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

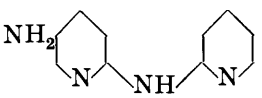
By Sir Gilbert Morgan and Jessie Stewart.

The α-amino-derivatives of pyridine, quinoline, and *iso*quinoline readily obtainable from these bases by the sodamide condensation (Tschitschibabin's reaction) are favourable starting materials in the preparation of substances having a pyridinic or quinolinic structure likely to be of interest as either colour intermediates or therapeutic agents.

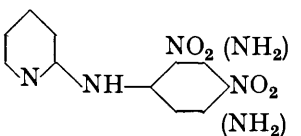
When condensed with 1-chloro-2 : 4-dinitrobenzene, these α-amino-compounds yield sparingly soluble dinitroamines which when suitably solubilised have tinctorial properties towards acetate rayon similar to the Dispersol yellows.

The condensation products with 1-chloro-2 : 4 : 6-trinitrobenzene (picryl chloride) readily lose the elements of nitrous acid to furnish dinitro-derivatives of a new group of hydroaromatic bases—the pyrido(1′ : 2′ : 1 : 2)benziminazoles (cyclic 1 : 3-diazalines). Successive reduction and diazotisation lead to elimination of the nitro-substituents with formation of the parent diamines, of which pyrido(1′ : 2′ : 1 : 2)benziminazole (1 : 2-pyrido-4 : 5-benz-1 : 3-diazaline) is the simplest member. This condensation with picryl chloride has been generalised by application to 2-amino-3-methylpyridine, 2-aminoquinoline, 1-amino*iso*quinoline, and 9-aminophenanthridine, giving rise to increasingly complex 1 : 3-diazalines with three, four, and five rings respectively. The various amino-derivatives of this group of 1 : 3-diazalines are convenient starting points for the synthesis of more complicated heterocyclic bases suitable for trials in chemotherapy.

In an attempt to prepare new bases of the pyridine series utilisable in the production of chemotherapeutic substances, 2-aminopyridine and 5-*amino*-2 : 2′-*dipyridylamine* (I), prepared by catalytic reduction of the corresponding nitro-compound, are each condensed



(I.)



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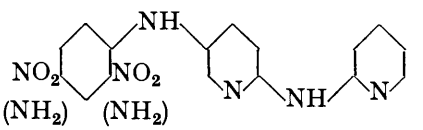
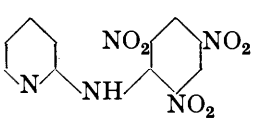
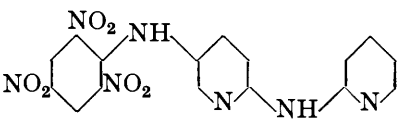


(III.)

with 1-chloro-2 : 4-dinitrobenzene and with 1-chloro-2 : 4 : 6-trinitrobenzene (picryl chloride) to form the corresponding N-2′ : 4′-*dinitrophenyl* (II and III) and N-2′ : 4′ : 6′-*trinitrophenyl* derivatives (IV and V) of the respective primary amines.

(IV.)





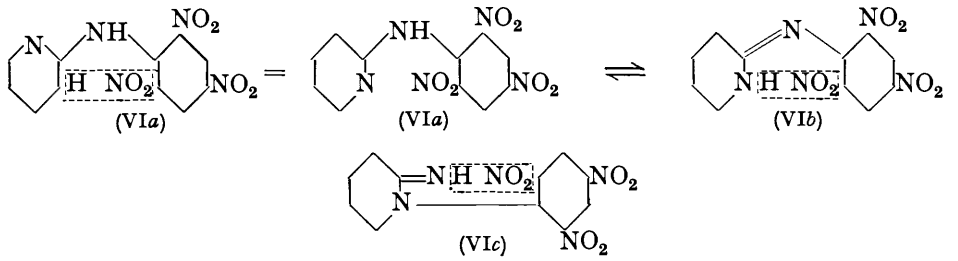
(V.)

A method is worked out for the nitration of 2 : 2′-dipyridylamine to give a mononitro-derivative, the identity of which as 5(or β′)-nitro-2 : 2′-dipyridylamine is established by comparison with the known β-nitro-compound synthesised by Tschitschibabin and Preobrashensky (*Ber.*, 1928, **61**, 199) from 2-aminopyridine and 2-chloro-5-nitropyridine and first prepared by these authors in small quantities by direct nitration of 2 : 2′-dipyridylamine. *N*-2′ : 4′-Dinitrophenyl-2-aminopyridine (II) and *N*-2″ : 4″-dinitrophenyl-5-amino-2 : 2′-dipyridylamine (III) are reduced catalytically in alcoholic suspension with hydrogen under pressure to N-2′ : 4′-*diaminophenyl-2-aminopyridine* (II) and N-2″ : 4″-*diaminophenyl-5-amino-2 : 2′-dipyridylamine* (III).

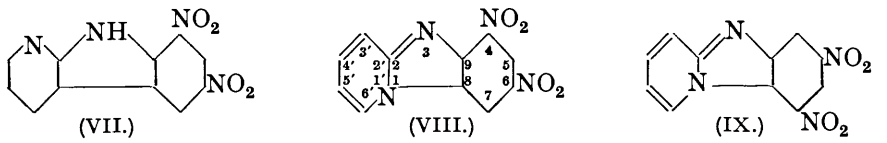
By treatment with methyl iodide *N*-2′ : 4′ : 6′-trinitrophenyl-2-aminopyridine (IV) is converted in alcoholic caustic potash solution into a N-*methyl* derivative, but under comparable conditions *N*-2′ : 4′-dinitrophenyl-2-aminopyridine (II) remains unattacked by methyl iodide.

(I) *Ring Closure with Picryl Derivatives.*—*N*-2′ : 4′ : 6′-Trinitrophenyl-2-aminopyridine (IV) loses the elements of nitrous acid with very great ease, and is converted thereby into a *dinitro*-compound, differing in this respect too from the extremely stable *N*-2′ : 4′-dinitrophenyl-2-aminopyridine (II).

N-Picryl-2-aminopyridine may be represented in the tautomeric forms (VI*a* and VI*b*) on the supposition that the hydrogen atom of the picramido-group migrates to the adjacent



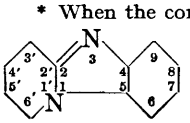
nitrogen atom of the pyridine ring. A dinitro-α-carboline (VII) would result from the loss of nitrous acid from a picryl compound of the former structure (VI*a*), the hydrogen atom withdrawn being from position 3 of the pyridine ring. Ring closure of a picryl compound of



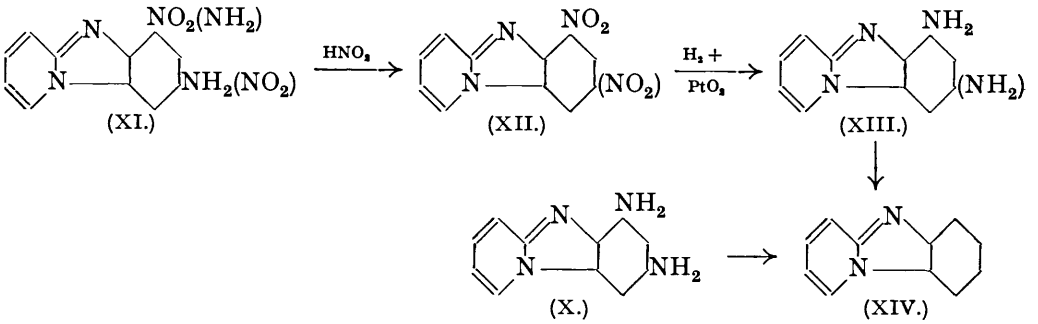
the alternative constitution (VI*b*) would involve the hydrogen attached to the nuclear nitrogen atom of the pyridine ring and a nitro-group in the *o*-position of the benzene ring, giving rise to an isomeric dinitro-compound represented by structure (VIII), to which the designation pyrido(1′ : 2′ : 1 : 2)benziminazole (cyclic 1 : 3-diazaline *) is assigned.

(II) *Cyclic 1 : 3-Diazalines. Pyridine Series.*—Ring closure of *N*-picryl-2-aminopyridine is of the latter type, for the dinitro-compound, 4 : 6-*dinitropyrido*(1′ : 2′ : 1 : 2)*benziminazole* (1 : 2-*pyrido*-7 : 9-*dinitro*-4 : 5-*benz*-1 : 3-*diazaline*) (VIII), into which it passes is reduced catalytically in alcoholic solution with hydrogen under pressure in presence of platinic oxide to the corresponding *primary diamine* (X), and either simultaneous removal of both amino-groups from this diamine, by the method of diazotisation devised by Schoutissen (*J. Amer. Chem. Soc.*, 1933, **55**, 4535), and decomposition of the solid diazonium salt with alcohol, or partial reduction of the dinitro-compound in acetone suspension with aqueous

* When the compound is named as a cyclic 1 : 3-diazaline, the numbering of the ring is as follows:

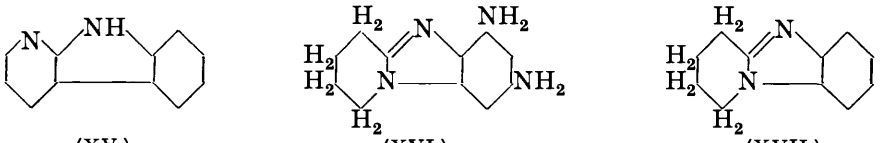


sodium sulphide and sulphur to the *nitroamino*-derivative (XI), followed by successive removal of substituent groups, leads to a base (XIV), m. p. 178—179°, which is not identical



(XI.) (XII.) (XIII.) (X.) (XIV.)

but isomeric with the known α-carboline (XV), m. p. 210°, prepared by Lawson, Perkin, and Robinson (J., 1924, **125**, 626) by pyrolysis of 1-α-pyridylbenztriazole.

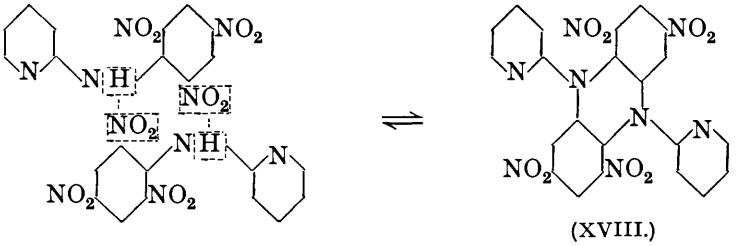


(XV.) (XVI.) (XVII.)

Solutions of the former base, *pyrido*(1′ : 2′ : 1 : 2)*benziminazole* (1 : 2-*pyrido*-4 : 5-*benz*-1 : 3-*diazaline*) (XIV)—the first of a series of colourless cyclic 1 : 3-diazalines prepared from the appropriate picryl derivatives of bases containing cyclic nitrogen and amino-groups in adjacent positions as in 2-aminopyridine—lack the intense blue fluorescence exhibited by solutions of α-carboline in neutral solvents. Characteristic also of α-carboline is the magenta coloration, turning to deep blue, produced when this base (XV) is reduced with sodium and *iso*amyl alcohol and treated with *p*-dimethylaminobenzaldehyde in presence of alcohol and dilute hydrochloric acid. Reduction of the diazaline (XIV) under comparable conditions does not lead to the development of a blue colour with *p*-dimethylaminobenzaldehyde.

Another possible alternative with regard to the formation of *N*-picryl-2-aminopyridine is dismissed as less probable, since it involves the assumption that the picryl residue attaches itself to the nuclear rather than to the substituent nitrogen atom of 2-aminopyridine, the latter reacting in the imino-form. Withdrawal of the elements of nitrous acid from picryl-2-aminopyridine if it were formed in this way (VIc) would give a dinitrodiazaline (IX), isomeric with the 7 : 9-dinitro-compound (VIII) but differing from it only in the positions (6 : 8) of the nitro-groups, so that this isomerism would disappear on removal of the substituent groups from the respective structures (VIII) and (IX).

The molecular weight of the parent diazaline (XIV) determined by the Rast and Beckmann methods is in agreement with the unimolecular structure formulated above and accords with the view that ring closure of picryl-2-aminopyridine with loss of nitrous acid is a unimolecular and not a bimolecular reaction. The latter chemical change would give a



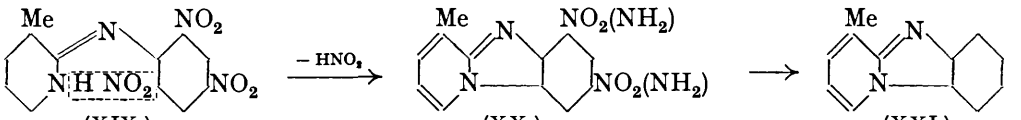
(XVIII.)

substance of a type indicated by the complex structure (XVIII). 4 : 6-Dinitropyrido(1′ : 2′ : 1 : 2)benziminazole [1 : 2-Pyrido-7 : 9-dinitro-4 : 5-benz-1 : 3-diazaline]

(VIII) is reduced catalytically in alcoholic solution with hydrogen under pressure to a *tetrahydro-primary diamine* (XVI), elimination of the amino-groups from the latter diamine resulting in a colourless *base*, m. p. 107°, believed to be 3′ : 4′ : 5′ : 6′-*tetrahydropyrido*-(1′ : 2′ : 1 : 2)*benziminazole* [3′ : 4′ : 5′ : 6′-*tetrahydro*-1 : 2-*pyrido*-4 : 5-*benz*-1 : 3-*diazaline*] (XVII). The preparation of the respective *bis-triazo*-compounds from the diamine and the tetrahydro-diamine supports the view that the double bonds of the pyridine ring become saturated while that at positions 2 and 3 remains unaffected. Were the latter double bond saturated with production of an imino-group at position 3, adjacent to an amino-group at position 4, in all probability ring closure across the 3 and 4 positions would occur on diazotisation. This evidence is admissible only if one amino-group is in position 4. No comparable ring closure would take place in the case of a tetrahydro-5 : 7-diamine, even with an imino-group at position 3.

(III) *Cyclic* 1 : 3-*Diazalines*. β-*Picoline Series*.—Zeide (*Ber.*, 1924, **57**, 1802; compare Philips, *Annalen*, 1895, **288**, 264) has shown that the base (b. p. 95°/8 mm.) prepared by the direct action of sodamide on β-picoline is 2-amino-3-methylpyridine and not 6-amino-3-methylpyridine.

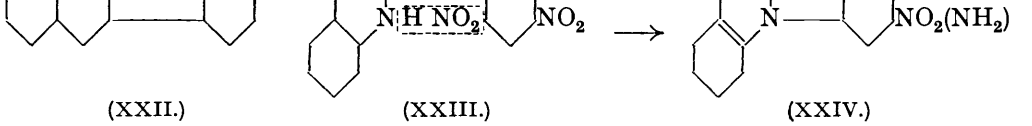
N-2′ : 4′ : 6′-*Trinitrophenyl*-2-*amino*-3-*methylpyridine* (XIX) is the picryl derivative of a base, the structure of which precludes the formation of a substituted α-carboline. Nevertheless it loses the elements of nitrous acid with great facility and undergoes ring closure in a precisely similar manner to that of picryl-2-aminopyridine to the 4 : 6-*dinitro*-3′-*methyl*-



(XIX.) (XX.) (XXI.)

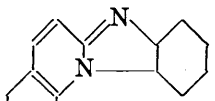
pyrido(1′ : 2′ : 1 : 2)*benziminazole* [3′-*methyl*-1 : 2-*pyrido*-7 : 9-*dinitro*-4 : 5-*benz*-1 : 3-*diazaline*] (XX). This is converted by catalytic reduction into the corresponding *diamine* (XX) and by milder reduction with sodium sulphide and sulphur into the *nitroaminodiazaline*. 3′-*Methylpyrido*(1′ : 2′ : 1 : 2)*benziminazole* [3′-*methyl*-1 : 2-*pyrido*-4 : 5-*benz*-1 : 3-*diazaline*] (XXI) is prepared both by reduction of the bis-diazonium salt from the primary diamine and by successive elimination of substituents from the nitroaminodiazaline.

(IV) *Cyclic* 1 : 3-*Diazalines*. *Quinoline Series*.—N-*Picryl*-2-*aminoquinoline*, like *N*-picryl-2-aminopyridine, offers the possibility of ring closure of α-carboline type as well as of diazaline type, the position adjacent to the amino-group of 2-aminoquinoline carrying an



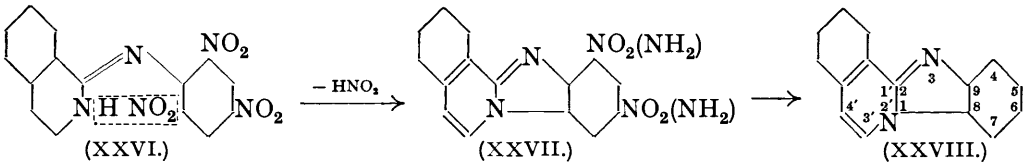
(XXII.) (XXIII.) (XXIV.)

available hydrogen atom. Gabriel and Eschenbach (*Ber.*, 1897, **30**, 3020) and Lawson, Perkin, and Robinson (J., 1924, **125**, 627) have prepared quinindoline (XXII), a benzo-α-carboline crystallising in yellow leaflets, m. p. 346°, the former investigators by reduction and simultaneous ring closure of 2 : 2′-dinitrocyanodibenzyl, the latter by pyrolysis of 1-α-quinolylbenztriazole. Ring closure of *N*-picryl-2-aminoquinoline (XXIII) by loss of the elements of nitrous acid furnishes a *dinitro*-compound (XXIV) of diazaline type. *Quinolo*(1′ : 2′ : 1 : 2)-*benziminazole*(1 : 2-*quinolo*-4 : 5-*benz*-1 : 3-*diazaline*) (XXV), the colourless cyclic 1 : 3-diazaline isomeric with quinindoline (XXII), is obtainable either directly from the corresponding *diamine* (XXIV), which results from catalytic reduction of the dinitro-compound (XXIV); or in successive stages from the nitroaminodiazaline.



(XXV.)

(V) *Cyclic* 1 : 3-*Diazalines. iso*Quinoline *Series.*—N-2′ : 4′ : 6′-*Trinitrophenyl*-1-*amino*-iso*quinoline* (XXVI, tautomeric form) resembles *N*-2′ : 4′ : 6′-trinitrophenyl-2-amino-3-methylpyridine (XIX) in that it is derived from a base, the structure of which permits loss of the elements of nitrous acid from the corresponding picryl compound with ring closure of diazaline type but precludes α-carboline formation, and, like the latter picryl compound, it undergoes with great facility transformation to a *dinitro-diazaline* (XXVII).

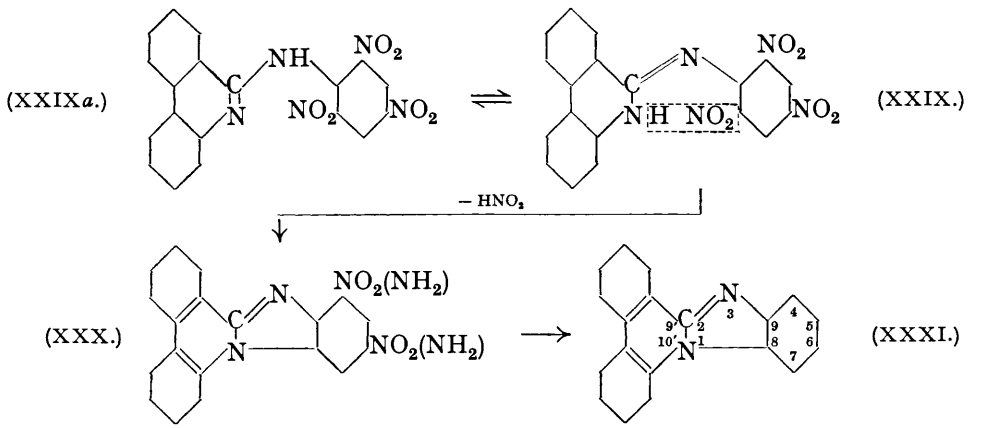


(XXVI.) (XXVII.) (XXVIII.)

Catalytic reduction of an alcoholic suspension of 4 : 6-*dinitro*iso*quinolo*(2′ : 1′ : 1 : 2)-*benziminazole* [1 : 2(2′ : 1′)iso*quinolo*-7′ : 9-*dinitro*-4 : 5-*benz*-1 : 3-*diazaline*] (XXVII) to the corresponding primary *diamine* (XXVII) and subsequent removal of the substituent amino-groups from the latter give the parent base of the series, iso*quinolo*(2′ : 1′ : 1 : 2)*benzimin-azole* [1 : 2(2′ : 1′)iso*quinolo*-4 : 5-*benz*-1 : 3-*diazaline*] (XXVIII).

In the course of this investigation it has been found that coal-tar quinoline, however carefully purified, contains appreciable quantities of *iso*quinoline, and the presence of the latter base makes it extremely difficult to prepare from coal-tar quinoline by the method of Tschitschibabin and Zeide (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1216; Tschitschibabin and Zacepina, *ibid.*, 1920, **50**, 553) 2-aminoquinoline of m. p. 129·5° free from 1-amino*iso*quino-line of m. p. 124—125°. At an early stage of the investigation (*Chem. and Ind.*, 1937, **56**, 670) it was thought that two forms of 2-aminoquinoline had been isolated, the one (m. p. 129·5°) giving an insoluble yellow picryl derivative which did not melt below 280°, the other (the m. p. of which was raised ultimately to 124—125°) giving a readily soluble, brick-red picryl compound, m. p. 154—156°. The latter isomeride is now identified as *N*-picryl-1-amino*iso*quinoline, for there has been prepared from it a cyclic 1 : 3-diazaline, m. p. 129°, identical with the diazaline (XXVIII) obtained from authentic 1-amino*iso*quinoline pre-pared directly from *iso*quinoline. The primary amine from which the diazaline was derived is established as 1-amino*iso*quinoline (compare Tschitschibabin and Oparina, *J. Russ. Phys. Chem. Soc.*, 1920, **50**, 543).

(VI) *Cyclic* 1 : 3-*Diazalines. Phenanthridine Series.*—N-2′ : 4′ : 6′-*Trinitrophenyl*-9-*aminophenanthridine* (XXIX) is derived from a base in which the hydrogen required for α-carboline formation is already replaced by a benzenoid residue of the phenanthridine molecule. Nevertheless this picryl compound, like those of 2-amino-3-methylpyridine and 1-amino*iso*quinoline, loses the elements of nitrous acid with great facility. The dinitro-



derivative into which it is transformed is the corresponding 4 : 6-*dinitrophenanthrido*-(10′ : 9′ : 1 : 2)*benziminazole* [1 : 2(10′ : 9′)-*phenanthrido*-7 : 9-*dinitro*-4 : 5-*benz*-1 : 3-*diaz-*

aline] (XXX). Catalytic reduction of the latter compound to the *diamino-diazaline* (XXX), followed by diazotisation of this base and reduction of the resulting bis-diazonium salt, gives the parent diazaline of the phenanthridine series, *phenanthrido*(10′ : 9′ : 1 : 2)*benziminazole* [1 : 2(10′ : 9′)-*phenanthrido*-4 : 5-*benz*-1 : 3-*diazaline*] (XXXI).

Morgan and Walls (J., 1932, 2227) record anomalies in the behaviour of 9-aminophenanthridine which suggest that the base may not be a true primary amine but an internal amidine. In accordance with this hypothesis, *N*-picryl-9-aminophenanthridine does not exist as represented by structure (XXIX*a*), but in a form which is capable of ring closure to a dinitro-diazaline without prior tautomeric change. Even if it were incorrect in consequence to disregard entirely in this instance the possibility of attachment of the picryl residue to the nuclear nitrogen atom of the heterocyclic ring of the phenanthridine molecule, the question of α-carboline formation does not arise. The only possible isomerism on withdrawal of the elements of nitrous acid is that of (7 : 9) or (6 : 8) substitution in the resulting dinitro-diazaline, and such isomerism disappears on removal of substituent groups from the diamino-diazaline into which the dinitro-diazaline is converted by catalytic reduction.

The values found by the Rast method for the molecular weights of tetrahydropyridobenziminazole [tetrahydro-1 : 2-pyrido-4 : 5-benz-1 : 3-diazaline] (XVII) and of diamino- and parent diazalines of the β-picoline, quinoline, *iso*quinoline, and phenanthridine series are all in agreement with the unimolecular structures formulated above and assigned to these series of substances (compare p. 1294, formula XVIII).

Experimental.

5-Nitro-2 : 2′-dipyridylamine.—2 : 2′-Dipyridylamine was obtained in 55% yield, calculated on the weight of 2-aminopyridine actually condensed, by refluxing equimolecular amounts of 2-aminopyridine and 2-aminopyridine hydrochloride at 250—280° for 6—7 hours. Longer periods were detrimental to the yield and purity of the product (compare Tschitschibabin and Vorobiev, *J. Russ. Phys. Chem. Soc.*, 1920, **50**, 519; Tschitschibabin and Preobrashensky, *Ber.*, 1928, **61**, 199). 5-Nitro-2 : 2′-dipyridylamine was prepared in 58—60% yield by gradual addition, with stirring and cooling to 10°, of nitric acid (49 g., *d* 1·5) in sulphuric acid (300 c.c., *d* 1·84) to 2 : 2′-dipyridylamine (60 g.) in sulphuric acid (600 c.c., *d* 1·84) (cf. Tschitschibabin and Preobrashensky, *loc. cit.*). After three days at room temperature the mixture was poured into water, made almost neutral to Congo-red with 6N-sodium hydroxide, filtered from precipitated dinitro-derivatives, the mononitro-compound separated from the filtrate by further addition of sodium hydroxide, collected, and crystallised from alcohol. There was no depression of m. p. (198°) on admixture of authentic mononitro-derivative from the condensation of 2-aminopyridine with 2-chloro-5-nitropyridine (cf. Tschitschibabin and Preobrashensky, *loc. cit.*).

5-Amino-2 : 2′-dipyridylamine (I).—The foregoing mononitro-compound, suspended in absolute alcohol (6 l.), was reduced at 50° in the presence of platinic oxide (3 g.) or Nuchar charcoal (10 g.) containing colloidal palladium equivalent to palladium chloride (1 g.) with hydrogen under pressure maintained between 15 and 10 atm. until this gas was no longer absorbed. The filtrate from suspended catalyst was distilled to small bulk, the base in the liquid residue precipitated by successive addition of ether and hydrochloric acid (*d* 1·16), and the hydrochloride crystallised from the minimum amount of hot water, deposition of solid being completed by addition of alcohol or alcohol–ether. The colourless *base*, regenerated by precipitation with sodium hydroxide (50%) from a cold aqueous solution of the hydrochloride, was crystallised from benzene–light petroleum (b. p. 40—60°); m. p. 91° (Found : C, 64·6; H, 5·7; N, 29·8. $C_{10}H_{10}N_4$ requires C, 64·5; H, 5·4; N, 30·1%).

N-2′ : 4′-Dinitrophenyl-2-aminopyridine (II).—An intimate mixture of 2-aminopyridine (18 g.) and 1-chloro-2 : 4-dinitrobenzene (40 g.) was heated in an oil-bath to 105°, raised gradually to 120° as the reaction subsided, and maintained at 120° for 2 hours. The mass was extracted successively with water and alcohol until all tarry matter was removed; the residue of *N-2′ : 4′-dinitrophenyl-2-aminopyridine* (II) crystallised from toluene in golden needles, m. p. 156—157° (Found : C, 50·9; H, 3·2; N, 21·8. $C_{11}H_8O_4N_4$ requires C, 50·8; H, 3·1; N, 21·5%). Larger batches of the reagents reacted with such violence that the condensation was repeated in toluene solution as described for the preparation of the analogous trinitro-compound.

N-2″ : 4″-Dinitrophenyl-5-amino-2 : 2′-dipyridylamine (III).—A solution of the base (I) (36 g.) in absolute alcohol (500 c.c.) was boiled under reflux for 3 hours with 1-chloro-2 : 4-dinitro-

benzene (40 g.). The red crystalline product (31 g., m. p. 196°) was collected from the hot reaction mixture. A further deposit (4 g.) of the yellow hydrochloride of the latter substance separated slowly from the cooled filtrate, and from this hydrochloride the red *dinitro*-derivative (3·3 g., m. p. 194°) was regenerated. Crystallisation from toluene raised the m. p. to 198° (Found: C, 54·8; H, 3·4; N, 24·1. $C_{16}H_{12}O_4N_6$ requires C, 54·6; H, 3·4; N, 23·9%).

The dinitroamines (II) and (III) were tested as dyes for acetate rayon by the Dyestuffs Group of Imperial Chemical Industries and found to possess tinctorial properties in common with Dispersol Fast Yellow AS and Dispersol Yellow 3GS.

N-2′ : 4′-*Diaminophenyl*-2-*aminopyridine* (II).—The corresponding dinitro-compound (II) (10 g.), suspended in absolute alcohol (300 c.c.) at 50°, was reduced in the presence of platinic oxide (0·5 g.) or palladium–charcoal (4 g.) by hydrogen at 5—3 atms. until absorption was complete. The filtrate from suspended catalyst was concentrated under reduced pressure, the newly formed *base* separating from the concentrate in minute crystals, m. p. 150° (Found: C, 66·0; H, 6·3; N, 27·7. $C_{11}H_{12}N_4$ requires C, 66·0; H, 6·0; N, 28·0%).

N-2″ : 4″-*Diaminophenyl*-5-*amino*-2 : 2′-*dipyridylamine* (III).—The corresponding dinitro-compound (III) was reduced catalytically in alcoholic suspension to the primary *diamine* (m. p. 187°) in a manner similar to that described for the reduction of the analogous dinitrophenyl-2-aminopyridine (Found: C, 65·0; H, 5·4; N, 28·4. $C_{16}H_{16}N_6$ requires C, 65·75; H, 5·5; N, 28·8%).

N-2′ : 4′ : 6′-*Trinitrophenyl*-2-*aminopyridine* (IV).—A solution of picryl chloride (48 g.; 1 mol.) in benzene (150 c.c.) was added gradually to 2-aminopyridine (36 g.; 2 mols.) dissolved in benzene (150 c.c.), and boiled under reflux for 1 hour. The benzene solution of *N*-picryl-2-aminopyridine was decanted at room temperature from aminopyridine hydrochloride precipitated during condensation, and crystallisation was promoted by concentration and finally by precipitation with light petroleum (b. p. 40—60°). Recrystallised from benzene solution, the *picryl* compound formed large rhombic crystals, m. p. 135° (Found: C, 43·4; H, 2·5; N, 23·0. $C_{11}H_7O_6N_5$ requires C, 43·3; H, 2·3; N, 22·95%). A concentrated aqueous solution of that portion of the original base recovered as hydrochloride was precipitated with solid sodium hydroxide, and the aminopyridine purified by crystallisation from benzene and distillation under reduced pressure.

N-2″ : 4″ : 6″-*Trinitrophenyl*-5-*amino*-2 : 2′-*dipyridylamine* (V).—Solutions of picryl chloride (2·5 g.) and 5-amino-2 : 2′-dipyridylamine (I) (3·7 g.) each in dry toluene (50 c.c.) were mixed and boiled for ½ hour. The *picryl* compound (V), which separated from the hot filtrate in ruby-red plates, was recrystallised from toluene; m. p. 224° (Found: C, 48·45; H, 2·7; N, 23·5, 23·0. $C_{16}H_{11}O_6N_7$ requires C, 48·4; H, 2·8; N, 24·7%).

N-2′ : 4′ : 6′-*Trinitrophenyl*-N-*methyl*-2-*aminopyridine*.—Methyl iodide (4·5 c.c.) was added to the deep red solution of picryl-2-aminopyridine (IV) (10 g.) in absolute alcohol (260 c.c.) containing potassium hydroxide (2 g.). Methylation took place readily on warming with precipitation of bright red needles, but a further addition of methyl iodide was made after 2 hours to ensure completion of this reaction. The crude product (8·3 g.) was washed with alcohol, crystallised from nitrobenzene and finally from alcohol; m. p. 243° (Found: C, 45·1; H, 3·0; N, 21·8. $C_{12}H_9O_6N_5$ requires C, 45·1; H, 2·8; N, 21·95%).

Pyrido(1′ : 2′ : 1 : 2)benziminazoles.

4 : 6-*Dinitropyrido*(1′ : 2′ : 1 : 2)*benziminazole* (VIII).—A solution of picryl-2-aminopyridine (VI*a* or VI*b*) (50 g.) in dimethylaniline (100 c.c.) was boiled under reflux for 2—2½ hours, oxides of nitrogen being evolved. The *dinitro-diazaline* crystallised almost quantitatively from the boiling mixture and after being washed successively with dimethylaniline and alcohol and recrystallised from nitrobenzene, formed bright yellow needles (35 g.), m. p. > 300° (Found: C, 51·4; H, 2·7; N, 21·7. $C_{11}H_6O_4N_4$ requires C, 51·2; H, 2·3; N, 21·7%). Dimethylaniline in nitrobenzene, phenol in nitrobenzene, and phenol alone were equally effective reagents for the withdrawal of the elements of nitrous acid from the picryl compound.

Loss of nitrous fumes and formation of a product identical with the foregoing dinitro-diazaline (VIII) occurred when picryl-2-aminopyridine (7 g.) was heated gradually to its m. p. (135°) in an air-oven, maintained at that temperature till frothing had ceased and the mass resolidified, then gradually raised to 200—220°. The solid (m. p. > 300°) was crystallised from nitrobenzene (Found: C, 51·7; H, 2·95; N, 21·4%).

When benzene was replaced by toluene as solvent in the foregoing condensation between picryl chloride and 2-aminopyridine, oxides of nitrogen were evolved and the aminopyridine hydrochloride which separated was admixed with appreciable quantities of the dinitro-diazaline

(VIII); the latter was purified by aqueous extraction of aminopyridine hydrochloride and crystallised from nitrobenzene (Found: C, 51·8; H, 2·8; N, 21·05%).

4 : 6-*Diaminopyrido*(1′ : 2′ : 1 : 2)*benziminazole* (X).—A suspension of the foregoing dinitro-diazaline (VIII) (10 g. in absolute alcohol, 2 l.) was preheated to the b. p. and then allowed to absorb hydrogen in presence of platinic oxide (0·45 g.) in an autoclave (working capacity, 2½ l.) until the pressure had fallen from 5 to 1 atm. After filtration from suspended catalyst the solution was concentrated to small bulk and the newly formed *diamine*, which separated rapidly on cooling, was collected, washed repeatedly with light petroleum (b. p. 40—60°), crystallised from xylene, in which it was sparingly soluble, and finally from absolute alcohol, forming yellow needles, m. p. 204—205° [Found: C, 66·44; H, 4·8; N, 28·47 (total, 99·71). $C_{11}H_{10}N_4$ requires C, 66·66; H, 5·05; N, 28·28% (total, 99·99)].

4 : 6(or 6 : 4)-*Nitroaminopyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XI).—A solution of sodium sulphide (24 g.) in boiling water (100 c.c.) containing flowers of sulphur (12 g.) was added slowly to a hot suspension of finely powdered dinitro-diazaline (VIII) (20 g.) in acetone (100 c.c.), and the mixture boiled under reflux for 2 hours. A red solid, collected after removal of acetone, was washed with water, dissolved in 4N-sulphuric acid, and reprecipitated with 4N-ammonia. When crystallised from nitrobenzene, the resulting *base* (13 g.) separated in dark red needles, m. p. > 280° (Found: C, 58·3; H, 3·7; N, 22·8. $C_{11}H_8O_2N_4$ requires C, 57·9; H, 3·5; N, 24·6%). This nitroamine was used without further purification for elimination of the amino-group.

4(or 6)-*Nitropyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XII).—This nitro-diazaline was prepared originally by boiling the foregoing finely powdered nitroamino-diazaline (32 g.) with hydrochloric acid (40 c.c., *d* 1·16) and water (100 c.c.) and, after rapid cooling and addition of ice (100 g.), diazotising the salt by the rapid introduction of sodium nitrite (12 g.) in water (100 c.c.). The excess of sodium nitrite was destroyed with urea and the yellow solution of the diazonium chloride was reduced by warming with absolute alcohol (400 c.c.), filtered from suspended brown solid, and rendered alkaline with 2N-ammonia. Bright yellow *mononitro-diazaline* was dissolved out from the resulting crude material (25—26 g.) by repeated extraction with toluene (Found: C, 62·0; H, 3·4; N, 19·8. $C_{11}H_7O_2N_3$ requires C, 62·0; H, 3·3; N, 19·7%). Later it was found advantageous to employ the method of diazotisation devised by Schoutissen (*loc. cit.*) and accordingly solutions at — 10° of the nitroamino-diazaline (13·8 g.) and sodium nitrite (6 g.), each in sulphuric acid (60 c.c., *d* 1·84), were mixed and added dropwise with stirring to well-cooled phosphoric acid (180 c.c., *d* 1·75), the temperature not being allowed to exceed + 5°. The yellow diazonium salt, precipitated by addition of the diazotised solution to a well-cooled mixture of alcohol and ether, was reduced by boiling with alcohol–water (50%), and the solution left overnight to allow of complete separation of coloured material, and filtered; the yellow mononitro-diazaline (11·5 g., m. p. 260—262°), precipitated at 60° by addition of 4N-ammonia, was recrystallised from pyridine.

4(or 6)-*Aminopyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XIII).—A suspension of finely powdered mononitro-diazaline (XII) (10 g.) in absolute alcohol (1600 c.c.) was reduced catalytically at 70° in presence of platinic oxide (0·45 g.) by hydrogen at 5—3 atms. until absorption of gas had ceased. The filtrate from suspended catalyst deposited the *amine* on concentration. The latter (7 g.), washed free from tarry matter with light petroleum (b. p. 40—60°) and crystallised from xylene, separated in lustrous yellow needles (5 g.), m. p. 229—230°. It has not yet been ascertained whether the colour is due entirely to superficial oxidation of the base, for it was not diminished appreciably by repeated washing with petroleum [Found: C, 72·3; H, 5·06; N, 23·0 (total, 100·36). $C_{11}H_9N_3$ requires C, 72·13; H, 4·92; N, 22·95%].

Pyrido(1′ : 2′ : 1 : 2)*benziminazole* (XIV).—This base, the parent diazaline of the pyridine series, was prepared originally by diazotising a paste of the monoamino-diazaline (XIII) (0·9 g.), hydrochloric acid (1 c.c., *d* 1·16), and water (1 c.c.) at — 5° with sodium nitrite (0·4 g.) in water (2 c.c.) and destroying the excess of nitrite with urea. The filtered solution of diazonium chloride was reduced by boiling with absolute alcohol in presence of aluminium powder, refiltered, made alkaline with 2N-sodium hydroxide, and evaporated to drynesss. The crude brown residue gave a blue fluorescence with alcohol, benzene, toluene or light petroleum, but colourless long slender needles of the *diazaline* (XIV), m. p. 178—179°, isolated by sublimation, dissolved sparingly in water, and in organic solvents to solutions which were practically non-fluorescent. The base was readily soluble in dilute mineral acids [Found: C, 78·37; H, 5·0; N, 16·36 (total, 99·73); *M*, 201 (Rast method), 160 (Beckmann method). $C_{11}H_8N_2$ requires C, 78·57; H, 4·76; N, 16·66%; *M*, 168].

When it was found advantageous to diazotise amino-diazalines in presence of phosphoric acid (cf. Schoutissen, *loc. cit.*), mixed solutions of monoamino-diazaline (XIII) (1·8 g.) and sodium

nitrite (1 g.), each in sulphuric acid (10 c.c., *d* 1·84), were added at − 10° to phosphoric acid (20 c.c.), the temperature not being allowed to exceed + 5°. The white diazonium salt isolated by addition of the diazotised solution of the monoamine to well-cooled alcohol–ether, was dissolved in water and reduced with alcohol. Volatile organic liquids were removed by distillation, the residual liquid filtered from coloured material and concentrated to half the original volume, and the crude product precipitated with sodium hydroxide solution (50%). It was extracted in petroleum (b. p. 100—120°) and crystallised (1·2 g.) from light petroleum (b. p. 40—60°), and the crude diazaline (0·8 g.) purified by crystallisation from water, from light petroleum (b. p. 40—60°), and finally by sublimation to give colourless needles (m. p. 179°) identical with the base prepared by reduction of the diazonium chloride from the monoamine (XIII).

The diazaline prepared by simultaneous removal of two substituent amino-groups from the diamine (X) by addition with constant stirring of mixed solutions of diamine (1 g.) in sulphuric acid (5 c.c., *d* 1·84) and sodium nitrite (0·7 g.) in sulphuric acid (7 c.c., *d* 1·84) to phosphoric acid (20 c.c.) initially at − 10°, the temperature not being allowed to exceed 0°, was identical with that obtained from the monoamine. For its isolation the diazonium solution, diluted by pouring on ice, was reduced by boiling with alcohol. Volatile solvents were distilled off, and the liquid made alkaline with aqueous ammonia (*d* 0·88) and extracted with ether. The residue after removal of ether was dissolved in 2N-hydrochloric acid, and the solution decolourised with wood charcoal and made alkaline with 2N-ammonia. The crude diazaline (m. p. 170°) purified by sublimation formed colourless needles, m. p. 178—179° either alone or admixed with the diazaline from the monoamine of the series.

Pyrido(1′ : 2′ : 1 : 2)benziminazole (XIV) has been compared with α-carboline (XV) (Lawson, Perkin, and Robinson, *loc. cit.*). The authors are indebted to Professor Robinson for a specimen of the latter base. The m. p. (178—179°) of the diazaline was depressed by admixture of α-carboline (m. p. 210°); that of the picrate prepared from the diazaline was depressed by admixture of the picrate from α-carboline. The vapour of the diazaline possessed a characteristic odour of aniseed type, that of α-carboline was odourless. Unlike α-carboline, the diazaline did not exhibit pronounced blue fluorescence when dissolved in neutral solvents, nor did it on reduction develop the characteristic deep blue coloration with *p*-dimethylaminobenzaldehyde.

4 : 6-*Diamino*-3′ : 4′ : 5′ : 6′-*tetrahydropyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XVI).—A suspension of the dinitro-diazaline (VIII) (30 g.) in absolute alcohol (400 c.c.) was reduced at 50° in presence of platinic oxide (0·6 g.) by hydrogen at 10—8 atms. until absorption of gas had ceased. The crude *diamine* (m. p. 193°), which possessed a light green-yellow superficial coloration, crystallised from pyridine in well-defined needles, m. p. 201—202°, depressed by admixture of the diamino-diazaline (X) (m. p. 205°), and dissolved in 2N-hydrochloric acid on warming to a sparingly soluble hydrochloride, separable from the cooled solution, in this respect differing from the hydrochloride of the diamine (X). Crude acetyl derivatives of the two diamines depressed one another in m. p. [Found: C, 65·03; H, 6·75; N, 28·2 (total, 99·98); *M* (Rast method), 287. $C_{11}H_{14}N_4$ requires C, 65·34; H, 6·93; N, 27·73%; *M*, 202].

Attempts to reduce the tetrahydrodiamino-diazaline (XVI) catalytically to the hexahydro-state by submitting it to pressures of 30, 40, 50, 70 atms. of hydrogen at 70° and finally 120 atms. at 100° were unsuccessful. At pressures up to 70 atms. the base became colourless, but under more intensive treatment a brown superficial coloration developed [Found: C, 65·85; H, 6·45; N, 27·8% (total, 100·10)].

When submitted to an initial pressure of 120 atms. of hydrogen and raised to 200°, an alcoholic suspension of the dinitro-diazaline (VIII) was not reduced catalytically beyond the tetrahydro-diamino-state.

3′ : 4′ : 5′ : 6′-*Tetrahydropyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XVII).—The tetrahydrodiamino-diazaline (XVI) (3 g.) in sulphuric acid (15 c.c., *d* 1·84) was diazotised at 0° by the method of Schoutissen (*loc. cit.*) using sodium nitrite (2·8 g.) in sulphuric acid (28 c.c., *d* 1·84) and phosphoric acid (50 c.c.). The diazonium salt (originally yellow but rapidly turning red) precipitated by addition of the diazonium solution to alcohol–ether was reduced in aqueous solution by boiling with alcohol. Volatile organic liquids were distilled off, and the crude *diazaline* precipitated from the filtered solution by addition of ammonia, dried in a vacuum over sulphuric acid, and purified by extraction with petroleum (b. p. 100—120°) and finally by sublimation, to form white plates, m. p. 107°, depressed by admixture of the unreduced diazaline (XIV) [Found: C, 76·38; H, 6·85; N, 16·77 (total, 100·00); *M* (Rast method), 210. $C_{11}H_{12}N_2$ requires C, 76·74; H, 6·98; N, 16·27%; *M*, 172].

4 : 6-*Bistriazopyrido*(1′ : 2′ : 1 : 2)*benziminazole*.—The diamino-diazaline (X) (0·5 g.) in sulphuric acid (2·5 c.c., *d* 1·84) was diazotised at − 15° with sodium nitrite (0·4 g.) in sulphuric

acid (4 c.c., *d* 1·84) by addition of the mixed solutions to phosphoric acid (10 c.c.). After addition of urea the diazonium solution was poured on ice, and an aqueous solution of sodium azide (0·35 g.) added; after evolution of nitrogen, addition of 4N-ammonia precipitated the colourless *bistriazo*-compound (decomp. 167°), which darkened rapidly and crystallised from petroleum (b. p. 80—100°) in needles, decomp. 167—170° [Found: C, 53·37; H, 3·04; N, 43·96 (total, 100·37). $C_{11}H_6N_8$ requires C, 52·8; H, 2·4; N, 44·8%].

4 : 6-*Bistriazo*-3′ : 4′ : 5′ : 6′-*tetrahydropyridobenziminazole*.—The tetrahydrodiamino-diazaline (XVI) (1 g.) in sulphuric acid (5 c.c., *d* 1·84) was converted similarly into the corresponding *bistriazo*-compound by sodium nitrite (0·8 g.) in sulphuric acid (8 c.c., *d* 1·84), phosphoric acid (20 c.c.), and sodium azide (0·7 g.) in aqueous solution. The crude product darkened on exposure, but crystallised from petroleum (b. p. 100—120°) in well-defined slender needles, p. 132°, depressed by admixture of the bistriazo-compound prepared from the diamino-diazaline (X) [Found: C, 52·86; H, 4·44; N, 42·7 (total, 100·00). $C_{11}H_{10}N_8$ requires C, 51·97; H, 3·93; N, 44·09%].

3′-*Methylpyrido*(1′ : 2′ : 1 : 2)*benziminazoles*.

N-2′ : 4′ : 6′-*Trinitrophenyl*-2-*amino*-3-*methylpyridine* (XIX).—Solutions of 2-amino-3-methylpyridine (86 g.) and picryl chloride (100 g.), each in benzene (400 c.c.), were condensed in the usual manner, the yellow product N-*picryl*-2-*amino*-3-*methylpyridine* (XIX) (m. p. 142—143° and subsequent solidification at 180°) being separated from the final benzene concentrate by precipitation and repeated washing with light petroleum (b. p. 40—60°) and crystallised from benzene–light petroleum (b. p. 40—60°) (Found: C, 45·3; H, 2·7; N, 21·9. $C_{12}H_9O_6N_5$ requires C, 45·1; H, 2·8; N, 21·9%).

4 : 6-*Dinitro*-3′-*methylpyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XX).—Picryl-2-amino-3-methylpyridine (XIX) (50 g.) was converted into the corresponding *dinitro-diazaline* (XX) by the action of phenol (25 g.) in dry xylene (50 c.c.). The reaction was less smooth than in the pyridine series. The crude material crystallised from nitrobenzene to give ultimately yellow needles, m. p. 256—260° (Found: C, 53·2; H, 3·0; N, 20·6. $C_{12}H_8O_4N_4$ requires C, 52·9; H, 2·9; N, 20·6%).

4 : 6-*Diamino*-3′-*methylpyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XX).—A suspension of the dinitro-diazaline (XX) in absolute alcohol (2 l.) was reduced at 70° in presence of platinic oxide (0·45 g.) by hydrogen initially at 5 atms. to the corresponding *diamino-diazaline* (7·3 g.), a dark green-black base more difficult to purify than the diamino-diazalines of the pyridine, quinoline, and *iso*quinoline series. A sample was isolated as a yellow solid by extraction of the crude base (2 g.) with xylene and analysed after crystallisation from benzene (the m. p. was indefinite, but approximately 130°, the base darkening rapidly on heating) (Found: C, 67·8; H, 5·9; N, 24·7. $C_{12}H_{12}N_4$ requires C, 67·9; H, 5·7; N, 26·4%). The remainder was used without further purification for diazotisation and elimination of substituent groups.

4 : 6(or 6 : 4)-*Nitroamino*-3′-*methylpyrido*(1′ : 2′ : 1 : 2)*benziminazole*.—The dinitro-diazaline (XX) (8 g.) in acetone (250 c.c.) was reduced with sodium sulphide (9 g.) and sulphur (4·5 g.) in boiling water (50 c.c.). The *nitroamino-diazaline* present in the red solid collected after distillation of acetone was purified by precipitation with ammonia from a solution in 6N-sulphuric acid and used for conversion into nitro-diazaline. For analysis, a portion of the product (5·5 g. in all) was crystallised from pyridine and finally from xylene; m. p. 269—270° (Found: C, 59·5; H, 4·1; N, 22·4, 22·1. $C_{12}H_{10}O_2N_4$ requires C, 59·5; H, 4·1; N, 23·1%).

4(or 6)-*Nitro*-3′-*methylpyrido*(1′ : 2′ : 1 : 2)*benziminazole*.—For diazotisation, solutions of the foregoing nitroamino-diazaline (13·8 g.) and sodium nitrite (6 g.), each in sulphuric acid (60 c.c., *d* 1·84), were mixed at — 10°, added slowly to phosphoric acid (180 c.c.) cooled to — 5°, and poured into alcohol–ether to precipitate the yellow diazonium salt, an aqueous solution of which (300 c.c.) was reduced by boiling with alcohol (250 c.c.). The cooled filtrate from the reduction was made alkaline with 4N-ammonia, and the pale yellow *nitro-diazaline* (11·3 g.), m. p. 260—262°, crystallised from pyridine and finally—for analysis—from xylene (Found: N, 18·4, 18·9. $C_{12}H_9O_2N_3$ requires N, 18·5%).

4(or 6)-*Amino*-3′-*methylpyrido*(1′ : 2′ : 1 : 2)*benziminazole*.—The corresponding nitro-diazaline (8 g.), suspended in boiling absolute alcohol (1600 c.c.), was reduced catalytically at 70° with hydrogen initially at 5 atms. and in presence of platinic oxide (0·4 g.). The crude yellow primary *monoamine* (5·5 g.), m. p. 185—187°, isolated by concentration of the filtrate from suspended catalyst, was crystallised from toluene (yielding 3·2 g.) for conversion into the parent diazaline (XXI) and again from petroleum (b. p. 100—120°) for analysis [Found: C, 73·33; H, 5·62; N, 20·54 (total, 99·49). $C_{12}H_{11}N_3$ requires C, 73·09; H, 5·58; N, 21·32%].

3′-*Methylpyrido*(1′ : 2′ : 1 : 2)*benziminazole* (XXI).—Solutions of the foregoing amino-diazaline (1·5 g.) in sulphuric acid (15 c.c., *d* 1·84) and sodium nitrite (0·8 g.) in sulphuric acid (8 c.c., *d* 1·84) were mixed at − 5° and added very slowly to phosphoric acid (20 c.c.), the temperature being kept between − 5° and + 5°. The white diazonium salt precipitated by addition of the diazonium solution to alcohol–ether rapidly turned yellow; it was dissolved in water to a yellow solution (50 c.c.) and reduced by boiling with alcohol (100 c.c.). After distillation of volatile organic liquids the cooled filtrate was made alkaline with aqueous ammonia (*d* 0·88) and the red-brown solid dried and extracted with petroleum (b. p. 80—100°), the extract depositing, after removal of solvent, almost colourless needles, m. p. 150°; repeated crystallisation from light petroleum (b. p. 40—60°) yielded finally colourless needles, m. p. 162°, of the parent *diazaline* (XXI) [Found: C, 79·14; H, 5·33; N, 15·45 (total, 99·92); *M* (Rast method), 184. $C_{12}H_{10}N_2$ requires C, 79·12; H, 5·49; N, 15·38%; *M*, 182]. This diazaline was identical with the parent base [Found: C, 79·14; H, 5·63; N, 15·24%; *M* (Rast method), 200] isolated from the diamino-diazaline (XX) of the same series by diazotising the latter compound (2·1 g.) in sulphuric acid (10 c.c., *d* 1·84) with sodium nitrite (1·7 g.) in sulphuric acid (17 c.c., *d* 1·84) in presence of phosphoric acid (40 c.c.) at − 10° to + 10° and reducing an aqueous solution of the resulting bisdiazonium salt with alcohol. The slightly lower m. p. (158—159°) of the diazaline prepared directly from the diamino-diazaline (XX) was not depressed by admixture of that from the primary monoamine.

Quinolo(1′ : 2′ : 1 : 2)*benziminazoles.*

N-2′ : 4′ : 6′-*Trinitrophenyl-2-aminoquinoline* (XXIII).—2-Aminoquinoline (m. p. 129·5°) was prepared from coal-tar quinoline by the direct action of sodamide (cf. Tschitschibabin and Zeide; Tschitschibabin and Zacepina; *locc. cit.*) and freed from admixed 1-amino*iso*quinoline by dissolving out the latter impurity in benzene at room temperature and crystallising the undissolved 2-aminoquinoline repeatedly from hot benzene (Found: C, 74·6; H, 6·0; N, 19·5, 19·7. Calc. for $C_9H_8N_2$: C, 75·0; H, 5·5; N, 19·4%). When the base (100 g.; 2 mols.) in boiling benzene solution (400 c.c.) was condensed with picryl chloride (85 g.; 1 mol.) in benzene (200 c.c.), *picryl-2-aminoquinoline* separated, together with 2-aminoquinoline hydrochloride. The latter was extracted with hot water and the remaining yellow picryl compound (XXIII) (m. p. > 280°) (Found: C, 52·0; H, 2·8; N, 18·5. $C_{15}H_9O_6N_5$ requires C, 50·7; H, 2·5; N, 19·7%) was used without further purification from possible traces of dinitro-diazaline (XXIV) for complete conversion into the latter dinitro-diazaline.

4 : 6-*Dinitroquinolo*(1′ : 2′ : 1 : 2)*benziminazole* (XXIV).—Equal weights of picryl-2-amino-quinoline and phenol suspended in dry xylene, when heated together until evolution of oxides of nitrogen had ceased, passed into solution, the former to be reprecipitated as the sparingly soluble *dinitro-diazaline* (XXIV), yellow needles when crystallised from nitrobenzene; m. p. > 300° (Found: C, 58·2; H, 2·5; N, 18·1. $C_{15}H_8O_4N_4$ requires C, 58·4; H, 2·6; N, 18·2%).

4 : 6-*Diaminoquinolo*(1′ : 2′ : 1 : 2)*benziminazole* (XXIV).—A suspension of the dinitro-diazaline (XXIV) (8 g.) in absolute alcohol (1200 c.c.) was reduced catalytically at 70—80° in presence of platinic oxide (0·4 g.) by hydrogen initially at 31 atms. to a solution containing the corresponding primary *diamine*, which after filtration from suspended catalyst and concentration to small bulk deposited yellow feathery needles, m. p. 273—274°, in 75% yield. A sample was crystallised from toluene for analysis (m. p. unchanged thereby) [Found: C, 72·64; H, 4·89; N, 22·52 (total, 100·05). $C_{15}H_{12}N_4$ requires C, 72·58; H, 4·84; N, 22·58%]. The main bulk was recrystallised from pyridine–light petroleum (b. p. 40—60°).

4 : 6(or 6 : 4)-*Nitroaminoquinolo*(1′ : 2′ : 1 : 2)*benziminazole*.—The dinitro-diazaline (XXIV) (9 g.) in acetone (250 c.c.) was reduced with sodium sulphide (9 g.) and sulphur (4·5 g.) in water (50 c.c.). The brick-red nitroamino-diazaline, m. p. > 300°, extracted with pyridine from the solid remaining after distillation of acetone was crystallised from pyridine, precipitation being completed by addition of water, and used without further purification for conversion into the mononitrodiazaline.

4(or 6)-*Nitroquinolo*(1′ : 2′ : 1 : 2)*benziminazole*.—Solutions of the nitroamino-diazaline (5·5 g.) in sulphuric acid (25 c.c., *d* 1·84) and sodium nitrite (1·6 g.) in sulphuric acid (16 c.c., *d* 1·84), mixed and added at − 10° to phosphoric acid (100 c.c.), yielded a diazo-solution which, when poured gradually (after addition of urea) into alcohol–ether, yielded the yellow diazonium salt. This was reduced with alcohol–water (50%). The *mononitro-diazaline* (3·8 g.), collected and crystallised from toluene, absolute alcohol, and finally toluene, formed yellow needles (3·0 g.), m. p. 242—243° (Found: C, 67·7; H, 3·6; N, 16·3. $C_{15}H_9O_2N_3$ requires C, 68·4; H, 3·4; N, 16·0%).

4(or 6)-*Aminoquinolo*(1′ : 2′ : 1 : 2)*benziminazole*.—The foregoing mononitro-diazaline (6·3 g.) was reduced catalytically at 70° in absolute alcohol suspension (2 l.) in presence of platinic oxide (0·4 g.) with hydrogen initially at 31 atms. The filtered solution was concentrated to 25 c.c. without separation of the diamine. Addition of ether gave a small yellow-brown solid, but the main fraction (4·7 g.) was precipitated by introduction of 2N-sodium hydroxide. Crystallisation from toluene formed needles, m. p. 220—223°, darker in colour than the crude material. Solution in 2N-hydrochloric acid at room temperature and precipitation with 2N-sodium hydroxide restored the pale yellow colour but lowered the m. p. to 130°, a change suggestive of possible hydrate formation, reversed by crystallisation of the dried material from toluene, absolute alcohol, or dry pyridine to yield yellow-green needles, m.p. 223° [Found : C, 76·9; H, 5·0; N, 17·8 (total, 99·7). $C_{15}H_{11}N_3$ requires C, 77·25; H, 4·7; N, 18·0%].

Quinolo(1′ : 2′ : 1 : 2)*benziminazole* (XXV).—The parent diazaline (XXV) of this series was best prepared by diazotising the foregoing monoamine (1·15 g.) in sulphuric acid (6 c.c., *d* 1·84) at — 15° with sodium nitrite (0·5 g.) in sulphuric acid (5 c.c., *d* 1·84) in presence of phosphoric acid (20 c.c.), precipitating the white diazonium salt by addition of the diazo-solution to alcohol–ether, and reducing the latter solid with alcohol–water (50%). The colourless *diazaline* (XXV) precipitated from the filtrate after distillation of volatile liquids, and purified by repeated crystallisation from light petroleum (b. p. 40—60°) to give a product (0·55 g.) of m. p. 92°, followed by crystallisation from 50% alcohol–water (and decolourisation with wood charcoal), yielded colourless needles, m. p. 102° [Found : C, 82·5; H, 4·5; N, 12·4; *M* (Rast method), 238. $C_{15}H_{10}N_2$ requires C, 82·6; H, 4·6; N, 12·8%; *M*, 218], depressed by admixture with quinindoline (XXII) (for which sample, yellow leaflets, m. p. 346°, the authors are indebted to Professor Robinson), the benzo-α-carboline with which this diazaline of the quinoline series is isomeric.

The identical diazaline (XXV) was also obtained in small yield directly from the diamino-diazaline (XXIV) by elimination of both amino-groups by diazotisation of the latter base (1·24 g.) in sulphuric acid (8 c.c., *d* 1·84) at — 10° to 0° with sodium nitrite (0·8 g.) in sulphuric acid (8 c.c., *d* 1·84) in presence of phosphoric acid (20 c.c.) and decomposition of the diazonium salt with 50% alcohol–water. This diazaline becomes faintly yellow on exposure to light and air.

iso*Quinolo*(2′ : 1′ : 1 : 2)*benziminazole*.

N-2′ : 4′ : 6′-*Trinitrophenyl*-1-*amino*iso*quinoline* (XXVI).—Solutions of 1-amino*iso*quinoline (m. p. 123°), prepared by the direct action of sodamide on *iso*quinoline (Tschitschibabin and Oparina, *J. Russ. Phys. Chem. Soc.*, 1920, **50**, 543) (100 g.; 2 mols.), and picryl chloride (85 g.; 1 mol.), each in benzene (400 c.c.), were condensed to give amino*iso*quinoline hydrochloride and a solution from which red rhombic crystals of *picryl*-1-*amino*iso*quinoline* (XXVI), m. p. 156°, separated (Found : C, 51·5; H, 2·8; N, 19·4. $C_{15}H_9O_6N_5$ requires C, 50·7; H, 2·5; N, 19·7%).

4 : 6-*Dinitro*iso*quinolo*(2′ : 1′ : 1 : 2)*benziminazole* (XXVII), prepared by withdrawal of the elements of nitrous acid from the foregoing picryl compound (XXVI) suspended in xylene in presence of phenol, crystallised from nitrobenzene in golden flattened needles, m. p. > 280° (Found : C, 58·95; H, 2·8; N, 18·0. $C_{15}H_8O_4N_4$ requires C, 58·4; H, 2·6; N, 18·2%).

4 : 6-*Diamino*iso*quinolo*(2′ : 1′ : 1 : 2)*benziminazole* (XXVII).—The corresponding dinitro-diazaline (XXVII) (30 g.) in absolute alcohol suspension (400 c.c.) was reduced catalytically at 70° in 80% yield by hydrogen initially at 15 atms. The main portion of the *diamine* crystallised from solution admixed with catalyst, from which it was separated in colourless needles, m. p. 249—250°, by crystallisation from pyridine. The remainder was isolated by concentration of the alcoholic filtrate [Found : C, 72·86; H, 4·6; N, 22·7 (total, 100·16); *M* (Rast method), 252. $C_{15}H_{12}N_4$ requires C, 72·58; H, 4·84; N, 22·58%; *M*, 248].

iso*Quinolo*(2′ : 1′ : 1 : 2)*benziminazole* (XXVIII).—The diaminodiazaline (XXVII) (2·5 g.), dissolved in sulphuric acid (10 c.c., *d* 1·84), was diazotised with sodium nitrite (1·6 g.) in sulphuric acid (16 c.c., *d* 1·84) by gradual addition of the mixed solutions at — 10° to + 5° to phosphoric acid (40 c.c.), the diazo-solution added to alcohol–ether, and the precipitated diazonium salt dissolved in water and reduced with absolute alcohol (30 c.c.). The filtrate from distillation of volatile organic liquids was made alkaline with 2N-ammonia, and the precipitate extracted repeatedly with petroleum (b. p. 80—100°). The residue (0·8 g., m. p. 105°) from petroleum solution was crystallised from the same solvent, from alcohol–water (50%), and finally from light petroleum (b. p. 40—60°) to give the *diazaline* (XXVIII) in colourless needles, m. p. 129°, which acquired a faintly pink-buff coloration on exposure to light and air [Found : C, 82·85; H, 4·67; N, 12·67 (total, 100·19); *M* (Rast method), 269. $C_{15}H_{10}N_2$ requires C, 82·57; H, 4·59; N, 12·84%; *M*, 218].

In order to establish completely the identity of the primary monoamine (m. p. 123°) prepared from authentic *iso*quinoline with that (m. p. 124—125°. Found: C, 74·8; H, 5·6; N, 19·9. Calc. for $C_9H_8N_2$: C, 75·0; H, 5·5; N, 19·4%) from coal-tar quinoline, the elements of nitrous acid were withdrawn from the picryl derivative (m. p. 156°. Found: C, 51·25; H, 2·5; N, 19·5. Calc. for $C_{15}H_9O_6N_5$: C, 50·7; H, 2·5; N, 19·7%) prepared from the latter base. The resulting dinitro-diazaline (Found: C, 58·6; H, 2·85; N, 18·5. Calc. for $C_{15}H_8O_4N_4$: C, 58·4; H, 2·6; N, 18·2%) was reduced catalytically to diamino-diazaline [m. p. 246°. Found: C, 72·47; H, 4·65; N, 22·66 (total, 99·78). Calc. for $C_{15}H_{12}N_4$: C, 72·58; H, 4·84; N, 22·58%], from which the two substituent groups were removed, giving the colourless parent diazaline [m. p. 129°. Found: C, 82·9; H, 4·6; N, 12·8; *M* (Rast method), 225. Calc. for $C_{15}H_{10}N_2$: C, 82·6; H, 4·6; N, 12·8%; *M*, 218]. Not only was the m. p. (124—125°) of the primary monoamine from coal-tar quinoline not depressed by admixture of 1-amino*iso*quinoline (m. p. 123°) from authentic *iso*-quinoline, but that (246°) of the diamino-diazaline prepared from the former base caused no depression below 246° of the m. p. (249—250°)of 4:6-diamino*iso*quinolo(2′:1′:1:2)benziminazole; and the respective unsubstituted diazalines derived from these diamino-diazalines melted at 129° either alone or mixed the one with the other.

Phenanthrido(10′ : 9′ : 1 : 2)*benziminazoles.*

N-2′ : 4′ : 6′-*Trinitrophenyl*-9-*aminophenanthridine* (XXIX).—9-Aminophenanthridine (30 g.; 2 mols.) (Morgan and Walls, *loc. cit.*), dissolved in boiling xylene (340 c.c.), was condensed with picryl chloride (18·7 g.; 1 mol.) in xylene (34 c.c.), the sparing solubility of the base in benzene necessitating the use of the higher-boiling solvent. The increased temperature of reaction resulted in spontaneous evolution of oxides of nitrogen. The major portion of the product separated from solution together with 9-aminophenanthridine hydrochloride (combined weight, 30 g.), from which it was purified by aqueous extraction of the latter hydrochloride. The remainder crystallised from the xylene filtrate from the foregoing mixed product when this solution was concentrated to crystallising point, more oxides of nitrogen being evolved, however, during the process. This crude picryl-9-aminophenanthridine was thus admixed with the corresponding dinitro-diazaline (XXX). It was used without further purification for complete conversion into the dinitro-diazaline (XXX).

It was possible, however, to prepare the sparingly soluble, very infusible, deep yellow *picryl*-9-*aminophenanthridine* (XXIX) in small quantities, free from dinitro-diazaline (XXX). 9-Aminophenanthridine (4·4 g.) in xylene (50 c.c.) was condensed with picryl chloride (2·75 g.) in xylene (5 c.c.). The major portion of the product (5 g.) separated from solution during the condensation and consisted of picryl-9-aminophenanthridine together with 9-aminophenanthridine hydrochloride (Found after aqueous extraction of 9-aminophenanthridine hydrochloride: N, 16·8, 16·5. $C_{19}H_{11}O_6N_5$ requires N, 17·3%). The remainder of the picryl derivative (1 g.) crystallised from the xylene filtrate at room temperature (Found: N, 17·1%). Crystallisation from nitrobenzene was detrimental, being accompanied by ring closure of the compound with loss of nitrous acid (Found after crystallisation: N, 16·6. $C_{19}H_{11}O_6N_5$ requires N, 17·3. $C_{19}H_{10}O_4N_4$ requires N, 15·6%).

4 : 6-*Dinitrophenanthrido*(10′ : 9′ : 1 : 2)*benziminazole* (XXX).—Picryl-9-aminophenanthridine (10 g.) containing some dinitro-diazaline (XXX) was boiled with dimethylaniline (25 c.c.) until oxides of nitrogen ceased to escape. The reaction proceeded sooothly. The *dinitro-diazaline* (XXX) (7 g.), which separated on cooling, crystallised from nitrobenzene in deep yellow needles, m. p. > 280° (Found: C, 63·9; H, 2·7; N, 15·9, 15·6. $C_{19}H_{10}O_4N_4$ requires C, 63·7; H, 2·8; N, 15·6%). Dimethylaniline was distilled from the reaction mixture, and the concentrate left to deposit a second fraction of the dinitro-diazaline.

4 : 6-*Diaminophenanthrido*(10′ : 9′ : 1 : 2)*benziminazole* (XXX).—The foregoing dinitro-diazaline (XXX) was reduced catalytically to the corresponding *diamino-diazaline* (XXX) by subjecting a suspension of the dinitro-compound (8 g.) in boiling absolute alcohol (1600 c.c.) containing platinic oxide (0·8 g.) to the action of hydrogen initially at 31 atms. at 80—90°. The highly infusible diamine (XXX) (6·1 g.) crystallised from solution together with admixed catalyst, from which it was separated by solution in pyridine and precipitation with light petroleum (b. p. 40—60°). It was purified from possible traces of unreduced dinitro-diazaline by solution in 2N-hydrochloric acid and reprecipitation with 2N-ammonia, washed with hot water, in which it was not appreciably soluble, dried in a vacuum over sulphuric acid, and crystallised from pyridine; the resulting yellow needles were washed with water to remove all traces of solvent [Found: C, 76·7; H, 4·52; N, 18·5 (total, 99·72). $C_{19}H_{14}N_4$ requires C, 76·51; H, 4·7; N, 18·78%].

Phenanthrido(10′ : 9′ : 1 : 2)*benziminazole* (XXXI).—The diamino-diazaline (XXX) was diazotised by adding mixed solutions of the primary diamine (2 g.) in sulphuric acid (10 c.c., *d* 1·84) and sodium nitrite (1·3 g.) in sulphuric acid (13 c.c., *d* 1·84), cooled to − 10°, very slowly to phosphoric acid (30 c.c.) at − 5° to + 5°. The dark yellow diazonium salt was precipitated by means of alcohol–ether and reduced in aqueous suspension with alcohol (175 c.c.), and the volatile alcohol and aldehyde distilled off. The cooled filtrate from coloured material was decolourised with wood charcoal at room temperature and made alkaline with 4N-ammonia, and the precipitated crude white *diazaline* (XXXI) (0·5 g.) extracted with light petroleum (b. p. 40—60°) to give, after removal of solvent, a colourless residue (0·35 g.), m. p. 148—150°, which was crystallised from petroleum and finally from alcohol–water. The parent diazaline of the phenanthridine series was prepared originally by using as starting material diamino-diazaline (XXX) derived from dinitro-diazaline (XXX) resulting from ring closure of that portion of the picryl compound which had separated from solution during condensation of 9-aminophenanthridine with picryl chloride and was then admixed with 9-aminophenanthridine hydrochloride, separable by aqueous extraction. The base (XXXI) crystallised in colourless needless, m. p. 153—154° [Found : C, 84·65; H, 4·77; N, 10·3 (total, 99·72); *M* (Rast method), 306. $C_{19}H_{12}N_2$ requires C, 85·07; H, 4·48; N, 10·44%; *M*, 268]. Prepared in precisely similar manner from the diamino-diazaline (XXX) of the series derived from the dinitro-diazaline (XXX) obtained in turn by ring closure of that portion of picryl-9-aminophenanthridine which crystallised from xylene solution after filtration of the reaction mixture resulting from condensation of 9-aminophenanthridine and picryl chloride, it melted at 155° [Found : C, 85·04; H, 4·54; N, 10·48% (total, 100·06); *M* (Rast method), 286], and there was no depression of m. p. below 154—155° on mixing the two samples of the parent substance of the series.

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