement of 1-*Bromo- to* 3-*Bromo-pyrrolo*[1,2-a]-*quinoxaline in a Solution of Lithium Bromide in Dimethylformamide*.—1-Bromopyrrolo[1,2-*a*]quinoxaline (0·40 g.) was added to a hot solution of lithium bromide (*ca.* 2·5 g.) in dimethylformamide (10 ml.) and the mixture was heated under reflux for 1 hr. Cooling and dilution gave a precipitate of 3-bromopyrrolo[1,2-*a*]quinoxaline (0·24 g., 60%), m.p. 184—185° [from light petroleum (b.p. 100—120°; 10 ml.)].

Similar treatment of 1,3-dibromopyrrolo[1,2-*a*]quinoxaline with lithium bromide in dimethylformamide also gave the 3-bromo-compound.

In both of these experiments addition of solid sodium hydrogen carbonate to the reaction mixture resulted in recovery of the starting bromo-compound.

Pyrrolo[1,2-a]*quinoxalin*-1(5H)-*one*.—(a) *From* 1-*Chloropyrrolo*[1,2-a]*quinoxaline*. The 1-chloro-compound (2·50 g.) was dissolved in a solution of potassium hydroxide (2·50 g.) in dimethyl sulphoxide (23 ml.) and water (2 ml.). The mixture was heated under reflux for 30 min., then cooled, and diluted with water (100 ml.). The pH was adjusted to 5 with acetic acid and the resulting orange precipitate was filtered off and washed with water and chloroform. The *product* (0·50 g., 20%), after crystallisation from aqueous dimethylformamide and aqueous methanol, decomposed when heated above 230° (Found: C, 65·2; H, 4·8; N, 14·2. $C_{11}H_8N_2O,H_2O$ requires C, 65·3; H, 5·0; N, 13·9%). Some discolouration occurred when the sample was dried at 110°/0·1 mm. for 4 hr. (Found: C, 71·8; 72·3; H, 4·6, 4·9; N, 14·3, 14·9. $C_{11}H_8N_2O$ requires C, 71·7; H, 4·4; N, 15·2%).

(b) *From* β-*Quinoxalin*-2-*ylpropionic acid*. A stirred mixture of the propionic acid (1·00 g.) in polyphosphoric acid (10 g.) was heated at 110° for 30 min. The mixture was cooled and poured into ice–water, and the pH was adjusted to 7 with conc. ammonia solution. The precipitate was filtered off and extracted with an excess of sodium hydrogen carbonate solution to give the quinoxalinone (0·85 g., 85%).

The quinoxalinone was converted (35%) into 1-chloropyrrolo[1,2-*a*]quinoxaline on treatment with boiling phosphoryl chloride for 3 hr.

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