975. *Heterocyclic Imines. Part I. Imino-derivatives of* iso*Indoline and their Reaction with Primary Bases.*

By J. A. Elvidge and R. P. Linstead.

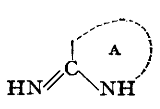
3-Imino-1-keto*iso*indoline (II) condensed readily with phenylhydrazine, hydrazine, hydroxylamine, aniline, and 2-aminopyridine, with elimination of ammonia, to yield the *N*-substituted 3-imino-1-keto*iso*indolines (IV). With the diacid bases, *m*-phenylenediamine and 2 : 6-diaminopyridine, (II) condensed twice, to afford the 3-unit compounds (V) and (VII).

Experiments on the synthesis of 1 : 3-di-imino*iso*indoline (III) from phthalonitrile and its imidic ester are described. Condensation of the di-imine (III) with two mols. of aniline and of 2-aminopyridine afforded the 3-unit compounds (VIII) and (X). The latter formed a dimethiodide (XI) and two nickel derivatives (XII) and (XIII).

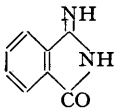
Light absorption data are given. Structures have been substantiated by quantitative degradations.

This series of papers will be concerned with cyclic imines of the type (I) and complications of this. We first became concerned with such compounds, particularly where ring A is pyrrole, as intermediates in the synthesis of azaporphins and other macrocycles. But the substances are of wider interest and their comparison with the amidines which they resemble is instructive. The present paper deals with two *iso*indole compounds containing the grouping (I), namely, 3-imino-1-keto*iso*indoline (the older name 3-iminophthalimidine will not be used in our papers) (II) and 1 : 3-di-imino*iso*indoline (III).

The exocyclic imino-group of (II) is known to be reactive. Linstead and Rowe (*J.*, 1940, 1070) found that the compound condensed with the methylene groups of malonic and acetoacetic esters, with elimination of ammonia, to give products containing a C:C link. W. O. Jones (B.P. 615,697) observed that it condensed with aryl-hydrazines and -amines to give azomethine dyes. As a preliminary to the examination of the more interesting di-imino-compound (III) we have studied further Jones's condensation reaction.



(I)



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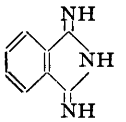
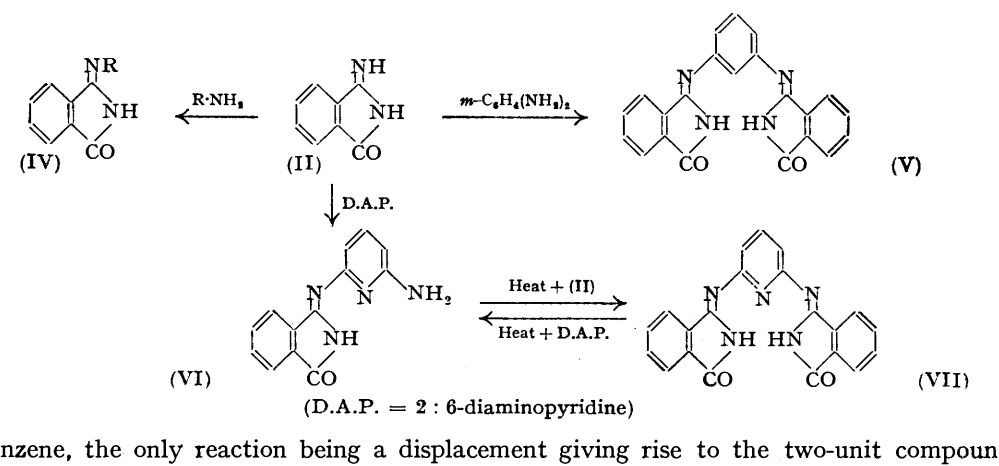


(III)

From 3-imino-1-keto*iso*indoline in alcoholic phenylhydrazine, ammonia is evolved slowly at room temperature and a yellow condensation product (IV; R = NHPh) crystallises out. Condensations with hydrazine, hydroxylamine, aniline, and 2-aminopyridine proceed similarly, rapidly on heating, to give high yields of analogous products (IV; R = NH_2, OH, Ph, and 2-C_5H_4N, severally). The colourless product of the reaction with hydroxylamine is oximinophthalimide, m. p. 257—258°, prepared by Müller (*Ber.*, 1886, **19**, 1491) from ethyl *o*-cyanobenzoate and hydroxylamine. (The structure of this compound was investigated by Thiele and Falk, *Annalen*, 1906, **347**, 712.) The products from hydrazine and 2-aminopyridine are also colourless. All the products are soluble in hot hydrochloric acid and the solutions yield phthalimide when boiled. 1-Keto-3-2′-pyridylimino*iso*indoline (IV; R = 2-C_5H_4N) was shown to give equivalent amounts of phthalimide and 2-aminopyridine in high yield, which supports structure (IV).

With *m*-phenylenediamine in boiling alcohol, two mols. of (II) reacted, to yield the 3-unit bis-condensation product (V). A similar treatment with 2 : 6-diaminopyridine gave only a 2-unit monocondensation product (VI). However, when this was boiled in *n*-butanol with more 3-imino-1-keto*iso*indoline it gave the bis-condensation product (VII). Both (VI) and (VII) readily gave phthalimide on acid hydrolysis.

The carbonyl groups of these condensation products showed no tendency to react with bases with the elimination of water. In particular, it had been thought possible that a self-condensation of (VI) might lead to a four-unit condensation product, perhaps (by elimination of two mols. of water) to a four-unit macrocycle. In fact, however, (VI) could be distilled at atmospheric pressure with only slight charring and was unaffected by prolonged heating in boiling nitrobenzene. Moreover the three-unit product (VII), with two terminal keto-groups, failed to condense with 2 : 6-diaminopyridine in boiling nitrobenzene, the only reaction being a displacement giving rise to the two-unit compound (VI). The striking superiority of the imino-group over the carbonyl in reactivity lent special interest to the examination of the di-imine (III).

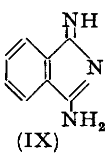


(D.A.P. = 2 : 6-diaminopyridine)

This compound, 1 : 3-di-imino*iso*indoline, had not been reported when our work started. For its preparation we first examined the Pinner reaction on phthalonitrile, which, contrary to a statement by Shriner and Neumann (*Chem. Reviews*, 1944, **35**, 351), has not previously been studied. Reaction of the nitrile in chloroform with dry ethanolic hydrogen chloride gave a product which was not homogeneous. Its chlorine content corresponded approximately to that required for diethyl phthaldi-imidoate dihydrochloride ($C_{12}H_{18}O_2N_2Cl_2$) but the yield of phthalimide obtained from it on hydrolysis was too high for this. Attempted crystallisation changed it to a homogeneous compound, $C_8H_7ON_2Cl$, identified as 3-imino-1-keto*iso*indoline hydrochloride. This monohydrochloride condensed with aniline as readily as did the parent base (II), to give 1-keto-3-phenylimino*iso*indoline (IV; R = Ph). The crude bisimidoate dihydrochloride which was its precursor, on the other hand, reacted readily with aniline to yield the yellow monohydrochloride of a bis-condensation product, $C_{20}H_{16}N_3Cl$. This compound, encountered again subsequently, was the hydrochloride of 1 : 3-diphenylimino*iso*indoline (VIII).

With an excess of ammonia in dry alcohol the bisimidoate dihydrochloride gave ammonium chloride and an alcohol-soluble hydrochloride which was essentially the monohydrochloride of di-imino*iso*indoline, as was shown by chlorine analysis, quantitative hydrolysis to phthalimide, and conversion into the characteristic nitrate described below. The di-imino*iso*indoline hydrochloride and aniline gave the hydrochloride of the diphenylated base (VIII), already described.

At this stage, two important discoveries came to our notice. The Bayer Farbenfabriken (Indian P. 43,679) described the preparation of a nitrate (and other salts) of 1-amino-3-imino*iso*indolenine (IX), as well as the liberation of the free base by the action of alkali on the nitrate. Imperial Chemical Industries Limited, Dyestuffs Division (personal communication), described a number of methods for the preparation of the free base (III), the simplest of which was by heating phthalonitrile with methanolic ammonia under pressure.*



(IX)

We have confirmed the latter method. The base so obtained gives a dihydrochloride under anhydrous conditions and a very sparingly soluble mononitrate,† m. p. 300° (decomp.), the latter identical with material prepared from our product of the Pinner reaction. A somewhat similar material was prepared by one of the Bayer methods—the reaction of phthalimide, urea, ammonium nitrate, and ammonium molybdate in nitrobenzene at 170°—but melted with decomposition at 252—254°. We have not been able to isolate the free base from the action of alkali on the insoluble nitrate (prepared by any of these methods) and in this respect our work differs from that reported in the Bayer patent. We have not pursued the identification of the Bayer product, but in the work described below have used the free base which is very readily prepared by the addition of ammonia to phthalonitrile and is of certain constitution (III) apart from questions of fine structure.

Condensation of di-imino*iso*indoline (III) with aniline in boiling ethanol gave the expected bis-condensation product, isolated as the yellow hydrochloride (VIII). This was identical with the material prepared by two other routes already described. 2-Aminopyridine and (III) in boiling butanol readily gave 1 : 3-di-2′-pyridylimino*iso*indoline (X), which was also prepared, though in poor yield, by reaction in the cold of 2-aminopyridine with the crude product of the Pinner reaction on phthalonitrile. Structure (X) follows from the easy acid hydrolysis to phthalimide and two mols. of 2-aminopyridine. With methyl iodide the new base gave a dimethiodide (XI), acid hydrolysis of which yielded phthalimide and two equivalents of 2-amino-1-methylpyridinium salt. This fission shows that the pyridine nitrogen atoms and not the aza-links are involved in the quaternisation. The dimethiodide (XI) showed no tendency to pass into an azacyanine by loss of the elements of hydrogen iodide, even when treated with triethylamine. However, we are studying such possibilities further among related compounds.

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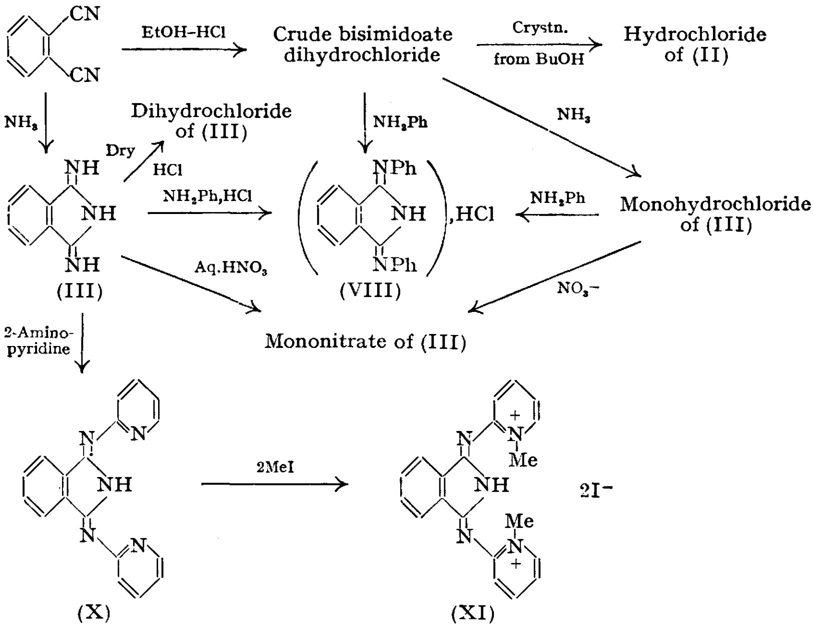
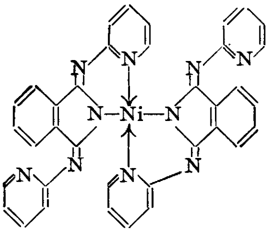
* Patent application pending.

† The insolubility is so high that the base is almost as good as nitron for the gravimetric precipitation of nitrate ion.

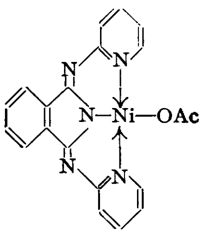
Condensation of di-imino*iso*indoline with appropriate diamines leads to macrocyclic compounds, the first of which is described in the following paper.

Dipyridylimino*iso*indoline (X) readily formed metallic compounds. With nickel acetate in formamide–methanol it gave two products: one, $C_{36}H_{24}N_{10}Ni$, sparingly soluble, crystallised in maroon prisms, m. p. 393°; the second, $C_{20}H_{15}O_2N_5Ni$, more soluble, formed brownish-yellow needles. With nickel chloride in formamide only the former was obtained. For this, which contains two molecules of base to one atom of nickel, formula (XII) is proposed. The yellow product clearly contains an acetic residue and structure (XIII) seems probable. It will be noted that in structure (XII) the stereochemical arrangement of the pyridine rings with respect to the *iso*indole nucleus must be *syn-anti* to permit of the disposal of two molecules of base about the metal with the four effective nitrogen atoms in one plane. For the other compound (XIII) the configuration is *syn-syn* as in the analogous macrocycles. There is presumably some departure from planarity in the two pyridine rings of (XII) not involved in holding the metal.





(XII)



(XIII)

The absorption of visible and ultra-violet light by the various compounds described above has been measured (see Table).

The derivatives of di-imino*iso*indoline described in this paper are structurally related to the linear "diamidides" recently described by Short and Peak (*J.*, 1951, 391; 1952, 215). Considerable differences seem to be that diamidides with unsubstituted imino-groups seem difficult to obtain, and that substituted diamidides do not show the reactivity of the type encountered above. This great reactivity of the heterocyclic di-imines in comparison with related compounds is being further investigated.

Light absorption data.

Compound	Solvent	$\lambda_{max.}$, Å	ϵ
(IV; R = Ph)	EtOH	2470 2510	18,200
		2800	5,500
		2920 *	5,500
		3020	6,200
		3240 3380	4,450
(IV; R = 2-C_5H_4N)	EtOH	2510 2570	11,100
		3300	16,300
		3360 *	15,000
(VI)	EtOH	2510 2580	12,400
		2670	16,000
		3630 *	11,400
		3840	12,400
(V)	Dioxan	2520 2570	33,000
		3020	9,500
		3300 3380	8,400
(VII)	Dioxan	2510 2570	15,800
		2800	7,900
		3020	8,800
		3330 3450	10,300
(VIII)	AcOH	3490	23,200
		3620 *	16,600
		3980	20,000
(X) †	EtOH	2310	31,300
		2740	19,800
		2840 *	18,500
		3300	16,900
		3450	18,300
		3640	20,500
		3830	21,800
(XI)	MeOH	2510 2570	8,450
		2800	9,600
		3280 3370	16,300
(XIII)	H·CO·NMe_2	2820	8,300
		3150 *	11,200
		3300	12,900
		3380 *	11,200
		4360 4680	14,500
(XII)	H·CO·NMe_2	2800	29,500
		3040	32,800
		3250	39,300
		4350	44,500
		4570	39,300

* Inflexion. † Similar values were obtained in acetic acid solution but the extinction values fell, presumably owing to hydrolysis.

EXPERIMENTAL

3-Imino-1-keto*iso*indoline (II), m. p. 203°, was prepared by thermal isomerisation, at 200°, of purified *o*-cyanobenzamide (Braun and Tcherniac, *Ber.*, 1907, **40**, 2709).

Products from (II) *and Monoacid Bases.*—(a) *Preparations.* (i) Phenylhydrazine (0·8 c.c.) was added to a warm solution of (II) (0·5 g.) in methanol (15 c.c.). After 3 days at ordinary temperature, the mixture smelled strongly of ammonia, and yellow needles of 1-*keto*-3-*phenylhydrazono*iso*indoline* (IV; R = NHPh) (0·4 g.) had separated, which after recrystallisation from ethyl acetate–ether had m. p. 234° (Found : C, 70·7; H, 4·7; N, 17·95. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·7; N, 17·7%). Jones (*loc. cit.*) records m. p. 227—228°, but no analysis. (ii) Similarly, (II) (0·5 g.) in methanol (15 c.c.) and hydrazine hydrate (1 c.c.) yielded 3-*hydrazono*-1-*keto*iso*indoline* (IV; R = NH_2) which formed colourless needles, m. p. 267°, from ethanol (charcoal) (Found : C, 59·7; H, 4·4; N, 25·9. $C_8H_7ON_3$ requires C, 59·7; H, 4·4; N, 26·1%). The compound fluoresced an intense blue in ultra-violet light. (iii) A solution of (II) (0·5 g.) and hydroxylamine hydrochloride (0·5 g.) in methanol (15 c.c.) was heated under reflux for 1·5 hours, then kept at room temperature for 15 hours. 3-Hydroxyimino-1-keto*iso*indoline (IV; R = OH) separated from ethanol as colourless laths, m. p. 260° (decomp.) (Found : C, 59·5; H, 3·9; N, 17·3. Calc. for $C_8H_6O_2N_2$: C, 59·3; H, 3·7; N, 17·3%), and was identical with " oximinophthalimide " (Müller, *loc. cit.*; Thiele and Falk, *loc. cit.*). (iv) A methanolic solution of (II) containing aniline slowly deposited a yellow solid. From ethanol, 1-*keto*-3-*phenylimino*iso*indoline* (IV; R = Ph) crystallised as pale yellow needles, m. p. 170—171° (Found: C, 75·2; H, 4·4; N, 12·9. $C_{14}H_{10}ON_2$ requires C, 75·65; H, 4·5; N, 12·6%). (v) A solution of (II) (0·5 g.) and 2-aminopyridine (0·5 g.) in ethanol (20 c.c.) was heated under reflux for 20 hours. Ammonia was evolved. When the solution was cooled, 1-*keto*-3-2′-*pyridylimino*iso*indoline* (IV; R = 2-C_5H_4N) (0·65 g.) separated and from methanol–water (charcoal) crystallised as colourless needles, m. p. 128° (Found : C, 69·9; H, 4·1; N, 19·1. $C_{13}H_9ON_3$ requires C, 69·9; H, 4·1; N, 18·8%).

(b) *Hydrolyses.* Each of the products (IV) dissolved in warm dilute hydrochloric acid and, when the solutions were heated to boiling and then cooled, colourless needles of phthalimide separated (m. p.s and mixed m. p.s 230—231°).

215 Mg. of 1-keto-3-2′-pyridylimino*iso*indoline (IV; R = 2-C_5H_4N) were treated for 2 min. with boiling 7·5N-hydrochloric acid (8 c.c.), and the solution was cooled in ice. Phthalimide (119 mg., 0·84 mol.) crystallised (m. p. and mixed m. p. 230—231°), and from the filtrate, on addition of an excess of cold saturated aqueous picric acid, 2-aminopyridine picrate was precipitated (231 mg., 0·74 mol.; m. p. and mixed m. p. 216—217°).

Condensation Products from Diacid Bases.—Interaction of 3-imino-1-keto*iso*indoline (II) (0·5 g.) with *m*-phenylenediamine (0·2 g.) in boiling ethanol (15 c.c.) for 20 hours afforded m-*di*-(1-*keto*-3-iso*indolinylidene*)*aminobenzene* (V) (0·4 g.), which separated from dioxan–ether as very pale yellow minute felted needles, m. p. 309—310° (Found: C, 71·6; H, 4·1; N, 15·4. $C_{22}H_{14}O_2N_4$ requires C, 72·1; H, 3·85; N, 15·3%). Reaction of (II) (3 g.) in ethanol (50 c.c.) with 2 : 6-diaminopyridine (1 g.) under similar conditions afforded only the monocondensation product (2·8 g.), m. p. 245—250°: from ethanol–acetone, the 3-(2-*amino*-6-*pyridylimino*)-1-*keto*iso*indoline* (VI) formed yellow needles, m. p. 254° (Found: C, 65·8; H, 4·3; N, 23·2. $C_{13}H_{10}ON_4$ requires C, 65·5; H, 4·2; N, 23·5%). By evaporation of the reaction mother-liquors, 3-imino-1-keto*iso*indoline (II) (0·3 g.) was recovered (m. p. and mixed m. p. 200—203°). From (VI) (0·3 g.) with (II) (0·2 g.) in boiling *n*-butanol, ammonia was evolved steadily during 12 hours. When the solution was cooled, 2 : 6-*di*-(1-*keto*-3-iso*indolinylidene*)*aminopyridine* (VII) (0·3 g.) separated, which from dioxan–ether or *n*-butanol formed clusters of golden prisms, m. p. 285° (Found: C, 68·6; H, 3·9; N, 18·8. $C_{21}H_{13}O_2N_5$ requires C, 68·6; H, 3·6; N, 19·1%).

3-(2-Amino-6-pyridylimino)-1-keto*iso*indoline (VI) was recovered almost completely (m. p. and mixed m. p. 252—253°) after being distilled at ordinary pressure and after being heated for 4 hours in boiling nitrobenzene.

After 2 : 6-di-(1-keto-3-*iso*indolinylidene)aminopyridine (VII) (100 mg.) and 2 : 6-diaminopyridine (50 mg.) had been heated together in boiling nitrobenzene (4 c.c.) for 6 hours and the solution then kept at room temperature overnight, only 3-(2-amino-6-pyridylimino)-1-keto-*iso*indoline (VI) was isolated, as yellow needles, m. p. and mixed m. p. 253—254°.

Each of the compounds (V), (VI), and (VII) dissolved in boiling 2N-hydrochloric acid. The yellow colours faded and, on cooling, phthalimide crystallised (m. p. and mixed m. p. 230—231°).

Reaction Product from Phthalonitrile and Ethanolic Hydrogen Chloride.—(a) *Preparation.* A solution of phthalonitrile (19·2 g.; distilled) in chloroform (300 c.c.; dried over P_2O_5) containing dry ethanol (19·5 c.c.) was saturated at 0—5° with dry hydrogen chloride, and after 6 days at 0°, the crude product (crop A) was collected (7·5 g.); it melted at *ca.* 200°, becoming dark blue. Addition of dry ether to the filtrate precipitated crop B (13 g.), of similar m. p. In subsequent experiments, " crude diethyl phthalimidoate dihydrochloride " refers to crops A and B combined.

(b) *Hydrolyses.* A portion of crop A (404·3 mg.) was treated with boiling N-nitric acid (15 c.c.) for 30 seconds and the solution allowed to cool. The mixture was finally chilled in ice and the phthalimide collected, washed with water, and dried (242·8 mg.; m. p. and mixed m. p. 230—231°). To the filtrate, silver nitrate (1 g.) in water was added and the mixture warmed on the steam for 30 minutes. The silver chloride was then collected, washed with water and dried (598·2 mg.). Crop B (303·8 mg.) was treated with boiling N-nitric acid (15 c.c.) for 90 seconds and the solution worked up similarly, to afford phthalimide (178·4 mg.), m. p. and mixed m. p. 230—232°, and silver chloride (292·9 mg.). (Found, for crop A: phthalimide yield, 60·1; Cl, 27·3%. For crop B: phthalimide yield, 58·8; Cl, 23·8%. Calc. for $C_{12}H_{18}O_2N_2Cl_2$: phthalimide, 50·2; Cl, 24·2%).

(c) *Recrystallisation.* The crude imidoate dihydrochloride afforded 3-*imino*-1-*keto*iso*indoline hydrochloride* as plates, m. p. 230° (decomp.), from *n*-butanol (Found: C, 52·8; H, 3·9; N, 14·8. $C_8H_7ON_2Cl$ requires C, 52·6; H, 3·8; N, 15·3%). The same compound (m. p. and mixed m. p. 230—231°) was obtained by evaporating a solution of (II) in dry ethanolic hydrogen chloride, and also by keeping *o*-cyanobenzamide in ethanol with dry hydrogen chloride for 3 days at room temperature, filtering the solution, and evaporating it under reduced pressure. To an ethanol solution (40 c.c.) of the iminoketo*iso*indoline hydrochloride (0·5 g.), aniline (1 c.c.) was added. Next day, yellow needles had separated (0·35 g.), having m. p. 168—170° undepressed by 1-keto-3-phenylimino*iso*indoline. The same product (m. p. 168—170°) was isolated after a similar reaction mixture had been heated under reflux overnight.

(d) *Reaction with aniline.* The crude imidoate dihydrochloride (2 g.) was dissolved in ethanol (40 c.c.), and aniline (3 c.c.) added. Heat was evolved. Overnight, a deep yellow solid separated (1·5 g.), m. p. 260—263°. From glacial acetic acid, the 1 : 3-*diphenylimino*iso-

indoline hydrochloride (VIII) formed yellow prisms, m. p. 278° (Found: C, 72·2; H, 5·0; N, 12·6. $C_{20}H_{16}N_3Cl$ requires C, 72·0; H, 4·8; N, 12·6%).

1 : 3-*Di-imino*iso*indoline*.—(*a*) Liquid ammonia (40 c.c.) was added cautiously to the crude phthalimidoate dihydrochloride (10 g.), dissolved in ethanol (200 c.c.), and the solution kept for 4 days at room temperature with protection from atmospheric moisture. Ammonium chloride was removed and the filtrate evaporated under reduced pressure, to yield crude 1 : 3-di-imino*iso*indoline hydrochloride as a white solid (7 g.), m. p. 300—310°, becoming green. The salt dissolved in cold water and, when the solution was heated to boiling, ammonia was evolved and phthalimide subsequently crystallised from the solution.

The salt (265·5 mg.) was treated with boiling 2N-nitric acid (15 c.c.) for 2 minutes and the mixture allowed to cool. The crystalline precipitate of phthalimide was collected, washed with water, and dried (164·2 mg.; m. p. and mixed m. p. 229—231°). Silver nitrate (0·5 g.) in water was added to the filtrate, and the mixture warmed for 30 minutes. The silver chloride was then collected, washed and dried (427·2 mg.) (Found: phthalimide yield, 76·4; Cl, 17·4. $C_8H_8N_3Cl$ requires phthalimide, 81·0; Cl, 19·5%).

The *hydrochloride* (0·2 g.) in ethanol (20 c.c.) was heated with aniline (1 c.c.) under reflux for 16 hours. Yellow solid separated (0·2 g.), having m. p. 265—270°, and 265—275° when mixed with 1 : 3-diphenylimino*iso*indoline hydrochloride.

A portion of the di-imine hydrochloride was dissolved in 2N-sodium hydroxide, and 2N-nitric acid added. The white precipitate had m. p. 290° (decomp.), and 292° (decomp.) when mixed with the authentic nitrate described below.

(*b*) To a stirred mixture of phthalonitrile (100 g.) and methanol (600 c.c.), liquid ammonia (200 c.c.) was cautiously added, and the whole then heated in a stainless-steel autoclave at 90—100° for 4 hours. The cooled solution was filtered from a trace of blue pigment (phthalocyanine) and concentrated under reduced pressure. 1 : 3-*Di-imino*iso*indoline* (III) (110 g.) separated as a very faintly green crystalline powder, m. p. 194—195° (becoming green): from methanol–ether (charcoal) it gave colourless prisms, m. p. 196° (decomp.) (Found: C, 66·3; H, 4·85; N, 28·7. $C_8H_7N_3$ requires C, 66·2; H, 4·9; N, 28·9%).

The base (III) (0·15 g.) and aniline (0·4 c.c.) were heated together in boiling ethanol (10 c.c.) for 10 hours, during which ammonia was evolved. Ethanolic hydrogen chloride was added and the precipitate washed with glacial acetic acid and ether. The 1 : 3-diphenylimino*iso*indoline hydrochloride (0·33 g.) had m. p. and mixed m. p. 278—279°.

To a solution of the purified base (III) in ethanol, ethereal hydrogen chloride was added, and the white microcrystalline precipitate collected, washed with ether, and dried. 1 : 3-*Di-imino*iso*indoline dihydrochloride* had m. p. 326—328° (becoming green) (Found: C, 43·3; H, 4·6; N, 19·0. $C_8H_9N_3Cl_2$ requires C, 44·05; H, 4·2; N, 19·25%). A solution of the dihydrochloride (87·6 mg.) in water (10 c.c.) was heated on the steam-bath and, after 5 minutes, 2N-nitric acid (5 c.c.) was added. Heating was continued for 30 minutes and the hydrolysate solution then kept at 0—2° overnight. The phthalimide (m. p. and mixed m. p.) was collected, washed with water, and dried (43·4 mg., 73·5%). To the filtrate, silver nitrate (0·3 g.) in water (5 c.c.) was added and the mixture warmed for 30 minutes. After 2 hours, the silver chloride was collected, washed, and dried (114·1 mg.) (Found: Cl, 32·2. $C_8H_9N_3Cl_2$ requires Cl, 32·5%).

A solution of the base (III) (0·8 g.) in water (25 c.c.) at room temperature was filtered into 2N-nitric acid (10 c.c.), whereupon 1 : 3-*di-imino*iso*indoline nitrate* separated as a microcrystalline precipitate, m. p. 300° (decomp.) (Found: C, 45·9; H, 3·9; N, 26·5. $C_8H_8O_3N_4$ requires C, 46·15; H, 3·9; N, 26·9%). The nitrate was soluble in concentrated mineral salts.

(*c*) A mixture of phthalimide (73 g.), urea (90 g.), ammonium nitrate (45 g.), ammonium molybdate (0·15 g.), and nitrobenzene (250 g.) was kept at 170° for 14 hours, the mixture being stirred during the first 6 hours (cf. Bayer Farbenfabriken, Indian P. 43,679). The mixture was broken up and filtered at 80—90°, and the solid washed with hot nitrobenzene and then boiling methanol (2 × 100 c.c.), to yield a slightly discoloured nitrate (74 g.), m. p. 252—254° (decomp.), and 269—270° (decomp.) when mixed with the preceding di-imino*iso*indoline nitrate of m. p. 300° (decomp.).

Treatment of an aqueous suspension of the nitrate with sodium hydroxide, according to the directions of Bayer Farbenfabriken (*loc. cit.*), failed to yield any of the base. On stronger cooling to −5°, only ice crystals were obtained. On subsequent acidification with acetic acid, the sparingly soluble nitrate was reprecipitated and thus recovered.

1 : 3-*Di-2′-pyridylimino*iso*indoline* (X).—(a) *Preparation.* (i) 1 : 3-Di-imino*iso*indoline (3 g.) and 2-aminopyridine (4 g.) were heated together in boiling *n*-butanol (25 c.c.) for 4 hours, during

which ammonia was evolved. Evaporation under reduced pressure and crystallisation of the greenish residue (m. p. 178—182°) from ethanol yielded 1 : 3-*di-2′-pyridyliminoisoindoline* (4 g.) as pale, slightly greenish, yellow needles, m. p. 182° (Found : C, 72·3; H, 4·6; N, 23·5. $C_{18}H_{13}N_5$ requires C, 72·2; H, 4·4; N, 23·4%). The compound dissolved freely in dilute nitric acid. (ii) The dipyridylimino*iso*indoline (0·3 g.), m. p. 178—180° (mixed m. p. undepressed), was also obtained by treating crude diethyl phthalimidoate dihydrochloride (2 g.) in chloroform (50 c.c.; dried over P_2O_5) with 2-aminopyridine (3 g.) for 36 hours, filtering from ammonium chloride, washing the solution with aqueous sodium carbonate and water, and evaporating the chloroform.

(*b*) *Hydrolysis*. The compound (X) (1 g.) was heated on the steam-bath with concentrated hydrochloric acid (10 c.c.) for 30 minutes and the solution then cooled in ice. Phthalimide crystallised (0·433 g., 0·88 mol.), m. p. and mixed m. p. 231—232°. The filtrate was evaporated to dryness under reduced pressure, and the residue taken up in water (5 c.c.) and treated with a solution of picric acid (1·8 g.) in water (90 c.c.). After 5 minutes, the yellow precipitate of 2-aminopyridine picrate was collected, washed with water, and dried (1·962 g., 1·90 mols.; m. p. and mixed m. p. 215—217°).

(*c*) *Methylation*. The dipyridylimino*iso*indoline (X) (0·55 g.) was heated with methyl iodide (4 c.c.) at 90—100° overnight. From methanol–ethyl acetate the *dimethiodide* (XI) (1 g.) crystallised as small orange-brown prisms, m. p. 251° (decomp.) (Found : C, 40·9; H, 3·9; N, 11·5; I, 43·5. $C_{20}H_{19}N_5I_2$ requires C, 41·2; H, 3·3; N, 12·0; I, 43·5%). After being heated in methanol with triethylamine, the dimethiodide was recovered (by evaporation) unchanged, m. p. and mixed m. p. 250—251° (decomp.).

When the dimethiodide (969 mg.) was heated on the steam-bath with 25% hydrochloric acid (15 c.c.) for 10 minutes and the solution cooled in ice, phthalimide separated (179 mg.) (m. p. 229—230°). The filtrate was evaporated to dryness under reduced pressure, and the residue taken up in water (12 c.c.) and filtered from undissolved phthalimide (31 mg.; m. p. 229—230°; total yield of phthalimide, 210 mg., 0·86 mol.). To the filtrate, saturated aqueous picric acid was added until precipitation ceased and the 2-amino-1-methylpyridinium picrate was collected (615 mg.; m. p. 200—201°); concentration of the filtrate to small bulk, under reduced pressure, afforded a second crop (110 mg.), m. p. 200—201° (total yield, 725 mg.; 1·30 mols.). Recrystallised from water, the picrate formed golden-yellow needles, m. p. 201° (Found : C, 42·8; H, 3·4. Calc. for $C_{12}H_{11}O_7N_5$: C, 42·75; H, 3·3%). Tschitschibabin, Konowalowa, and Konowalowa (*Ber.*, 1921, **54**, 814) record m. p. 201°.

(*d*) *Nickel derivatives*. A solution of the dipyridylimino*iso*indoline (X) (0·6 g.) in hot methanol (40 c.c.) was treated with nickel acetate (0·4 g.) in formamide (4 c.c.), and the dark precipitate collected. Evaporation of the filtrate to small bulk, under reduced pressure, afforded a golden-brown solid which was washed with water and methanol. From nitrobenzene, the *nickel monoacetate* derivative (XIII) separated as slender brownish-yellow needles, m. p. 373° (decomp.) (Found: C, 57·9; H, 3·8; N, 16·75; Ni, 13·6. $C_{20}H_{15}O_2N_5Ni$ requires C, 57·75; H, 3·6; N, 16·8; Ni, 14·1%). Recrystallisation of the foregoing dark precipitate from nitrobenzene yielded maroon prisms, m. p. 393° of the *nickel* derivative (XII) (Found : C, 65·4; H, 3·8; N, 21·8; Ni, 8·8. $C_{36}H_{24}N_{10}Ni$ requires C, 66·0; H, 3·7; H, 21·4; Ni, 8·95%). The same compound, m. p. and mixed m. p. 393°, was the sole product of a similar reaction between (X) and nickel chloride in formamide.

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