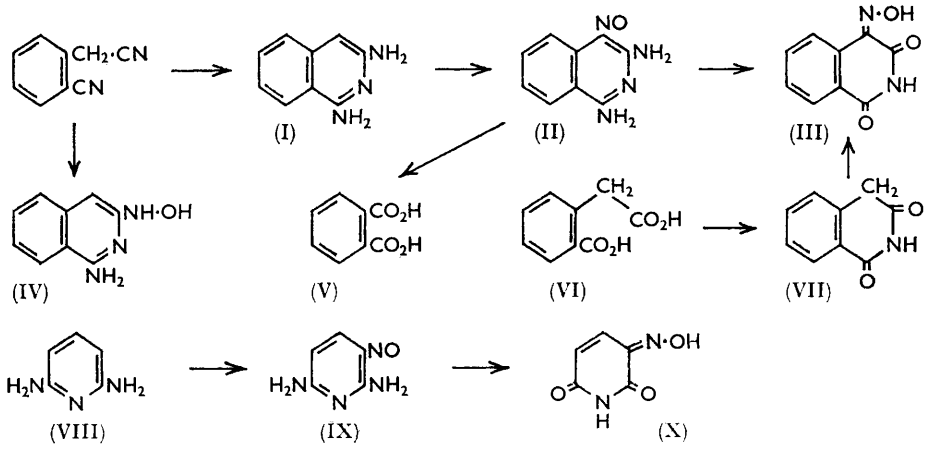
273. *Heterocyclic Imines and Amines. Part X.* 1,3-Diaminoisoquinoline, and the Fine Structures of Related Nitroso-compounds and Pyridine Derivatives.*

By J. M. Cox, J. A. Elvidge, and (in part) D. E. H. Jones.

1,3-Diaminoisoquinoline has been prepared for the first time, from *o*-cyanobenzyl cyanide and ammonia. The diamine was converted into the 4-nitroso-compound and thence degraded to "nitrosohomophthalimide" and to phthalic acid. The fine structures of these isoquinolines and of related pyridines have been deduced from proton magnetic resonance measurements, and with the assistance of ultraviolet and infrared spectra. Best representations for these several compounds are (I)—(III) and (VII)—(X).

It has been confirmed that hydroxylamine with *o*-cyanobenzyl cyanide yields 1-amino-3-hydroxylaminoisoquinoline.

Addition of ammonia to *o*-cyanobenzyl cyanide occurs less readily than to phthalonitrile [1] or glutaronitrile [2] and requires a temperature of 140° for 24 hr. The product, $C_9H_9N_3$, is not an imidine; it is the hitherto unknown 1,3-diaminoisoquinoline (I). This crystallises as yellow plates, m. p. 232°, is unaffected by boiling aqueous mineral acid or base, unlike an imidine, and has pK_a 5·70 (in 80% 2-methoxyethanol). 1,3-Di-iminoisoindoline and *m*-phenylenediamine have pK_a 7·47 and 4·88, respectively (in that solvent).[3] The new diamine forms a picrate, and hydrated dibenzoyl and diacetyl derivatives. Proton resonance data for the last are included in Table 1. The infrared (i.r.) spectrum of the base (I) (Table 2) confirms that it is an amine and an *o*-disubstituted benzene, and shows the absence of a nitrile function. The absorption envelope in the ultraviolet (u.v.) region is similar to that of 2,6-diaminopyridine (VIII) (Fig. 1) and bears the same relationship to the spectra of isoquinoline [4] and 1-aminoisoquinoline [5] as does the spectrum of 2,6-diaminopyridine to those of pyridine [6] and 2-aminopyridine,[5] there being successive bathochromic shifts with the introduction of each amino-substituent. The proton magnetic resonance (p.m.r.) spectrum of the new amine in dioxan (Table 1) also fully accords with



* Part IX, *J.*, 1959, 208.

[1] Elvidge and Linstead, *J.*, 1952, 5000.
[2] Elvidge, Linstead, and Salaman, *J.*, 1959, 208.
[3] Elvidge and Golden, *J.*, 1957, 700.
[4] Ewing and Steck, *J. Amer. Chem. Soc.*, 1946, **68**, 2181.
[5] Steck and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397.
[6] Miller, Knight, and Roe, *J. Amer. Chem. Soc.*, 1950, **72**, 1629.

TABLE 1.

Proton magnetic resonance results at 60 Mc./sec. (for 5—10% solutions in *a* dioxan, *b* dimethyl sulphoxide, *c* MeOH, *d* CCl_4, *e* $CDCl_3$).

Compound	τ	Intensity	Multiplicity	Assignment
(I) [a]	5·37	2	broadened	3-NH_2
	4·30	2	,,	1-NH_2
	4·08	1	doublet, J 0·8 c./sec.	4-H
	3·3 to 2·3	4	complex	5-, 6-, 7-, 8-H's
(I) [b]	4·77	2	broadened	3-NH_2
	4·10	1	doublet, J 0·8 c./sec. (collapsed, by irradiation at 126 ± 5 c./sec. down-field)	4-H (∴ coupled to 8-H)
	3·58	2	broadened	1-NH_2
	3·3 to 2·6	3	complex	5-, 6-, 7-H's
	2·08	1	doublet, J_o 8 c./sec., showing finer splitting (collapsed, by irradiation at 58 ± 5 c./sec. upfield)	8-H (∴ 7-H is at *ca.* 3·03)
1,3-Diacetamido-isoquinoline- [c]	7·80	3	singlet	Ac (at 3)
	7·68	3	,,	Ac (at 1)
	2·8 to 1·8	5	complex	4-, 5-, 6-, 7-, 8-H's
	−0·07	2	broadened	1-, 3-NH's
(VIII) [b]	4·71	4	broadened	2-, 6-NH_2's
	4·33	2	doublet } J 8 c./sec.	3-, 5-, H's
	2·95	1	triplet }	4-H
(II) [b]	2·53	1	*ca.* double triplet	6-, 7-H's
	2·23	1	,, ,,	
	1·75	1	double doublet J_o 7·8, J_m 1·8 c./sec.	8-H
	1·23	1	,, ,,	5-H
	1·45	2	broadened	1-NH_2
	1·82	1	,,	3-NH
	−2·38	1	,,	3-NH (proton bonded to 4-NO)
(IX) [b]	3·77	1	doublet } J 9 c./sec.	5-H
	1·79	1	,, }	4-H
	2·25	3	broadened	2-NH, 6-NH_2
	−0·58	1	,,	2-NH (proton bonded to 3-NO)
(VII) [b]	5·96	2	singlet	4-CH_2
	2·76 to 2·14	3	complex	5-, 6-, 7-H's
	1·96	1	*ca.* double doublet, J_o 7·5 c./sec.	8-H (?)
	−1·28	1	broadened	NH
(III) [b]	2·36 to 2·01	2	complex	6-, 7-H's
	1·78	1	*ca.* double doublet } J_o 7 c./sec.	8-H (?)
	1·00	1	*ca.* ,, }	5-H (?)
	−1·67	1	broadened	NH } (?)
	ca. 1·6 to −4	*ca.* 1	very broad	=NOH }
(X) [b]	3·67	1	double doublet, $J_{4,5}$ 10·25, $J_{1,5}$ 1·9 c./sec.	5-H
	2·29	1	doublet	4-H
	−1·47	1	broadened	NH } (?)
	ca. 1·6 to −4·7	*ca.* 1	very broad	=NOH }
(IV) [b]	6·42	*	broadened	H_2O
	3·68	1	singlet	4-H
	3·36	2	broadened	1-NH_2
	3·05 to 2·55	3	complex	5-, 6-, 7-H's
	2·33	2	slightly broadened singlet	3-NHOH
	1·96	1	doublet, lines slightly broadened J_o 8 c./sec.	8-H
o-Cyanotoluene [d]	7·48	3	singlet	CH_3
	around 2·5	4	complex	ring protons
o-Cyanobenzyl chloride [d]	5·28	2	singlet	CH_2Cl
	around 2·44	4	complex	ring protons
o-Cyanobenzal chloride [d]	2·99	1	singlet	$CHCl_2$
	2·70 to 1·90	4	complex	ring protons
o-Cyanobenzyl cyanide [e]	5·98	2	singlet	CH_2·CN
	around 2·32	4	complex	ring protons

* Intensity dependent upon state of hydration of the compound (IV).

the 1,3-diaminoisoquinoline structure (I) in that it shows the presence of two, differently shielded, amino-groups, a group of four benzenoid protons, and, to higher-field, the lone 4-proton (τ 4·08). The change in the spectrum in dimethyl sulphoxide (Table 1) is attributable to chelation of this solvent with the 1-amino-group: the signal from the latter has moved down-field, 0·12 p.p.m. further than the 3-amino-signal, and the signal from one benzenoid proton appears separately from the others as a low-field double-doublet (τ 2·08). This is evidently the 8-proton now additionally deshielded: the 4-proton (adjacent to the 3-amino-group) is virtually unchanged in position at τ 4·10. A further feature of these spectra is the fine splitting of the signal from the 4-proton (J = 0·8 c./sec.). Double irradiation showed that the coupling is to the lowest-field benzenoid proton, and this we have deduced is that in the 8-position. Analogous long-range coupling has been detected in quinoline, indole, and benzofuran, and a pyrrolothiophen.[7]

P.m.r. data for 2,6-diaminopyridine (VIII) are included in Table 1, for comparison with that of the new diamine (I).

TABLE 2.

Infrared absorptions (Nujol mull; measured with a Grubb-Parsons double-beam S4 spectrometer, NaCl optics).

Compd.	Max. (cm.$^{-1}$)
(I)	3363, 3270, 3152, 3030w, 1729w, 1649, 1622s, 1559, 1507, 1347, 1199, 1130w, 1022w, 977, 943w, 864, 807s, 764w, 736
(VIII)	3410, 3350, 3230, 3140, 1644, 1635, 1600s, 1582, 1560, 1357, 1312, 1272, 1180w, 1122, 1070, 992, 975w, 864, 845, 800, 750, 725.
(II)	3340, 3198, 3151, 1691, 1614, 1587s, 1503s, 1323w, 1304, 1255, 1203, 1172w, 1153s, 1133w, 1119, 1040, 1020, 983s, 871w, 824w, 773, 733w, 674
(IX)	3233, 3125w, 1712, 1611s, 1529w, 1418w, 1334, 1255s, 1216, 1167s, 1137s, 1063, 964w, 950w, 803, 772, 732, 678
(VII)	3138, 3050, 1843w, 1703s, 1678, 1609, 1337, 1316w, 1292s, 1194w, 1139, 1033w, 966w, 927w, 886, 865w, 806, 761s, 742s, 724w, 686, 671
(III)	3147, 3040w, 1709, 1689s, 1590, 1321s, 1299s, 1284w, 1249w, 1216w, 1146, 1102, 1042s, 1022w, 869w, 819, 798, 783, 746, 724w, 686, 670w
(X)	3147, 3067w, 1821w, 1724, 1685s, 1617, 1420s, 1345w, 1294s, 1210, 1140, 1123, 1022s, 935w, 856, 812, 796, 767, 739, 725w, 694w, 671w
(IV)	3373, 3275, 3077, 1657s, 1612s, 1574w, 1512, 1369, 1272, 1208, 1159, 1114, 957w, 862w, 806, 747

1- and 3-Aminoisoquinoline are converted by nitrite in sulphuric acid into the corresponding isoquinolones.[8,9] The new diamine (I), however, behaves like 2,6-diaminopyridine (VIII) and undergoes *C*-nitrosation at the *m*-position to the ring-nitrogen. That this is a position of high electron density, as in the pyridine, is shown by the comparably high τ values for the 4-proton in (I) and the 3-proton in (VIII) (see Table 1).

The nitrosation product, 1,3-diamino-4-nitrosoisoquinoline (II), resembles 2,6-diamino-3-nitrosopyridine (IX) in being a red crystalline solid which gives dark green solutions in polar solvents. The two compounds have similar u.v. absorptions (Fig. 2), and in the i.r. region each shows a band of medium intensity near 1700 cm.$^{-1}$ which is either an overtone or represents a combination transition. That the pyridine derivative has the fine structure (IX) is demonstrated by p.m.r. The spectrum (Table 1) shows an AB quartet, as expected from the 4- and 5-proton, and two low-field signals. These last comprise a broadened three-proton signal at τ 2·25 from three of the amino-group protons, and a broadened signal of unit intensity at τ −0·58 from that proton on the 2-amino-group nearest and probably chelated to the 3-nitroso-group. No other tautomeric form of the molecule fits these observations. The p.m.r. spectrum of the diaminonitrosoisoquinoline

[7] Anet, *J. Chem. Phys.*, 1960, **32**, 1274; Elvidge and Foster, *J.*, 1963, 590; Gutowsky and Porte, *J. Chem. Phys.*, 1961, **35**, 839.
[8] Jansen and Wibaut, *Rec. Trav. chim.*, 1937, **56**, 699; Wibaut and Haaijman, *ibid.*, 1943, **62**, 466.
[9] Baumgarten, Murdoch, and Dirks, *J. Org. Chem.*, 1961, **26**, 803.

(II) shows four coupled benzenoid protons, all at lower field than in the parent compound (I), significantly no lone proton at higher field (demonstrating 4-substitution), a broadened two-proton signal at τ 1·45 from the 1-amino-group, and two (unit) signals, at τ 1·82 and −2·38. These last two are assigned to the differently shielded protons of the 3-amino-group, one probably being chelated to the adjacent 4-nitroso-group. The alternative 1-amino-4-hydroxyimino-3-imino- and 3-amino-4-hydroxyimino-1-imino-tautomeric forms, possibly also compatible with the p.m.r. data, are rejected because the u.v. absorption of (II) lacks any resemblance to that of 1,2-[10] or 1,4-naphthaquinone.[11] We conclude that the best representation of the new diaminonitrosoisoquinoline is (II), analogous to (IX) for the pyridine.

When the reaction mixture containing the nitrosation product (II) was boiled with sodium hydroxide, ammonia was evolved: subsequently phthalic acid was isolated in rather less than 50% yield. Expected changes were hydrolysis to "nitrosohomophthalimide" (which as we show below exists in the hydroxyimino-form) and thence to α-hydroxyiminohomophthalic acid, followed by decarboxylation. This could yield either the oxime of phthaldehydic acid which might then undergo a Cannizzaro disproportionation to *o*-carboxybenzhydroxamic acid (as one product) which would hydrolyse to phthalic acid, or it might afford *o*-cyanobenzoic acid and thence phthalic acid. This second possibility,[11a] however, provides no immediate reason for a restricted yield.

By keeping the diaminonitrosoisoquinoline (II) in aqueous acid for some days, "nitrosohomophthalimide" was obtained in good yield, identical with the product from the nitrosation of homophthalimide (VII). We assign to this nitrosation product the hydroxyimino-imide structure (III) for several reasons. The compound is colourless. The u.v. absorption envelope has a similar shape to that of homophthalimide, although there is a general bathochromic shift (Fig. 3). The infrared absorption curve in the carbonyl and in the 670—870 cm.$^{-1}$ region closely resembles that of homophthalimide: the C=N absorption in compound (III) presumably comes under the imide double peak and is responsible for the slight broadening as compared with the corresponding band in the spectrum of homophthalimide. The structure of homophthalimide, assumed to be (VII), appears certain because the u.v. absorption (in neutral solution) is similar to that of the *N*-ethyl derivative and to homophthalic anhydride,[12] and the i.r. absorption indicated the presence of the true imide function rather than an enolic form of this.[13] Moreover, the p.m.r. spectrum of homophthalimide (VII) (Table 1) demonstrates that there is a 4-methylene group in the heterocyclic ring, by a singlet at τ 5·96 of intensity two. This signal is not of course given by the nitrosation product (III), but neither does that compound give a one-proton signal attributable to the 4-proton in a 4-nitrosohomophthalimide structure. Hence the hydroxyimino-imide form (III) for the nitrosation product is strongly indicated.

The conversion of the diaminonitrosoisoquinoline (II) into the homophthalimide derivative (III) resembled the hydrolysis of 2,6-diamino-3-nitrosopyridine (IX) to the corresponding "2,6-dihydroxy-3-nitrosopyridine,"[14,15] which compound we suggest is best represented as the hydroxyiminoimide (X). This compound is colourless, and it has u.v. and i.r. spectral characteristics similar to those of homophthalimide (VII) and the 4-hydroxyimino-derivative (III) (Fig. 3 and Table 2). Hence it appears to be a glutaconimide rather then a 6-hydroxy-2-pyridone. This recalls another pyridone which was best regarded as γ-ethoxy-*N*-phenylglutaconimide.[16] Furthermore, the p.m.r. spectrum of compound (X)

[10] Bader, *J. Amer. Chem. Soc.*, 1951, **73**, 3731.
[11] Daglish, *J. Amer. Chem. Soc.*, 1950, **72**, 4859.
[11a] Rapoport and Nilsson, *J. Org. Chem.*, 1962, **27**, 629; Jordan and Hauser, *J. Amer. Chem. Soc.*, 1936, **58**, 1304.
[12] Buu-Hoï, *Bull. Soc. chim. France*, 1945, **12**, 313.
[13] Mason, *J.*, 1957, 4874.
[14] Gattermann and Skita, *Ber.*, 1916, **49**, 494.
[15] Titov, *J. Gen. Chem. U.S.S.R.*, 1938, **8**, 1483.
[16] Butt, Elvidge, and Foster, *J.*, 1963, 3069.

(Table 1) shows that two strongly-coupled protons are present (J = 10·25 c./sec.)—those *cis* to one another in the 4- and 5-position (significantly the coupling is larger than $J_{\beta\gamma}$ for a true pyridine ring)[17]—and that the higher-field 5-proton is weakly coupled (J = 1·9 c./sec.) to one other proton. The latter cannot be a proton attached to a ring-carbon atom because

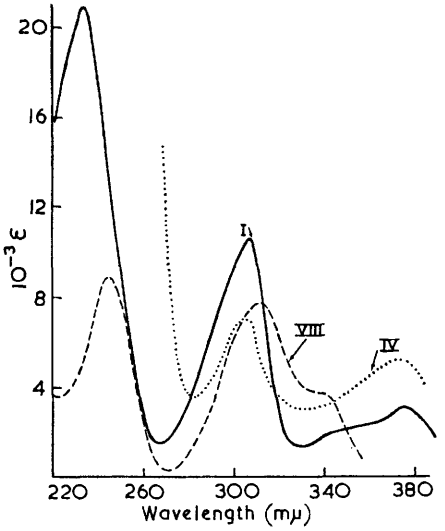


FIG. 1,

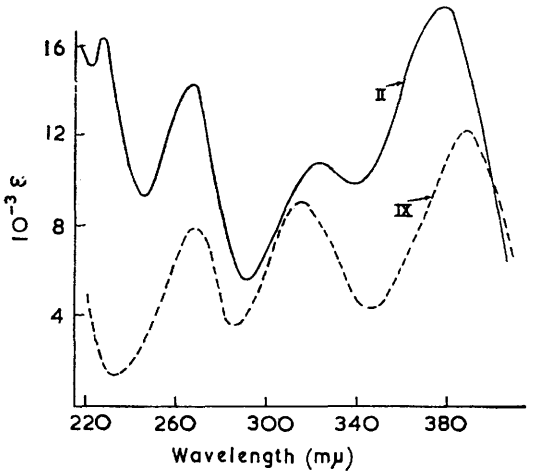


FIG. 2.

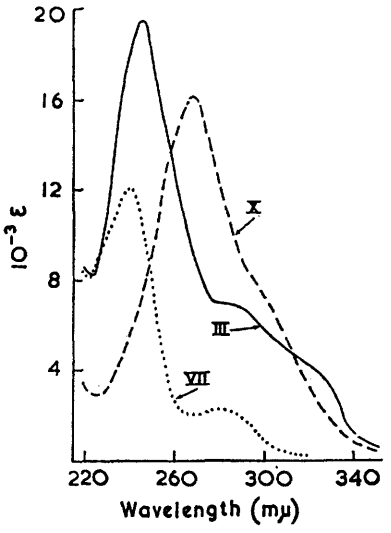


FIG. 3.

Ultraviolet absorptions (in ethanol)
(Perkin-Elmer Spectracord 4000 and Unicam S.P. 500)

Compd.	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	Compd.	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$
(I)	234	20·9	(IX)	267	7·9
	307	10·6		322	10·7
	375	3·2		377	17·8
(VIII)	246	8·7	(III)	246	19·5
	312	7·7		282in	6·6
	335in	3·8		325sh	3·7
(IV)	235	34·8	(X)	269	16·1
	264	29·5		305sh	6·3
	305	7·0	(VII)	240	12·2
	375	5·2		279	2·4
(II)	228	16·2			
	268	14·3			
	315	9·0			
	388	12·2			

in = inflection
sh = shoulder

an appropriate signal does not appear in the spectrum and, moreover, there is no detectable second-order coupling to the 4-proton. In protonated pyridones, weak coupling is found between the NH proton and the *meta*-proton (in the 3-position), across the carbonyl group.[18] Hence it appears that the weak coupling of the 5-proton in (X) is to the *meta*-imide proton (at the 1-position). The latter evidently gives rise to the broadened signal

[17] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co. Inc., New York, 1959, p. 266.
[18] Katritzky and Reavill, *J.*, 1963, 753.

at τ −1·47. The imide proton in homophthalimide (VII) has τ −1·28. The compound (III) gives an analogous signal at τ −1·67. These values are in a correct order. Dr. D. W. Turner (of this Department) informs us from his experience with a series of imides that the nitrogen relaxation should be sufficiently rapid for the NH-proton signal to appear as a reasonably sharp band. Our presumed imide-proton signals have a width (at half-height) of about 0·17 p.p.m. The remaining proton in compound (III) and in (X) was not certainly located in the spectra, although the integral trace in each case suggested the presence of a very considerably broadened signal covering the region from τ 1·6 to about τ −4. We identify this with the exchangeable proton of the hydroxyimino-group. The corresponding proton in salicylaldoxime, for example, gives a much broadened signal,[19] although the width is not so great as we believe it to be in the present examples. We intend in due course to seek further evidence for the foregoing tentative assignments. The present proton resonance results are sufficient for our immediate purpose in that they are not inconsistent with the hydroxyimino-forms (III) and (X) which the u.v. and i.r. spectral results strongly indicate.

A product from the addition of hydroxylamine to *o*-cyanobenzyl cyanide, to which Eichelbaum [20] gave an unlikely structure, was suggested by Knott [21] to be 1-amino-3-hydroxylaminoisoquinoline (IV): certainly, mechanistic considerations lead to that structure. We have now confirmed the isoquinoline nature of compound (IV) by showing that the u.v. and i.r. absorption envelopes are similar to those of 1,2-diaminoisoquinoline (I) (Fig. 1 and Table 2), and have proved the positions of the substituents by p.m.r. spectroscopy. The spectrum (Table 1) shows an amino-group signal at τ 3·36, compared to 3·58 for the 1-amino-group in (I), and a lower-field signal (as expected) from the protons of the hydroxylamino-group (at τ 2·33). The rest of the spectrum resembles that of the diamine (I) except that all the signals are shifted to lower-field. This is the result of replacing an electron-donating amino-group by hydroxylamino in structure (IV). Significantly, the largest down-field shift is for the signal from the 4-proton. The 3-hydroxylamino-constitution (IV) therefore appears certain.

Experimental

(D. E. H. Jones rendered assistance with preparations marked *.)

* o-*Cyanobenzyl Chloride* (cf. ref. 22).—*o*-Cyanotoluene (100 g.) was heated to 130° and irradiated with a 150-w spotlight, whilst chlorine was passed in until the liquid had n_D^{25} 1·5577—1·5595. When cooled, the product slowly solidified. The solid was slurried with a little ethanol and collected. The *o*-cyanobenzyl chloride (80—53 g.; 60—40%) had m. p. 55—60°, raised to 60° by crystallisation from ethanol. Attempted fractionation of the ethanolic washings and mother-liquors gave a liquid (47 g.), b. p. 115—125°/25 mm., n_D^{20} 1·5600, which p.m.r. spectroscopy showed was a 1 : 3·0 : 3·7 mixture of *o*-cyano-toluene, -benzyl chloride, and -benzal chloride.

When *o*-cyanotoluene (98 g.) was treated as before with chlorine for 7 hr., the product failed to solidify and had b. p. 260—263°, n_D^{25} 1·5666 (yield, 62 g.). The p.m.r. spectrum indicated that it was *o*-cyanobenzal chloride.

* 1,3-*Diaminoisoquinoline* (I).—*o*-Cyanobenzyl cyanide [23] (7·65 g.) was heated with a solution of liquid ammonia (32 c.c.) in methanol (125 c.c.) for 24 hr. at 140°. The solution was evaporated to small bulk (10 c.c.), and the dark green solid (6 g., 70%) was crystallised from chlorobenzene (charcoal) to give yellowish plates (4 g.), m. p. 231·5—232·5° (Found: C, 68·1; H, 5·75; N, 26·35. $C_9H_9N_3$ requires C, 67·9; H, 5·7; N, 26·4%).

The diamine had pK_a 5·70, determined by potentiometric titration of an M/800-solution in purified 80% (v/v) 2-methoxyethanol [24] with N/100-hydrochloric acid in the same solvent.

[19] Bhacca, Johnson, and Shoolery, " Nuclear Magnetic Resonance Spectra Catalog," Varian Associates, Palo Alto, 1962, No. 156.
[20] Eichelbaum, *Ber.*, 1889, **22**, 2973.
[21] Knott, *J.*, 1947, 1196.
[22] Barkenbus and Holtzclaw, *J. Amer. Chem. Soc.*, 1925, **47**, 2189.
[23] Gabriel and Otto, *Ber.*, 1887, **20**, 2222.
[24] Ruehle, *Ind. Eng. Chem. Analyt.*, 1938, **10**, 130.

The *picrate*, prepared in nitromethane, crystallised from nitromethane as orange prisms, m. p. 242° (Found: C, 46·7; H, 3·4; N, 21·9. $C_{15}H_{12}N_6O_7$ requires C, 46·4; H, 3·1; N, 21·6%).

* *Dibenzoyl Derivative.*—The diamine (0·25 g.), suspended in water (10 c.c.) containing sodium hydroxide (0·12 g.), was stirred vigorously with benzoyl chloride (0·43 g.) for 3 hr. The 1,3-dibenzamidoisoquinoline (0·3 g.) crystallised from ethanol as the *hydrate*, m. p. 190° (Found: C, 71·3; H, 4·6. $C_{23}H_{17}N_3O_2,H_2O$ requires C, 71·7; H, 5·0%).

Diacetyl Derivative.—The diamine (0·5 g.) was boiled with acetic acid (10 c.c.), acetic anhydride (5 c.c.), and acetyl chloride (15 c.c.) for 3·5 hr. The golden-yellow solid (0·4 g.), m. p. 258·5—260°, was dissolved in a minimum volume of water, and the solution basified with 10% sodium hydroxide. From ethanol–water, the 1,3-diacetamidoisoquinoline crystallised as needles of the *hydrate*, m. p. 222° (Found: C, 60·0; H, 6·2; N, 16·1. $C_{13}H_{13}N_3O_2,H_2O$ requires C, 59·8; H, 5·8; N, 16·1%).

1,3-*Diamino*-4-*nitrosoisoquinoline* (II).—The diamine (1 g.) was dissolved in a mixture of glacial acetic acid (4 c.c.), concentrated hydrochloric acid (3 c.c.), and water (8 c.c.). To the solution, at −5°, sodium nitrite (0·44 g., 1 Equiv.) in water (3 c.c.) was added slowly, and the mixture was then kept at −2° overnight. The pinkish precipitate was dissolved in water (40 c.c.) and an excess of aqueous sodium hydrogen carbonate added. The flocculent olive-green solid was washed with water (3 × 30 c.c.) by centrifugation, and crystallised from dimethyl sulphoxide–water to give reddish-purple needles (0·96 g., 81%), m. p. 279—281° (decomp.) of 1,3-*diamino*-4-*nitrosoisoquinoline* (Found: C, 57·5; H, 4·55; N, 29·8; O, 8·6. $C_9H_8N_4O$ requires C, 57·4; H, 4·3; N, 29·8; O, 8·5%).

2,6-*Diamino*-3-*nitrosopyridine* [25] (IX) crystallised from water as red needles (70%), decomp. at 266° (Found: C, 43·6; H, 4·5; N, 41·3. Calc. for $C_5H_6N_4O$: C, 43·5; H, 4·4; N, 40·6%).

Homophthalimide [26] (VII) was obtained by pyrolytic distillation of diammonium homophthalate at 20 mm.; it crystallised from ethanol as platelets, m. p. 235°.

1,2,3,4-*Tetrahydro*-4-*hydroxyimino*-1,3-*dioxoisoquinoline* (III).—1,3-Diaminoisoquinoline (0·5 g.) was dissolved in concentrated hydrochloric acid (3 c.c.) and ethanol (12 c.c.). To the solution, at 0°, sodium nitrite (0·22 g., 1 Equiv.) in water (2 c.c.) was added, and the mixture kept at 0° for 30 min. and then for 11 days at room temperature. The pale buff precipitate (0·54 g., 86%) was crystallised from acetic acid (charcoal) to give prisms of 1,2,3,4-*tetrahydro*-4-*hydroxyimino*-1,3-*dioxoisoquinoline*, m. p. 259° (decomp.) (Found: C, 57·0; H, 3·3; N, 14·4. $C_9H_6N_2O_3$ requires C, 56·8; H, 3·2; N, 14·7%). Other workers record, without preparative details, m. p. 242—243° (decomp.) [27] and m. p. 318°.[28]

An identical product (i.r. spectrum) was obtained by treating homophthalimide (1·1 g.) in acetic acid (40 c.c.), ethanol (3 c.c.), and concentrated hydrochloric acid (1 c.c.), cooled to 0°, with sodium nitrite (0·52 g.) in water (5 c.c.). The solution turned yellow and the product began to separate. After 30 min., the solid was collected and washed with acetic acid, and ether; it (1·2 g.) then had m. p. 240—244° (decomp.). After one crystallisation from acetic acid, the product had m. p. and mixed m. p. 254—255° (decomp.).

1,2,3,6-*Tetrahydro*-3-*hydroxyimino*-2,6-*dioxopyridine* [14,15] (X).—2,6-Diaminopyridine (1 g.) in concentrated sulphuric acid (3 c.c.) and water (15 c.c.) was treated, similarly to the diaminoisoquinoline, with sodium nitrite (0·88 g.) in water (24 c.c.), and after 11 days the dark precipitate was collected. Crystallisation from aqueous sulphur dioxide gave the 3-hydroxyimino-compound (0·48 g., 44%), m. p. 264—266° (decomp.) (Found: C, 42·9; H, 3·0; N, 20·0. Calc. for $C_5H_4N_2O_3$: C, 42·9; H, 2·9; N, 20·0%).

Degradation of the Diaminonitrosoisoquinoline to Phthalic Acid.—A solution of 1,3-diaminoisoquinoline (0·42 g.) in concentrated sulphuric acid (2·9 c.c.) and water (12 c.c.) was treated at 0° with sodium nitrite (0·4 g., 2 Equivs.) in water (3 c.c.). The mixture was kept at 0° overnight, and then heated under reflux with an excess of aqueous 10% sodium hydroxide until evolution of ammonia ceased. Continuous extraction with ether afforded a crystalline acid (160 mg., 39%) (Found: C, 57·5; H, 3·65. Calc. for $C_8H_6O_4$: C, 57·8; H, 3·6%). The m. p., 206—208° (decomp.), was undepressed by phthalic acid (same m. p.), and the infrared spectra were identical.

[25] Tschitschibabin and Seide, *J. Russ. Phys. Chem. Soc.*, 1920, **50**, 522.
[26] Gabriel, *Ber.*, 1886, **19**, 1653.
[27] Meyer and Vittenet, *Ann. Chim. (France)*, 1932, **17**, 344.
[28] Décombe and Fournier, *Compt. rend.*, 1963, **256**, 1545.

* 1-*Amino*-3-*hydroxylaminoisoquinoline* [20] (IV).—*o*-Cyanobenzyl cyanide (1·42 g.), hydroxylamine hydrochloride (2·8 g.), and sodium carbonate (2·12 g.) were boiled in aqueous methanol for 4 hr. The solution was evaporated under reduced pressure, the residue extracted with ethanol (2 × 10 c.c.), and the extract filtered through charcoal and evaporated to a small bulk. 1-Amino-3-hydroxylaminoisoquinoline crystallised (1·37 g., 78%), and was recrystallised from water (charcoal) to give needles, m. p. 95°, of the *dihydrate* (Found: C, 51·4; H, 6·4; N, 20·4. $C_9H_9N_3O,2H_2O$ requires C, 51·2; H, 6·2; N, 19·9%), which gave the *hemihydrate* at 56°/0·5 mm. (Found: C, 58·3; H, 5·6; N, 23·05. $C_9H_9N_3O,\frac{1}{2}H_2O$ requires C, 58·4; H, 5·4; N, 22·8%).

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