228. *Pyrido*(1′ : 2′ : 1 : 2)*benziminazoles and Allied Compounds (Cyclic* 1 : 3-*Diazalines). Part II.*

By Sir Gilbert Morgan and Jessie Stewart.

The object of the present investigation was to ascertain whether the condensation described in Part I (J., 1938, 1292), yielding cyclic 1 : 3-diazalines, could be generalised still further and an extension has now proved to be practicable. The *N*-2′ : 4′-dinitrophenyl derivatives of 2-aminopyridine, 2-aminoquinoline and 1-amino*iso*quinoline can be made to lose the elements of nitrous acid, giving rise by ring closure to the corresponding 7-nitro-4 : 5-benz-1 : 3-diazalines, which are convertible successively into 7-amino-4 : 5-benz-1 : 3-diazalines and into the unsubstituted 4 : 5-benz-1 : 3-diazalines.

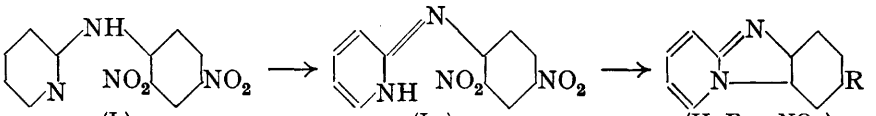
Moreover *N*-2′ : 4′-dinitro-1′-naphthyl derivatives of the foregoing α-aminopyridine and analogues undergo similar condensations to cyclic 1 : 3-diazalines containing a naphthalenoid residue.

The replacement of picryl chloride in these reactions by the readily available 1-chloro-2 : 4-dinitrobenzene is a matter of considerable technical utility in the application of cyclic 1 : 3-diazalines as intermediates for the production of dyes or therapeutic agents.

The employment of 1-chloro-2 : 4-dinitronaphthalene in such condensations indicates further that this diazaline reaction is capable of wide application to other *N*-2 : 4-nitro-aryl derivatives of α-aminopyridine and analogous bases.

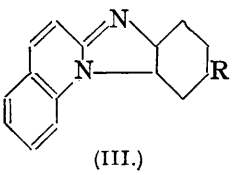
In Part I (J., 1938, 1292) the *N*-picryl derivatives of the α-amino-compounds of pyridine, β-picoline, quinoline, *iso*quinoline and phenanthridine were shown to lose the elements of nitrous acid with ring closure, thereby furnishing dinitro-derivatives of a group of hydroaromatic diamines, the pyrido(1′ : 2′ : 1 : 2)benziminazoles (cyclic 1 : 3-diazalines). Subsequent experiments have proved that under suitable conditions *N*-2′ : 4′-dinitrophenyl-2-

aminopyridine (I) may be made to undergo ring closure to the corresponding 1 : 2-*pyrido*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (II, R = NO_2).



(I.) (Ia.) (II, R = NO_2.)

(I) *Replacement of Picryl Chloride by* 1-*Chloro*-2 : 4-*dinitrobenzene*.—This simpler condensation has now been extended to the *N*-2′ : 4′-*dinitrophenyl* derivatives of 2-aminoquinoline and 1-amino*iso*quinoline with the result that 1 : 2-*quinolo*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (III, R = NO_2) and 1 : 2(2′ : 1′)-iso*quinolo*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (V; R = H, R′ = NO_2) are now obtainable by a ring closure which leaves no ambiguity in either case with respect to the position of the nitro-group, so that subsequent reduction yields a base of known constitution (III, R = NH_2, and V, R = H, R′ = NH_2).



(III.)

(A) 1 : 2-*Pyrido*-1 : 3-*diazalines*.—By the preparation of 1 : 2-pyrido-7-nitro-4 : 5-benz-1 : 3-diazaline (II, R = NO_2) from *N*-2′ : 4′-dinitrophenyl-2-aminopyridine (I) an ambiguity left over from the picryl-2-aminopyridine condensation (J., 1938, 1294) has been clarified. The immediate product of the latter ring closure was 1 : 2-pyrido-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline, and when this dinitro-compound was partially reduced to a nitroamine there remained the uncertainty as to which of the two nitro-groups had undergone reduction. Accordingly successive diazotisation of the nitroamine and elimination of the diazonium group still left the constitution of the resulting mononitrodiazaline uncertain. Its identity with the above 1 : 2-pyrido-7-nitro-4 : 5-benz-1 : 3-diazaline shows, however, that it was the 9-nitro-group which underwent reduction and subsequent elimination by means of the diazo-reaction. The amine resulting from the reduction of the 7-nitro-derivative will have the constitution (II, R = NH_2).

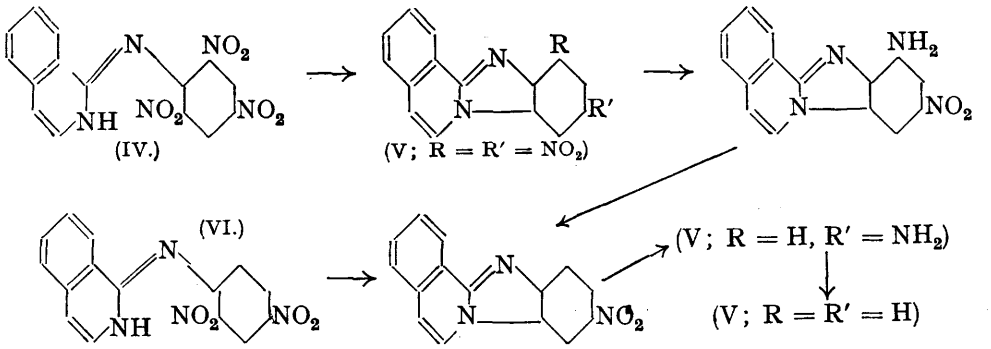
Finally the two series of derivatives, one from picryl-2-aminopyridine and the other from *N*-2′ : 4′ dinitrophenyl-2-aminopyridine, are proved to have the same 1 : 3-diazaline configuration by eliminating either both amino-groups from 1 : 2-pyrido-7 : 9-diamino-4 : 5-benz-1 : 3-diazaline (*loc. cit.*, p. 1293) or the single amino-group from 1 : 2-pyrido-7-amino-4 : 5-benz-1 : 3-diazaline (p. 1060); 1 : 2-pyrido-4 : 5-benz-1 : 3-diazaline (II, R = H) is obtained in both cases.

(B) 1 : 2-*Quinolo*-1 : 3-*diazalines*.—Ring closure with *N*-2′ : 4′-dinitrophenyl-2-aminoquinoline leads to 1 : 2-quinolo-7-nitro-4 : 5-benz-1 : 3-diazaline (III, R = NO_2), which is identical with the mononitrodiazaline formerly obtained (J., 1938, 1302) by eliminating the amino-group from a nitroamine then described as 1 : 2-quinolo-7 : 9(or 9 : 7)-nitro-amino-4 : 5-benz-1 : 3-diazaline. The ambiguity implied in the alternative rendering is removed, for the nitro-group and the amino-radical produced on reduction (III, R = NH_2) are now both located in position 7. That the ring closures from picryl-2-aminoquinoline and *N*-2′ : 4′-dinitrophenyl-2-aminoquinoline are both of diazaline type is proved by the fact that the unsubstituted diamine, 1 : 2-quinolo-4 : 5-benz-1 : 3-diazaline (III, R = H), is the end product in both series. It has now beeen obtained either by eliminating both amino-groups from 1 : 2-quinolo-7 : 9-diamino-4 : 5-benz-1 : 3-diazaline (*loc. cit.*, p. 1303) or by removing the single amino-group from 1 : 2-quinolo-7-amino-4 : 5-benz-1 : 3-diazaline (p. 1061).

(C) 1 : 2(2′ : 1′)-iso*Quinolo*-1 : 3-*diazalines*.—In the earlier communication it was pointed out (*loc. cit.*, p. 1296) that a ring closure with picryl-1-amino*iso*quinoline must be of diazaline type, since any α-carboline formation was precluded owing to the structure of *iso*quinoline. The dinitrodiazaline (V; R = R′ = NO_2) then obtained was reduced to a diamine which, on elimination of both amino-groups through the diazo-reaction, was converted into the unsubstituted 1 : 2(2′ : 1′)-*iso*quinolo-4 : 5-benz-1 : 3-diazaline (V; R = R′ = H).

In the present investigation 1 : 2(2′ : 1′)-*iso*quinolo-7 : 9-dinitro-4 : 5-benz-1 : 3-

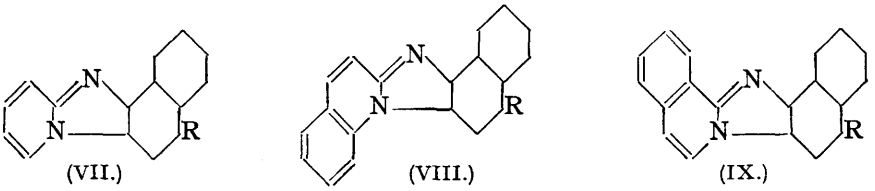
diazaline (V; R = R′ = NO_2) has been reduced in stages and the intermediate nitroamine has been shown to be 1 : 2(2′ : 1′)-iso*quinolo*-7-*nitro*-9-*amino*-4 : 5-*benz*-1 : 3-*diazaline* (V;



R = NH_2, R′ = NO_2) by eliminating its amino-group, since the resulting nitro-compound is identical with 1 : 2(2′ : 1′)-iso*quinolo*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (V; R = H, R′ = NO_2), obtained as the immediate product of the ring closure of N-2′ : 4′-*dinitrophenyl*-1-*amino*iso*quinoline* (VI).

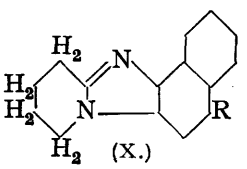
On reduction, this nitro-product (V; R = H, R′ = NO_2) of known constitution yields 1 : 2(2′ : 1′)-iso*quinolo*-7-*amino*-4 : 5-*benz*-1 : 3-*diazaline* (V; R = H, R′ = NH_2), from which by elimination of the amino-group 1 : 2(2′ : 1′)-*iso*quinolo-4 : 5-benz-1 : 3-diazaline (V; R = R′ = H) is obtained. This end product has now been obtained both from picryl-1-amino*iso*quinoline (IV) and from *N*-2′ : 4′-dinitrophenyl-1-amino*iso*quinoline (VI).

(II) *Replacement of Picryl Chloride by* 1-*Chloro*-2 : 4-*dinitronaphthalene*.—The diazaline condensation has been generalised still further by employing *N*-2′ : 4′-dinitro-1′-naphthyl-derivatives of 2-aminopyridine, 2-aminoquinoline, and 1-amino*iso*quinoline. Ring closure leads respectively to the formation of 1 : 2-*pyrido*-7-*nitro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (VII, R = NO_2), 1 : 2-*quinolo*-7-*nitro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (VIII, R = NO_2) and 1 : 2(2′ : 1′)-iso*quinolo*-7-*nitro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (IX, R = NO_2).



(D) Each of these three 7-nitro-8 : 9-benzo-4 : 5-benz-1 : 3-diazalines (VII, VIII, IX; R = NO_2) is reduced to the corresponding 7-*amino*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (VII, VIII, IX; R = NH_2) and by elimination of the primary amino-group from the latter base, each monoamino-8 : 9-benzo-4 : 5-benz-1 : 3-diazaline is converted into the unsubstituted *diazaline* (VII, VIII, IX; R = H) of a new series which contains a naphthalenoid nucleus arising from the use of 1-chloro-2 : 4-dinitronaphthalene.

(E) In the reduction of the three foregoing nitro-compounds (VII, VIII, IX; R = NO_2) hydrogen under moderate pressure was used in the presence of a platinum catalyst; but when in the case of 1 : 2-pyrido-7-nitro-8 : 9-benzo-4 : 5-benz-1 : 3-diazaline (VII, R = NO_2), the gas pressure was raised, hydrogenation proceeded further and a tetrahydro-derivative was obtained, which by analogy with a similar reduction product from 1 : 2-pyrido-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline (*loc. cit.*, p. 1295) is formulated as 1 : 2-*tetrahydropyrido*-7-*amino*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (X; R = NH_2). The amino-group of this compound is still in an aromatic ring, as is shown by the fact that it can be successively diazotised and eliminated, leaving 1 : 2-*tetrahydro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (X, R = H).



EXPERIMENTAL.

(I) *Condensations of 2-Aminopyridine and Analogues with 1-Chloro-2 : 4-dinitrobenzene.*

Pyridine Series. Ring Closure of N-2′ : 4′-Dinitrophenyl-2-aminopyridine.—Condensation of 2-aminopyridine (31 g.; 2 mols.) with 1-chloro-2 : 4-dinitrobenzene (34 g.; 1 mol.) in xylene solution (100 c.c.) is a great improvement both on the use of toluene as solvent and on the interaction of the two solids at 105—120° (J., 1938, 1297). The precipitated product was extracted with hot water to dissolve aminopyridine hydrochloride and uncondensed aminopyridine. When the crude *N*-2′ : 4′-dinitrophenyl-2-aminopyridine (I) (29—30 g.) was crystallised from xylene, a dark brown residue (2 g.) remained. This by-product was dissolved in boiling 6N-sulphuric acid and reprecipitated by addition of aqueous ammonia. The substance crystallised from nitrobenzene in minute yellow needles tinged with green (m. p. > 280°). It has not, however, been examined further.

1 : 2-*Pyrido*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (II, R = NO_2). A solution of *N*-2′ : 4′-dinitrophenyl-2-aminopyridine (I) (5 g.) in naphthalene or in diphenyl (5 g.) was boiled under reflux in a metal-bath at 300—310° until oxides of nitrogen ceased to escape; much of the solvent had then sublimed on to the walls of the condenser. The cooled mass was warmed with N-hydrochloric acid. The crude yellow nitrodiazaline (3·0—3·5 g., m. p. 250°) precipitated with 2N-ammonia from the filtered solution was free from *N*-2′ : 4′-dinitrophenyl-2-aminopyridine. When redissolved in N-hydrochloric acid at room temperature, filtered from a small amount of yellow solid, and reprecipitated with 2N-ammonia, the *diazaline* melted at 259° and after crystallisation from nitrobenzene it separated in feathery needles, m. p. 262—263° (Found: C, 61·9; H, 3·6; N, 19·8. $C_{11}H_7O_2N_3$ requires C, 62·0; H, 3·3; N, 19·7%), not depressed by admixture with the mononitrodiazaline (m. p. 262—263°) prepared (*loc. cit.*) by transformation of picryl-2-aminopyridine into 1 : 2-pyrido-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline, reduction of this dinitrodiazaline to nitroaminodiazaline, and removal of the amino-group from the nitroaminodiazaline by the diazotisation devised by Schoutissen (*J. Amer. Chem. Soc.*, 1933, **55**, 4535), followed by crystallisation of the product from nitrobenzene rather than from pyridine as described in the earlier communication (*loc. cit.*).

1 : 2-*Pyrido*-7-*amino*-4 : 5-*benz*-1 : 3-*diazaline*. The foregoing mononitrodiazaline (II, R = NO_2) was reduced in alcoholic suspension by hydrogen in presence of platinic oxide over a pressure range 5 atms. → 2·5 atms. to the corresponding 1 : 2-*pyrido*-7-*amino*-4 : 5-*benz*-1 : 3-*diazaline*, which crystallised from xylene in yellow needles (Found: C, 71·7; H, 5·2; N, 23·25. $C_{11}H_9N_3$ requires C, 72·1; H, 4·9; N, 22·95%), m. p. 227°. This m. p. was not depressed by admixture with the monoaminodiazaline (m. p. 229°) (*loc. cit.*) prepared by ring closure of picryl-2-aminopyridine to 1 : 2-pyrido-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline, reduction of the latter dinitrodiazaline to nitroaminodiazaline, elimination of the amino-group from the nitro-aminodiazaline, and catalytic reduction of the resulting mononitrodiazaline to the corresponding monoaminodiazaline, thus confirming that the nitroaminodiazaline into which the 7 : 9-dinitrodiazaline is converted by the action of sodium sulphide and sulphur is the 7-nitro-9-amino- and not the isomeric 9-nitro-7-amino-compound.

1 : 2-*Pyrido*-4 : 5-*benz*-1 : 3-*diazaline* (II, R = H). Conclusive evidence of the diazaline structure of the foregoing monoamine (II, R = NH_2) derived from *N*-2′ : 4′-dinitrophenyl-2-aminopyridine (I) (*v. supra*) has been provided by diazotisation of this base (1·8 g.) in sulphuric acid (18 c.c., *d* 1·84) at 0° with sodium nitrite (1 g.) in sulphuric acid (10 c.c., *d* 1·84) in presence of phosphoric acid (30 c.c., *d* 1·75). The diazonium salt was precipitated with alcohol–ether, collected, and reduced with alcohol. After distillation of alcohol and acetaldehyde, the unsubstituted base of the series was precipitated with sodium hydroxide solution (50%), crystallised from petroleum (b. p. 100—120°), from light petroleum (b. p. 40—60°), and finally sublimed to form colourless, long, slender needles m. p. 179° (Found: C, 78·4; H, 4·8; N, 17·1. Calc. for $C_{11}H_8N_2$: C, 78·6; H, 4·7; N, 16·7%), identical with 1 : 2-pyrido-4 : 5-benz-1 : 3-diazaline (II, R = H) derived originally (*loc. cit.*) from picryl-2-aminopyridine.

Quinoline Series. Ring Closure of N-2′ : 4′-Dinitrophenyl-2-aminoquinoline. N-2′ : 4′-*Dinitrophenyl-2-aminoquinoline.*—2-Aminoquinoline and 1-chloro-2 : 4-dinitrobenzene (molecular proportions 2 : 1) condense very slowly in boiling xylene solution but much more rapidly at the temperature of boiling nitrobenzene. When 2-aminoquinoline (12 g.), dissolved in nitrobenzene (100 c.c.), and 1-chloro-2 : 4-dinitrobenzene (8 g.) in nitrobenzene (30 c.c.) were boiled together under reflux for 5—6 hours and the yellow condensation product which separated from the cooled reaction mixture was freed from aminoquinoline hydrochloride and any unchanged

aminoquinoline by successive extraction with dilute hydrochloric acid and water, N-2′ : 4′-*dinitrophenyl-2-aminoquinoline* (7 g.) remained undissolved. It crystallised from xylene in minute orange needles, m. p. 221° (Found : C, 58·3; H, 3·2; N, 18·0. $C_{15}H_{10}O_4N_4$ requires C, 58·1; H, 3·2; N, 18·1%).

1 : 2-*Quinolo*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (III, R = NO_2). Ring closure of *N*-2′ : 4′-dinitrophenyl-2-aminoquinoline to 1 : 2-quinolo-7-nitro-4 : 5-benz-1 : 3-diazaline (III, R = NO_2) was demonstrated by heating the former substance (1 g.) in a metal-bath. Brown fumes were evolved at 340—360°, yellow needles (0·03 g.) sublimed, and charring occurred. Recrystallised from nitrobenzene, the sublimate melted at 238°. When extracted with boiling xylene, the charred residue yielded an extract from which petroleum (b. p. 100—120°) precipitated yellow needles (0·15 g.) identical with the recrystallised sublimate. The m. p. of each specimen was depressed to 185—190° by the original *N*-2′ : 4′-dinitrophenyl-2-aminoquinoline, but not depressed by the mononitrodiazaline derived (*loc. cit.*) from picryl-2-aminoquinoline. At the same time it was established that the 7 : 9(or 9 : 7)-nitro-aminodiazaline, an intermediate product of the picryl series, is the 7-nitro-9-amino-form. Accordingly the nitrodiazaline derived from it by eliminating the amino-group is 1 : 2-quinolo-7-nitro-4 : 5-benz-1 : 3-diazaline, which on catalytic reduction is transformed into the corresponding 7-amino-diazaline.

When *N*-2′ : 4′-dinitrophenyl-2-aminoquinoline was heated at 340—360°/20 mm., the sublimate of 1 : 2-*quinolo*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (IV) was approximately 66% of the calculated amount. This crude nitrodiazaline, which was extracted with xylene from a dark green-yellow insoluble solid, crystallised from the same solvent in yellow needles (Found : C, 68·1; H, 3·1; N, 15·85. $C_{15}H_9O_2N_3$ requires C, 68·4; H, 3·4; N, 16·0%), m. p. 243°, not depressed by the mononitrodiazaline (m. p. 243°) derived from ring closure of picryl-2-aminoquinoline (*loc. cit.*) after elimination of one of the two nitro-groups from the resulting dinitrodiazaline.

The non-volatile residue from the pyrolysis of *N*-2′ : 4′-dinitrophenyl-2-aminoquinoline at 340—360°/20 mm. was purified by repeated crystallisation from nitrobenzene, solution in hydrochloric acid at room temperature (much charred matter remaining undissolved), neutralisation of the filtered solution with aqueous ammonia, and crystallisation of the yellow product from nitrobenzene to form minute needles which have not been identified with certainty.

1 : 2-*Quinolo*-7-*amino*-4 : 5-*benz*-1 : 3-*diazaline* (III, R = NH_2). Catalytic reduction at 70° with hydrogen initially at 31 atms. and in presence of platinic oxide (0·5 g.) of an alcoholic suspension (2000 c.c.) of the mononitrodiazaline (7·3 g.) prepared by ring closure of *N*-2′ : 4′-dinitrophenyl-2-aminoquinoline gave *monoaminodiazaline* (III, R = NH_2) (6 g.), which separated on evaporation of the filtered solution to small bulk and, after solution in 2N-hydrochloric acid at room temperature and precipitation with 2N-sodium hydroxide, crystallised from xylene in clusters of pale yellow needles (5 g.) (Found : C, 77·5; H, 4·8; N, 17·8; *M*, Rast, 287. $C_{15}H_{11}N_3$ requires C, 77·25; H, 4·7; N, 18·0%; *M*, 233), m. p. 233°, not depressed by the monoaminodiazaline (m. p. 233°) derived from picryl-2-aminoquinoline (*loc. cit.*).

1 : 2-*Quinolo*-4 : 5-*benz*-1 : 3-*diazaline* (III, R = H).—Diazotisation of the foregoing monoamine (III, R = NH_2) (3·45 g.) in sulphuric acid (18 c.c., *d* 1·84) at 0° with sodium nitrite (1·5 g.) in sulphuric acid (15 c.c., *d* 1·84) in presence of phosphoric acid (50 c.c., *d* 1·75), precipitation of the diazonium salt with alcohol–ether, reduction of this with alcohol (150 c.c.) diluted with water (50 c.c.), distillation of alcohol and acetaldehyde, and precipitation of the filtered concentrate with aqueous ammonia (*d* 0·88) gave a buff precipitate (3·1—3·2 g., m. p. 90°), the unsubstituted base of the series. After solution in cold 2N-hydrochloric acid, filtration through wood charcoal, and precipitation with 2N-ammonia, it crystallised from petroleum (b. p. 100—120°) in colourless needles (2·3 g., m. p. 95°), from light petroleum (b. p. 40—60°) and finally from a large volume of alcohol–water in long slender needles, m. p. 102—103° (Found : C, 82·2; H, 5·1; N, 13·0; *M*, Rast, 254. Calc. for $C_{15}H_{10}N_2$: C, 82·6; H, 4·6; N, 12·8%; *M*, 218), identical with 1 : 2-quinolo-4 : 5-benz-1 : 3-diazaline (III, R = H) which was first prepared (*loc. cit.*, p. 1303) by elimination of both amino-groups from 1 : 2-quinolo-7 : 9-diamino-4 : 5-benz-1 : 3-diazaline, the diamine obtained by catalytic reduction of 1 : 2-quinolo-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline, the product of ring closure of picryl-2-aminoquinoline; and again from reduction of the dinitrodiazaline to nitroaminodiazaline and successive withdrawal of the two substituents from the latter product.

iso*Quinoline Series. Successive Elimination of Substituents from the Dinitrodiazaline.* 1 : 2(2′ : 1′)-iso*Quinolo*-7-*nitro*-9-*amino* (or 9-*nitro*-7-*amino*)-4 : 5-*benz*-1 : 3-*diazaline*.—An emulsion of 1 : 2(2′ : 1′)-*iso*quinolo-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline (V; R = R′ = NO_2) (9 g.) in boiling acetone (250 c.c.) was reduced with sodium sulphide (9 g.) and sulphur (4·5 g.) in

boiling water (50 c.c.). The brick-red solid which remained after distillation of acetone was extracted with 6N-sulphuric acid and the relatively small amount which dissolved was precipitated from the filtered solution with aqueous ammonia. The main bulk of solid remained undissolved as the yellow sulphate of the base and was suspended in hot water, to which was added 2N-ammonia in quantity sufficient to regenerate the brick-red *nitroaminodiazaline*. This was crystallised from pyridine, precipitation being completed by addition of water. The uniformity of the product was demonstrated by elimination of the amino-group from all three fractions of nitroaminodiazaline to give one and the same mononitrodiazaline, but there still remained need for distinguishing between 1 : 2(2′ : 1′)-*iso*quinolo-7-nitro-9-amino-4 : 5-benz-1 : 3-diazaline (V; R = NH_2, R′ = NO_2) and the isomeric 9-nitro-7-aminodiazaline, both of which are possible products of the foregoing partial reduction of the dinitrodiazaline (V; R = R′ = NO_2).

1 : 2(2′ : 1′)-iso*Quinolo*-7(or 9)-*nitro*-4 : 5-*benz*-1 : 3-*diazaline*.—A solution of the preceding nitroaminodiazaline (10·5 g.) in sulphuric acid (100 c.c., *d* 1·84) was diazotised with sodium nitrite (3·8 g.) in sulphuric acid (38 c.c., *d* 1·84) by gradual addition of the mixed solutions at −5° to well-cooled phosphoric acid (120 c.c., *d* 1·75). The yellow diazonium salt precipitated by addition of the diazo-solution to alcohol–ether was reduced with alcohol (200 c.c.), the major portion of the product—a red-brown solid—remaining undissolved. It was collected from the cooled suspension and extracted repeatedly with 6N-sulphuric acid, and the yellow nitrodiazaline (6·5 g., m. p. 264—267°) precipitated from acid solution with aqueous ammonia. From the main alcoholic filtrate, after distillation to remove alcohol and acetaldehyde, there was isolated by addition of 2N-ammonia a yellow solid, partly soluble in boiling 6N-sulphuric acid; neutralisation of the filtered solution yielded the mononitrodiazaline (1 g.). Crystallisation of the crude product from nitrobenzene gave 1 : 2(2′ : 1′)-iso*quinolo*-7(or 9)-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* in yellow needles, m. p. 271—272° (Found: C, 68·5; H, 3·2; N, 15·8. $C_{15}H_9O_2N_3$ requires C, 68·4; H, 3·4; N, 16·0%), the position of the nitro-group depending upon the orientation of the nitroaminodiazaline from which the amino-group had been withdrawn.

1 : 2(2′ : 1′)-iso*Quinolo*-7(or 9)-*amino*-4 : 5-*benz*-1 : 3-*diazaline*.—Reduction of a suspension of the foregoing mononitrodiazaline (7·5 g.) in absolute alcohol (2000 c.c.) preheated to 70°, by hydrogen initially at 31 atms. in presence of platinic oxide (0·5 g.) was extremely rapid. The filtrate from the suspended catalyst was distilled almost to dryness and the residual solid was collected, washed with light petroleum (b. p. 40—60°), dissolved in 2N-hydrochloric acid at room temperature, and precipitated from the filtered solution with 2N-ammonia. The *base*, colourless at first but pale yellow when collected, washed with water, and dried in a vacuum, crystallised from xylene in pale yellow needles (5 g.), m. p. 266—267° [Found: C, 77·3; H, 4·6; N, 18·2; *M* (Rast method), not determined, the base being insoluble in camphor. $C_{15}H_{11}N_3$ requires C, 77·25; H, 4·7; N, 18·0%].

Ring Closure of N-2′ : 4′-*Dinitrophenyl*-1-*amino*iso*quinoline*. N-2′ : 4′-*Dinitrophenyl*-1-*amino*iso*quinoline* (VI).—When a solution of 1-amino*iso*quinoline (12 g.) in xylene (50 c.c.) was boiled under reflux with 1-chloro-2 : 4-dinitrobenzene (8 g.) dissolved in xylene (25 c.c.), 1-amino*iso*quinoline hydrochloride (3 g.) separated and the solution developed a red colour. It is noteworthy that brown fumes of oxides of nitrogen were evolved after 2—3 hours if the mixed solutions were allowed to boil vigorously. At the end of 5—6 hours the reaction mixture was filtered while hot from 1-amino*iso*quinoline hydrochloride and left to crystallise. The crude product (8·0—8·5 g.) was extracted twice with N-hydrochloric acid (100 c.c.) to dissolve unchanged amino*iso*quinoline. N-2′ : 4′-*Dinitrophenyl*-1-*amino*iso*quinoline* remaining undissolved was washed with water, dried, and crystallised from xylene, forming red needles, m. p. 230—231° (Found: C, 59·1; H, 3·5; N, 17·6. $C_{15}H_{10}O_4N_4$ requires C, 58·1; H, 3·2; N, 18·1%). A small amount of yellow solid melting partially at 275—280° remained undissolved in xylene. The red needles were used without further purification for ring closure to the corresponding mononitrodiazaline.

While still hot, the combined hydrochloric acid extracts were filtered again from freshly precipitated yellow needles. The latter were dissolved in 6N-sulphuric acid (250—300 c.c.) and precipitated from the filtered solution with aqueous ammonia. This solid (0·5 g., m. p. >280°) has not yet been examined.

When 1-amino*iso*quinoline was recovered from the acid extracts by addition of excess of sodium hydroxide and purified by treatment with 2N-hydrochloric acid at room temperature, followed by addition of water to ensure complete solution of the hydrochloride of the base, a yellow solid remained undissolved. This was dissolved in 6N-sulphuric acid and reprecipitated (0·3 g.) with aqueous ammonia. It melted partially at 250—270° and possibly contained the

mononitrodiazaline product of ring closure of *N*-2′ : 4′-dinitrophenyl-1-amino*iso*quinoline (*v. infra*), but it was not examined further.

1 : 2(2′ : 1′)-iso*Quinolo*-7-*nitro*-4 : 5-*benz*-1 : 3-*diazaline* (V; R = H, R′ = NO_2).—Ring closure of *N*-2′ : 4′-dinitrophenyl-1-amino*iso*quinoline (VI) to this diazaline was demonstrated by distilling the dinitrophenyl compound (1 g.) at 340—360°/20 mm. and extracting both sublimate and residue with xylene. The undissolved charred residue has not been investigated, but the crude product from xylene solution (0·5 g.) melted at 262—264° and by repeated crystallisation from nitrobenzene formed yellow needles (Found : C, 67·9; H, 3·2; N, 15·7. $C_{15}H_9O_2N_3$ requires C, 68·4; H, 3·4; N, 16·0%), m. p. 271—272°, not depressed by the 7(or 9)-mononitrodiazaline (m. p. 271—272°) (*v. supra*) derived from 1 : 2(2′ : 1′)-*iso*quinolo-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline (V; R = R′ = NO_2) by reduction to nitroaminodiazaline and withdrawal of the amino-group from the latter substance; this identity of the two preparations of mononitrodiazaline revealing in addition that the nitroaminodiazaline concerned is 1 : 2(2′ : 1′)-iso*quinolo*-7-*nitro*-9-*amino*-4 : 5-*benz*-1 : 3-*diazaline* (V; R = NH_2, R′ = NO_2).

When distillation was carried out on a larger scale it was difficult to avoid sublimation of a small amount of unchanged *N*-2′ : 4′-dinitrophenyl-1-amino*iso*quinoline (VI) together with the more volatile mononitrodiazaline (V; R = H, R′ = NO_2), the m. p. of the crude product extracted with xylene (some 60% of the calculated amount of mononitrodiazaline) being depressed thereby to approximately 235—240° and raised only to 258—260° on crystallisation from nitrobenzene. Even so the latter product was reduced smoothly to the corresponding primary monoamine, which was isolated without difficulty and in a pure state from the reduction mixture.

1 : 2(2′ : 1′)-iso*Quinolo*-7-*amino*-4 : 5-*benz*-1 : 3-*diazaline* (V; R = H, R′ = NH_2).—Catalytic reduction of the nitrodiazaline (V; R = H, R′ = NO_2) (6 g.), suspended in absolute alcohol (2000 c.c.) preheated to 60°, with hydrogen initially at 31 atms. and in presence of platinic oxide (0·5 g.) was rapid and complete. On concentration of the alcoholic filtrate to small bulk the colourless *monoaminodiazaline* (3·6 g.) separated. A smaller quantity, less pure, was collected by distillation of the concentrate (5 c.c.) to dryness, the residual solid being washed with light petroleum (b. p. 40—60°). Purified by solution in 2N-hydrochloric acid at room temperature and precipitation with 2N-ammonia, the crude base melted at 258—260°; recrystallisation from xylene gave very faintly yellow needles, m. p. 266—267° (Found : C, 77·2; H, 4·6; N, 18·4. $C_{15}H_{11}N_3$ requires C, 77·25; H, 4·7; N, 18·0%), not depressed by the mononitrodiazaline (m. p. 266—267°) derived from ring closure of picryl-1-amino*iso*quinoline (IV) to the corresponding 7 : 9-dinitrodiazaline (V; R = R′ = NO_2) (*v. supra*), reduction of the dinitrodiazaline to nitroaminodiazaline (V; R = NH_2, R = NO_2), elimination of the newly formed amino-group, and catalytic reduction of the resulting nitrodiazaline to aminodiazaline, thus confirming that the latter monoamine is 1 : 2 (2′ : 1′)-*iso*quinolo-7-amino- and not 1 : 2(2′ : 1′)-*iso*quinolo-9-amino-4 : 5-benz-1 : 3-diazaline.

1 : 2(2′ : 1′)-iso*Quinolo*-4 : 5-*benz*-1 : 3-*diazaline* (V; R = R′ = H).—1 : 2(2′ : 1′)-*iso*Quinolo-7-amino-4 : 5-benz-1 : 3-diazaline (V; R = H, R′ = NH_2) (1·75 g.)—the base obtained by catalytic reduction of the product of ring closure of *N*-2′ : 4′-dinitrophenyl-1-amino*iso*quinoline (VI)—was dissolved in sulphuric acid (17 c.c., *d* 1·84) and diazotised with sodium nitrite (0·75 g.) in sulphuric acid (7·5 c.c., *d* 1·84) by gradual addition of the mixed solutions at 0° to phosphoric acid (30 c.c., *d* 1·75). The diazonium salt, precipitated by pouring the diazo-solution into alcohol–ether, was warmed with alcohol (75 c.c.); it gradually dissolved on reduction. The red filtrate from a small buff precipitate of water-soluble needles was distilled to remove alcohol and acetaldehyde; addition of 2N-ammonia to the residual liquid precipitated a buff-pink solid (1·6—1·7 g., m. p. 120°), from which colourless needles (1·2 g., m. p. 127—128°) were obtained by extraction with petroleum (b. p. 100—120°). Recrystallisation from the same solvent raised the m. p. to 129°, at which value it remained on crystallisation from light petroleum (b. p. 40—60°) (Found : C, 82·4; H, 4·5; N, 13·0; *M*, Rast, 235. Calc. for $C_{15}H_{10}N_2$: C, 82·6; H, 4·6; N, 12·8%; *M*, 218). This unsubstituted diazaline (V; R = R′ = H) was identical not only with that of m. p. 129° (Found : C, 82·45; H, 4·2; N, 12·9%; *M*, Rast, 247) prepared in precisely similar manner from the monoamine resulting from elimination of the amino-group from 1 : 2(2′ : 1′)-*iso*quinolo-7-nitro-9-amino-4 : 5-benz-1 : 3-diazaline (V; R = NH_2, R′ = NO_2) and catalytic reduction of the mononitrodiazaline formed thereby (*v. supra*) but also with that of m. p. 129° prepared originally (*loc. cit.*) by reduction of the bis-diazonium salt of 1 : 2(2′ : 1′)-*iso*quinolo-7 : 9-diamino-4 : 5-benz-1 : 3-diazaline, the diamine derived from the dinitrodiazaline (V; R = R′ = NO_2), the product of ring closure of picryl-1-amino*iso*quinoline (IV) with loss of the elements of nitrous acid.

(II) *Condensations of 2-Aminopyridine and Analogues with 1-Chloro-2 : 4-dinitronaphthalene.*

Providing that the temperature of reaction was closely controlled, 1-chloro-2 : 4-dinitronaphthalene was more readily accessible by the interaction of molecular proportions of 2 : 4-dinitro-α-naphthol and toluene-*p*-sulphonyl chloride in diethylaniline as described by Ullmann and Bruck (*Ber.*, 1908, **41**, 3932) than by successive nitration of toluene-*p*-sulphonyl-α-naphthylamine, hydrolysis of the resulting dinitro-derivative to 2 : 4-dinitro-α-naphthylamine (Ullmann and Bruck, *loc. cit.*), diazotisation of this as described by Hodgson and Walker (J., 1933, 1620), and decomposition of the diazonium chloride with cuprous chloride.

Pyridine Series. N-2′ : 4′-*Dinitro*-1′-*naphthyl*-2-*aminopyridine*.—2-Aminopyridine (30 g.; 2 mols.) condensed with 1-chloro-2 : 4-dinitronaphthalene (40 g.; 1 mol.) more satisfactorily in xylene solution (150 c.c.) than in benzene. Aminopyridine hydrochloride separated during the condensation, *N*-2′ : 4′-dinitro-1′-naphthyl-2-aminopyridine when the reaction mixture was cooled. The mixed product was digested with hot water to dissolve the former solid; the latter (45 g.) crystallised from xylene in yellow needles (40 g.), m. p. 192°, but was sufficiently pure after aqueous extraction of aminopyridine hydrochloride for conversion into the corresponding mononitrodiazaline (VII, R = NO_2).

When investigating the relative reactivity of aromatic nitro-compounds in ethyl-alcoholic solution, Mangini condensed 2-aminopyridine and 1-chloro-2 : 4-dinitronaphthalene (*Atti R. Accad. Lincei*, 1937, **25**, 387). The reaction proceeded slowly during 30 hours, the yield of *N*-2′ : 4′-dinitro-1′-naphthyl-2-aminopyridine (m. p. 189—190°) not exceeding 10% of the calculated amount.

1 : 2-*Pyrido*-7-*nitro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (VII, R = NO_2).—*N*-2′ : 4′-Dinitro-1′-naphthyl-2-aminopyridine (10 g.) in nitrobenzene (20 c.c.) was boiled in a metal-bath at 220° for *ca.* 1 hour, until the rapid evolution of oxides of nitrogen ceased. Golden-yellow needles of 1 : 2-*pyrido*-7-*nitro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (3·4—3·5 g., m. p. 236—238°) crystallised from the cooled mass and were washed with alcohol. Recrystallised from nitrobenzene, they melted at 240—241° (Found: C, 68·6; H, 3·6; N, 16·2. $C_{15}H_9O_2N_3$ requires C, 68·4; H, 3·4; N, 16·0%).

1 : 2-*Pyrido*-7-*amino*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline*.—The foregoing mononitrobenzodiazaline (7 g.), suspended in alcohol (1400 c.c.) preheated to 70°, was reduced in presence of platinic oxide (0·7 g.) with hydrogen initially at 5 atms. The resulting solution, after filtering from catalyst, was concentrated almost to dryness; the base which separated (4·5 g., m. p. 232—234°) was washed with light petroleum (b. p. 40—60°) and crystallised from xylene to form pale yellow, feathery needles, m. p. 238—239° (Found: C, 77·7; H, 4·6; N, 17·9; *M*, Rast, 323. $C_{15}H_{11}N_3$ requires C, 77·25; H, 4·7; N, 18·0%; *M*, 233).

1 : 2-*Tetrahydropyrido*-7-*amino*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (X, R = NH_2).—The mononitrobenzodiazaline (VII; R = NO_2) (10 g.), suspended in absolute alcohol (2000 c.c.), was treated at 70° in presence of platinic oxide (1 g.) with hydrogen initially at 32 atms. until absorption of gas ceased. The pasty mass which remained on concentration of the filtered solution solidified (5·1 g., m. p. 210—220°) on addition of light petroleum (b. p. 40—60°). Crystallisation from xylene formed yellow needles, m. p. 228—230° (Found: C, 76·8; H, 6·1; N, 17·4. $C_{15}H_{15}N_3$ requires C, 75·95; H, 6·3; N, 17·7%). That this nuclear hydrogenation is restricted to the dihydropyridine ring of the diazaline nucleus is confirmed by the following experiment under higher pressure. A solution of the base (X, R = NH_2) (5 g., m. p. 228—230°) in absolute alcohol (1000 c.c.) was submitted at 70° in presence of platinic oxide (0·5 g.) to hydrogen at 70 atms. The crude product (4·8 g., m. p. 219°), isolated in the foregoing manner from the concentrate, crystallised from xylene in needles, m. p. 226—227° (Found: C, 76·45; H, 6·0; N, 17·8%; *M*, Rast, 300), not depressed by admixture with the original base (X, R = NH_2) of m. p. 228—230° but depressed to 195—210° by admixture with 1 : 2-pyrido-7-amino-8 : 9-benzo-4 : 5-benz-1 : 3-diazaline (VII, R = NH_2) of m. p. 238—239°.

1 : 2-*Pyrido*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (VII, R = H).—A solution in sulphuric acid (23 c.c., *d* 1·84) of the monoamine (VII, R = NH_2) (2·3 g.) derived by catalytic reduction with hydrogen at 5 atms. of the nitrobenzodiazaline (VII, R = NO_2) was diazotised at 0° with sodium nitrite (1 g.), dissolved in sulphuric acid (10 c.c., *d* 1·84), in presence of phosphoric acid (30 c.c., *d* 1·75). The colourless diazonium salt, which on precipitation with alcohol–ether turned pale yellow, was dissolved in water (50 c.c.) and reduced with alcohol (150 c.c.). The filtered solution, distilled to remove alcohol and acetaldehyde, was treated with aqueous ammonia (*d* 0·88), and the buff precipitate (1·7 g.) extracted with petroleum (b. p. 100—120°). The extract deposited a very pale yellow *base* (1·25 g., m. p. 183—184°); crystallisation from

the same solvent raised the m. p. to 187° (Found : C, 81·9; H, 4·9; N, 12·85; *M*, Rast, 238. $C_{15}H_{10}N_2$ requires C, 82·6; H, 4·6; N, 12·8%; *M*, 218).

1 : 2-*Tetrahydropyrido*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (X, R = H).—Similar diazotisation of the tetrahydro-base (X, R = NH_2) (1·8 g.) prepared catalytically from the mononitrobenzodiazaline (VII, R = NO_2) under 32 atms.' pressure of hydrogen proceeded less smoothly and the crude product was dark and sticky. The colourless unsubstituted *diazaline* extracted therefrom with petroleum (b. p. 100—120°) crystallised from the same solvent and melted at 158—159° (Found : C, 80·9; H, 6·1; N, 13·2. $C_{15}H_{14}N_2$ requires C, 81·1; H, 6·3; N, 12·6%).

Quinoline Series. N-2' : 4'-*Dinitro*-1'-*naphthyl*-2-*aminoquinoline*.—Addition of a solution of 1-chloro-2 : 4-dinitronaphthalene (20 g.) in xylene (40 c.c.) to aminoquinoline (23 g.) dissolved in xylene (60 c.c.) caused immediate precipitation of yellow solid. The mixture was boiled under reflux for 1 hour and cooled, and the product collected. The solid (22 g.) remaining after extraction with boiling water to dissolve aminoquinoline hydrochloride was very sparingly soluble in xylene, separating in orange-yellow needles, m. p. 262° (Found : N, 15·5. $C_{19}H_{12}O_4N_4$ requires N, 15·55%), and was used without further purification for ring closure to the corresponding nitrobenzodiazaline (VIII, R = NO_2).

1 : 2-*Quinolo*-7-*nitro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (VIII, R = NO_2).—A mixture of *N*-2' : 4'-dinitro-1'-naphthyl-2-aminoquinoline (5 g.) and diphenyl (10 g.) was heated under reflux in a metal-bath for 1 hour. Oxides of nitrogen and water vapour were evolved simultaneously at 220—230°, the reaction tending towards sudden violence, but although the temperature of the bath was raised ultimately to 260—265° there was no further evolution of brown fumes at the higher temperature. The cooled mass was extracted with hot alcohol to remove diphenyl, and the undissolved *nitrobenzodiazaline* (VIII, R = NO_2) (2·7 g.) crystallised from nitrobenzene, forming pale yellow needles, m. p. >280° (Found : N, 13·8. $C_{19}H_{11}O_2N_3$ requires N, 13·4%).

1 : 2-*Quinolo*-7-*amino*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline*.—The mononitrobenzodiazaline (VIII, R = NO_2) (5 g.), suspended in absolute alcohol (1000 c.c.) preheated to 70°, was reduced catalytically in presence of platinic oxide (0·5 g.) with hydrogen initially at 31 atms.; the resulting solution of monoaminobenzodiazaline had a vivid green fluorescence. The crude base isolated from the concentrate was very sparingly soluble in 2N-sulphuric acid or 2N-hydrochloric acid even at the b. p., but addition of a few drops of hydrochloric acid (*d* 1·2) to the base suspended in water sufficed to produce a clear yellow-green solution. The *aminobenzodiazaline* was reprecipitated with 4N-ammonia; crystallisation from xylene gave yellow needles, m. p. 244—245° (Found : C, 80·65; H, 4·6; N, 14·8; *M*, Rast, not determined, the base being insoluble in camphor. $C_{19}H_{13}N_3$ requires C, 80·6; H, 4·6; N, 14·8%).

1 : 2-*Quinolo*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (VIII, R = H).—1 : 2-Quinolo-7-amino-8 : 9-benzo-4 : 5-benz-1 : 3-diazaline (VIII, R = NO_2) (1·4 g.), dissolved in sulphuric acid (14 c.c., *d* 1·84), was diazotised with sodium nitrite (0·5 g.) in sulphuric acid (5 c.c., *d* 1·84) by addition of the mixed solutions at 0° to phosphoric acid (20 c.c., *d* 1·75). On distillation of alcohol and acetaldehyde from the clear solution formed by reducing a suspension in alcohol (150 c.c.) and water (50 c.c.) of the yellow diazonium salt, precipitated with alcohol–ether from the diazo-solution, a buff-pink solid separated from the cooled concentrate. A solution of this product in boiling 2N-sulphuric acid (200 c.c.) was filtered into 2N-sodium hydroxide, and the resulting base extracted with petroleum (b. p. 100—120°); the unsubstituted *diazaline* (m. p. 164—166°) from the petroleum extract crystallised from the same solvent in buff needles, m. p. 166°, which darkened on exposure (Found : C, 85·15; H, 4·7; N, 10·4; *M*, Rast, 290. $C_{19}H_{12}N_2$ requires C, 85·1; H, 4·5; N, 10·45%; *M*, 268).

iso*Quinoline Series.* *N*-2' : 4'-*Dinitro*-1'-*naphthyl*-1-*amino*iso*quinoline*.—Mixed solutions of 1-amino*iso*quinoline (58 g.) in xylene (150 c.c.) and 1-chloro-2 : 4-dinitronaphthalene (50 g.) in xylene (100 c.c.) were boiled under reflux for 1 hour, then cooled to allow completion of the separation of the products of reaction. The solid (60 g.) remaining after extraction of 1-amino-*iso*quinoline hydrochloride with boiling water crystallised from xylene in nodules of flattened needles, m. p. 232° (Found : C, 64·2; H, 3·9; N, 14·8. $C_{19}H_{12}O_4N_4$ requires C, 63·3; H, 3·3; N, 15·55%), and was used without further purification for transformation into the nitrobenzodiazaline (IX, R = NO_2), oxides of nitrogen having been observed during the foregoing condensation.

1 : 2(2' : 1')-iso*Quinolo*-7-*nitro*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (IX, R = NO_2).—The foregoing *N*-2' : 4'-dinitro-1'-naphthyl-1-amino*iso*quinoline (15 g.) was boiled under reflux in a metal-bath at 245—250° with nitrobenzene (50 c.c.) containing phenol (15 g.) until oxides of

nitrogen were no longer evolved. The golden-yellow *mononitrobenzodiazaline* (IX, R = NO_2) (3 g.) which separated from the cooled mass was washed with alcohol and crystallised from nitrobenzene, forming feathery plates, m. p. >280° (Found: C, 73·1; H, 3·7; N, 13·4. $C_{19}H_{11}O_2N_3$ requires C, 72·8; H, 3·5; N, 13·4%). A solid precipitated with alcohol from the nitrobenzene–phenol filtrate has not been further examined.

1 : 2(2′ : 1′)-iso*Quinolo*-7-*amino*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (IX, R = NH_2).—The mononitrobenzodiazaline (VIII, R = NO_2) (10 g.), suspended in alcohol (2000 c.c.) preheated to 70°, was reduced in presence of platinic oxide (1 g.) with hydrogen initially at 70 atms. The major portion of the product separated from the concentrate; the remainder was isolated by addition of 2N-hydrochloric acid to the filtrate from this separation and precipitation of the solution with 2N-ammonia. The whole was redissolved in 2N-hydrochloric acid, precipitated with 2N-ammonia, washed with water, and boiled with a small amount of petroleum (b. p. 100—120°). The *base* was very sparingly soluble in benzene, but more soluble in xylene, separating from solution in minute, almost colourless needles, m. p. 252—253°. It was precipitated from solution in pyridine by addition of water [Found: C, 80·6; H, 4·8; N, 14·6; *M*, Rast, 338 (not a very accurate determination, the base darkening in camphor). $C_{19}H_{13}N_3$ requires C, 80·6; H, 4·6; N, 14·8%; *M*, 283].

1 : 2(2′ : 1′)-iso*Quinolo*-8 : 9-*benzo*-4 : 5-*benz*-1 : 3-*diazaline* (IX, R = H).—The foregoing monoaminobenzodiazaline (2·8 g.), dissolved in sulphuric acid (40 c.c., *d* 1·84), was diazotised with sodium nitrite (1 g.) in sulphuric acid (10 c.c., *d* 1·84), the mixed solutions being added at −5° to phosphoric acid (40 c.c., *d* 1·75). The colourless diazonium salt, precipitated with alcohol–ether, darkened rapidly. It was reduced in aqueous solution (50 c.c.) with alcohol (150 c.c.) and after distillation of alcohol and acetaldehyde the resulting red solution was filtered from a small quantity of suspended solid and made alkaline with 4N-ammonia. The almost colourless product (1·5 g.), which darkened on exposure, was extracted with petroleum (b. p. 100—120°); the *base* (0·7 g.) from the extract was crystallised from the same solvent and finally from light petroleum (b. p. 40—60°), melting ultimately at 184° but shrinking slightly at 170° (Found: C, 84·7; H, 4·7; N, 10·3; *M*, Rast, 315. $C_{19}H_{12}N_2$ requires C, 85·1; H, 4·5; N, 10·45%; *M*, 268).

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