o-Nitroaniline Derivatives. Part VI.[1] Cyanide-induced Cyclisation of *o*-Nitroanils

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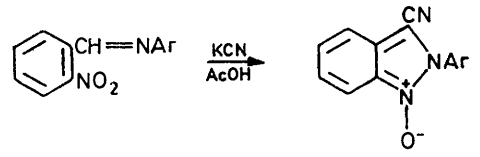
Schiff bases derived from *o*-nitroaniline generally react with cyanide ion, in methanolic solution, to give 2-aryl-1-hydroxybenzimidazoles in moderate to good yield; *N*-*p*-nitrobenzylidene-*o*-nitroaniline gives *N*-*p*-nitrobenzoyl-*o*-nitroaniline as well as the benzimidazole derivative. *N*-*o*-Nitrobenzylidene-*o*-nitroaniline and its simple analogues, however, react with methanolic cyanide to give 3-methoxy-4-(*o*-nitroarylamino)cinnoline 1-oxides and methyl *N*-(*o*-nitroaryl)-*o*-nitrobenzimidates as the only isolated products.

REACTIONS which involve chemical interaction between aromatic nitro-groups and *ortho*-side chains, and which lead to heterocyclic products, have considerable synthetic utility and are well documented.[2] Several such cyclisations are brought about by cyanide ion: in particular, *N*-*o*-nitrobenzylideneanilines (1) react with potassium cyanide in acetic acid to give 2-aryl-3-cyanoindazole 1-oxides (2),[3] and *N*-benzylidene-*o*-nitroaniline (3; Ar = Ph) is cyclised, by potassium cyanide in dry methanol, to 1-hydroxy-2-phenylbenzimidazole (4; Ar = Ph).[4]



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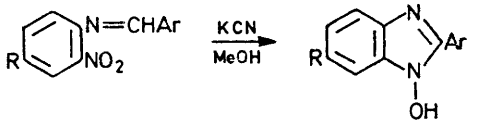


(3) R = H (4) R = H
(5) R = Me, Ar = Ph (6) R = Me, Ar = Ph

As a continuation of this earlier work,[4] we have now examined the reactions of a range of *o*-nitroanils with cyanide ion in methanol, to explore the generality of the reaction (3) ⟶ (4). The results (Table 1) indicate that, for a variety of substituted *o*-nitroanils, moderate to good yields of 2-aryl-1-hydroxybenzimidazoles are obtained. In general, these benzimidazoles are the sole products, and are isolated simply by dilution of the reaction mixture with water and acidification with hydrochloric acid.

In the case of *N*-*p*-nitrobenzylidene-*o*-nitroaniline (3; Ar = C_6H_4·NO_2-*p*), a second product is obtained, and is separable from the hydroxybenzimidazole by chromatography. This is *N*-*p*-nitrobenzoyl-*o*-nitroaniline (7), and its formation from the Schiff base evidently involves oxidation. Benzanilides result directly from the reaction of *N*-benzylideneanilines with cyanide ion in an oxidising solvent such as dimethyl sulphoxide,[4,5] but they are also formed indirectly from *N*-*p*-nitrobenzylideneanilines in methanol solution by the sequence shown in Scheme 1,[6,7] and the formation of (7) in our reaction may also be rationalised in terms of Scheme 1 if it is assumed that it is the α-cyano-anil (8; Ar = C_6H_4·NO_2-*o*) which is the primary product and that this undergoes hydrolysis during the chromatographic work-up.

Of particular interest is the reaction of *N*-*o*-nitrobenzylidene-*o*-nitroaniline (9; X = Y = H) with methanolic potassium cyanide, since in this case cyclisation involving either nitro-group is, in theory, possible. However, this reaction gives neither the indazole oxide (2; Ar = C_6H_4·NO_2-*o*) nor the hydroxybenzimidazole (4; Ar = C_6H_4·NO_2-*o*), but an orange-red compound, $C_{15}H_{12}N_4O_4$, which crystallises out of the cooled reaction mixture, and a yellow compound, $C_{14}H_{11}N_3O_5$, isolated by chromatography of the methanol-soluble material.

The compound $C_{15}H_{12}N_4O_4$ has an i.r. spectrum which shows N–H but no C≡N absorption. The mass spectrum

[1] (*a*) Part V, J. Machin, R. K. Mackie, H. McNab, G. A. Reed, A. J. G. Sagar, and D. M. Smith, preceding paper; (*b*) preliminary report, D. Johnston and D. M. Smith, *Tetrahedron Letters*, 1975, 1121; presented in part at the Chemical Society Autumn Meeting, Leicester, 1974.

[2] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389; E. Ochiai, 'Aromatic Amine Oxides,' Elsevier, Amsterdam, London, and New York, 1967, pp. 59—62; A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic *N*-Oxides,' Academic Press, London and New York, 1971, pp. 120—141; P. N. Preston and G. Tennant, *Chem. Rev.*, 1972, **72**, 627.

[3] G. Heller and G. Spielmeyer, *Ber.*, 1925, **58**, 834; K. Akashi, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1941, **20**, 798 (*Chem. Abs.*, 1949, **43**, 7934); L. C. Behr, E. G. Alley, and O. Levand, *J. Org. Chem.*, 1962, **27**, 65.

[4] R. Marshall and D. M. Smith, *J. Chem. Soc.* (*C*), 1971, 3510.

[5] J. S. Walia, L. Guillot, J. Singh, M. S. Chattha, and M. Satyanarayana, *J. Org. Chem.*, 1972, **37**, 135.

[6] Y. Ogata and A. Kawasaki, *J. Chem. Soc.* (*B*), 1971, 325.

[7] Y. Ogata and A. Kawasaki, *J.C.S. Perkin II*, 1972, 1792.

shows an intense molecular ion (*m/e* 312) and a significant $(M - 16)^+$ ion (a characteristic of *N*-oxides [8]), as well as an intense fragment ion at *m/e* 191 corresponding to $M - C_6H_3NO_2$. The ^1H n.m.r. spectrum contains NH (δ 9.44) and OCH_3 (δ 4.34) signals, the latter at unusually low field, and resonances for eight aryl protons which may be assigned, by scale expansion and spin decoupling, to the protons of two *ortho*-disubstituted rings. One of these aryl signals is a multiplet at exceptionally low field (δ 8.41), *i.e.* lower than that of a proton *ortho* to a nitro-group. Two structures for the compound are consistent with the spectroscopic data and are also conceivable on mechanistic grounds: 3-methoxy-4-(*o*-nitroanilino)cinnoline 1-oxide (10a) and 3-methoxy-4-(*o*-nitrophenyl)-5*H*-1,2,5-benzotriazepine 1-oxide (11a). The low-field one-proton multiplet in the n.m.r. spectrum enables a distinction between these structures to be made. Signals of this type have been observed in the n.m.r. spectra of quinoline *N*-oxides [9] and cinnoline 1-oxides [10] and have been assigned to the 8-proton, which is *peri* to the *N*-oxide function. Such an assignment in the present case is also reasonable, since the signal is shifted slightly to higher field, and is simplified, when the *N*-oxide group is removed by reaction with phosphorus trichloride. Clear indication that the low-field proton in the product was originally the 3-proton of the *o*-nitrobenzylidene group is obtained from the n.m.r. spectra of analogous products formed in the corresponding reactions of a series of *N*-*o*-nitrobenzylidene-*o*-nitroanilines carrying additional substituents. Substituents in the amine-derived ring have little effect on the low-field proton, but a 5-chloro-substituent in the nitrobenzylidene ring simplifies the low-field signal to a doublet (*J* 9 Hz). Thus the proton which is *peri* to the *N*-oxide originates in the aldehyde-derived ring, and the cinnoline structures (10) are correct. In particular, the n.m.r. spectrum of the product derived from *N*-(5-chloro-2-nitrobenzylidene)-4-methyl-2-nitroaniline (Table 4) is completely interpretable in terms of structure (10e): the alternative formulation (11e) requires that the *peri*-proton should show *meta*-splitting (*J* 2—3 Hz) only.

The yellow compound $C_{14}H_{11}N_3O_5$ has an i.r. spectrum which shows no N–H but C=O or C=N (1 675 cm^{-1}) and NO_2 (1 520 and 1 350 cm^{-1}) absorption. The n.m.r.

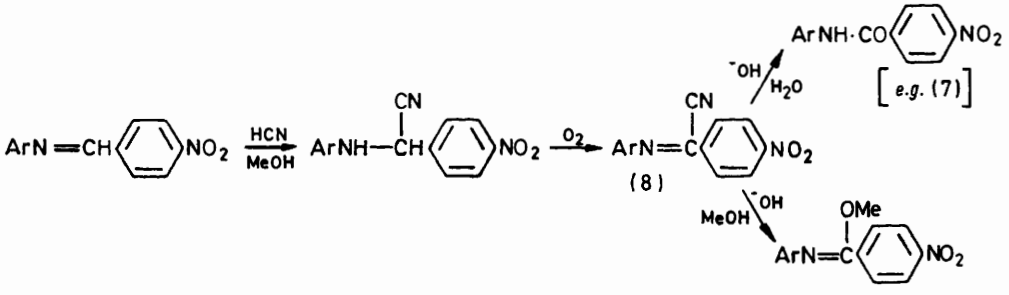
TABLE 1

2-Aryl-1-hydroxybenzimidazoles [(4) or (6)] prepared from *o*-nitroanils [(3) or (5)]

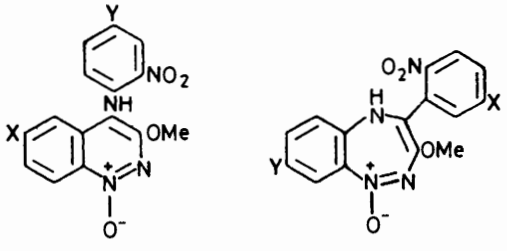
Compound	Yield (%)	M.p. (°C) (decomp.) (solvent) *	Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
(4) Ar = *o*-BrC_6H_4	64	251—252 (EtOH)	$C_{13}H_9BrN_2O$	53.8	3.2	9.4	54.0	3.1	9.7
o-ClC_6H_4	58	232—234 (EtOH)	$C_{13}H_9ClN_2O$	63.6	3.7	11.5	63.8	3.7	11.45
o-MeO·C_6H_4	72	220—222 (EtOH)	$C_{14}H_{12}N_2O_2$	69.7	5.1	11.5	70.0	5.0	11.7
p-ClC_6H_4 †	72	211—213 (EtOH–H_2O)	$C_{13}H_9ClN_2O$,HCl	55.1	3.9	9.85	55.5	3.8	10.0
p-MeO·C_6H_4	70	205 (EtOH–H_2O)	$C_{14}H_{12}N_2O_2$,H_2O	64.6	5.65	10.8	65.1	5.5	10.85
p-MeC_6H_4	61	224—226 (EtOH–H_2O)	$C_{14}H_{12}N_2O$	74.6	5.5	12.5	75.0	5.4	12.5
p-$O_2N·C_6H_4$	30	239—243 (DMF–H_2O) [a]							
(6) §	64	231—233 (DMF–H_2O)	$C_{14}H_{12}N_2O$	74.6	5.5	12.8	75.0	5.4	12.5

* DMF = dimethylformamide. † Hydrochloride. § Experiment carried out by Dr. R. Marshall.

[a] Lit. 243—246° (H. McNab and D. M. Smith, *J.C.S. Perkin I*, 1973, 1310).



SCHEME 1



(10) a; X = Y = H
e; X = Cl, Y = Me

(11) a; X = Y = H
e; X = Cl, Y = Me

[8] T. A. Bryce and J. R. Maxwell, *Chem. Comm.*, 1965, 206; *cf.* A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic *N*-Oxides,' Academic Press, London and New York, 1971, p. 17; M. H. Palmer, E. R. R. Russell, and W. A. Wolstenholme, *Org. Mass Spectrometry*, 1969, **2**, 1265.

[9] K. Tori, M. Ogata, and H. Kano, *Chem. and Pharm. Bull. (Japan)*, 1963, **11**, 681; P. Hamm and W. v. Philipsborn, *Helv. Chim. Acta*, 1971, **54**, 2363.

[10] M. Ogata, H. Kano, and K. Tori, *Chem. and Pharm. Bull. (Japan)*, 1963, **11**, 1527; M. H. Palmer and E. R. R. Russell, *Chem. and Ind.*, 1966, 157; *J. Chem. Soc.* (*C*), 1968, 2621.

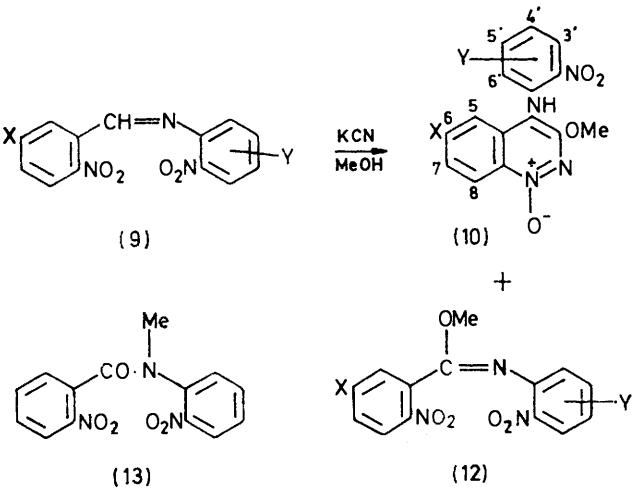
TABLE 2

Products from the cyclisation of *N*-*o*-nitrobenzylidene-*o*-nitroanilines (9) with methanolic potassium cyanide

		Yields (%)			
		Cinnoline 1-oxide (10)		Imidate ester (12)	
X	Y				
H	H	(10a)	25	(12a)	14
H	4'-Me	(10b)	32	(12b)	3
H	6'-Me	(10c)	21	(12c)	0
H	4'-OMe	(10d)	36	(12d)	Trace (<1)
Cl	4'-Me	(10e)	23	(12c)	12
Cl	4'-OMe	(10f)	31	(12f)	10

spectrum contains a three-proton singlet (δ 3.97) and signals for eight aromatic protons which may be assigned to the protons of two *ortho*-disubstituted rings. In view of the non-identity of this compound with *N*-methyl-*N*-*o*-nitrobenzoyl-*o*-nitroaniline (13), and by analogy with Scheme 1, it has been formulated as methyl *N*-(*o*-nitrophenyl)-*o*-nitrobenzimidate (12a). Analogous products have been isolated from the corresponding reactions of other anils of type (9).

The yields of cinnoline 1-oxides (10) and imidates (12) isolated from these reactions are shown in Table 2, and the properties of the products are collected in Tables 3—5. The corresponding reaction of *N*-*o*-nitrobenzylidene-*o*-nitroaniline with potassium cyanide in ethanol 1-oxide, and the only one of the three which uses a cyano-group as the source of the 2- and 3-atoms of the cinnoline system.



The simplest mechanism by which the formation of (10) and (12) may be rationalised is outlined in Scheme 2. The mechanism proposed for the imidate formation is based on the work of Ogata and Kawasaki [6,7] (Scheme 1),

TABLE 3

3-Methoxy-4-(*o*-nitroarylamino)cinnoline 1-oxides (10)

					Found (%)			Required (%)		
Compd.	M.p. (°C)	ν_{NH}/cm^{-1}	$\lambda_{max.}$ ($CHCl_3$)/nm (ε)	Formula	C	H	N	C	H	N
(10a)	249—250 [a]	3 400	424 (13 900)	$C_{15}H_{12}N_4O_4$	57.6	3.9	18.2	57.7	3.9	17.9
(10b)	246—248 [b]	3 380	438 (17 200)	$C_{16}H_{14}N_4O_4$	58.9	4.4	17.0	58.9	4.3	17.2
(10c)	195—197 [b,c]	3 300	448 (8 500)	$C_{16}H_{14}N_4O_4$	58.6	4.5	16.9	58.9	4.3	17.2
(10d)	198—200 [b]	3 290	445 (11 200)	$C_{16}H_{14}N_4O_5$	55.9	4.3	16.0	56.1	4.1	16.4
(10e)	238—240 [b]	3 310	440 (10 800)	$C_{16}H_{13}ClN_4O_4$	53.5	3.7	15.6	53.3	3.6	15.5
(10f)	220 [b,c]	3 320	444 (9 200)	$C_{16}H_{13}ClN_4O_5$	51.1	3.7	14.8	51.0	3.45	14.8

[a] From methanol. [b] From benzene–petroleum. [c] Decomp.

TABLE 4

^{1}H N.m.r. spectra of 3-methoxy-4-(*o*-nitroarylamino) cinnoline 1-oxides (10)

	δ ($CDCl_3$)										*J*/Hz
Compd.	N–H	OMe	H(5)	H(6)	H(7)	H(8)	H(3')	H(4')	H(5')	H(6')	
(10a)	9.44	4.34	←	7.5—7.7	→	8.41	8.26	6.95	7.36	6.61	(3',4'), 8; (4',5'), and (5',6'), 8.5; (3',5'), 1.5
(10b) *	9.50	4.34	←	7.5—7.8	→	8.38	8.20	[Me (2.57)]	8.00	7.34	(7,8) and (5',6'), 9; (3',5'), 2
(10c)	8.55 †	3.93	←	7.5—7.9	→	8.55 †	8.02	7.02	7.23	[Me (1.92)]	(3',4') and (4',5'), 8.5
(10d)	9.04	4.08	(←	7.5—7.8	→)§	8.58	(7.5—7.8)§	[OMe(3.83)]	7.04	6.49	(5',6'), 9
(10e)	9.03	4.08	7.72	(Cl)	7.50	8.55	8.08	[Me (2.33)]	7.20	6.40	(7,8), 9; (5,7) and (3',5'), 2; (5',6'), 8
(10f)	8.96	4.08	7.72¶	(Cl)	7.46	8.52	7.72 ¶	[OMe (3.85)]	7.05	6.45	(7,8) and (5',6'),9; (5,7) and (3',5'), 2

* Solvent CF_3·CO_2H. § H(5), H(6), H(7), and H(3') signals overlapping. ¶ H(5) and H(3') signals coincident. † NH and H(8) signals coincident.

gives the ethoxy-analogues of (10a) and (12a), in yields of 11 and 16% respectively.

This cinnoline 1-oxide synthesis provides a simple route to a group of cinnoline derivatives which are at present not accessible by any other method. Among the numerous recorded cyclisations of *o*-nitro-compounds,[2] it is only the third which leads to a cinnoline and that proposed for the cinnoline 1-oxide formation also has good literature analogy, especially in the well known Arndt synthesis of 1,2,4-benzotriazine 1-oxides [*e.g.* (14) ⟶ (15)] [11] and related reactions such as (16) ⟶ (17).[12] There is also a precedent for cyclisation of imidates such as (23), in the sequence (18) ⟶ (19).[13]

The reason why *N*-*o*-nitrobenzylidene-*o*-nitroanilines

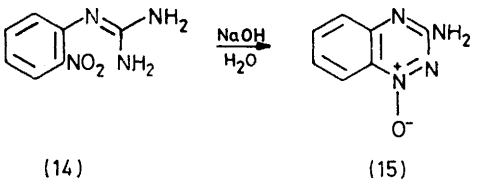
[11] F. Arndt, *Ber.*, 1913, **46**, 3522; *cf.* reviews in ref. 2.
[12] G. Tennant, *J. Chem. Soc.* (*C*), 1967, 1279.
[13] T. Okamoto and H. Takahashi, *Chem. and Pharm. Bull.* (*Japan*), 1971, **19**, 1809.

do not undergo cyclisation under these conditions to indazole oxides or hydroxybenzimidazoles presumably lies in the electron delocalisation in the intermediates (20)—(22) (Scheme 2), which are the necessary intermediates for such cyclisations. In each of these, the nucleophilic centre [the charged atom in (20) and (21), and the amino-nitrogen atom in (22)] is attached to an *o*-nitrophenyl group, and the nucleophilicity of this centre will thus be appreciably diminished. In addition there is likely to be appreciable steric hindrance to intramolecular nucleophilic attack by such a centre on the appropriate nitro-group.

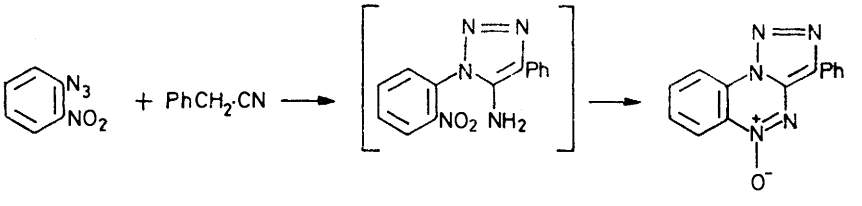
TABLE 5

Methyl *N*-(*o*-nitroaryl)-*o*-nitrobenzimidates (12)

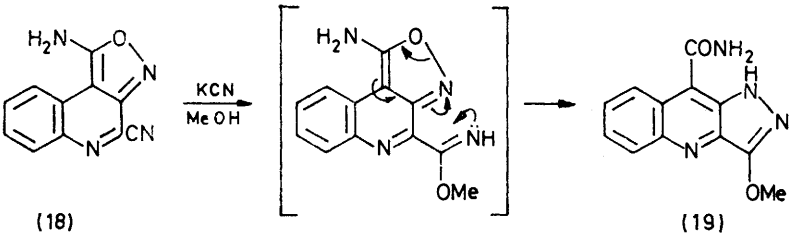
Compd.	M.p. (°C) (solvent)	$\nu_{C=N}$/cm^{-1}	Formula	Found (%) C	H	N	Required (%) C	H	N
(12a)	114—116 (EtOH–H_2O)	1 675	$C_{14}H_{11}N_3O_5$	55.9	3.8	13.9	55.8	3.7	13.95
(12b)	104—105 (EtOH)	1 675	$C_{15}H_{13}N_3O_5$	57.1	4.3	13.2	57.1	4.2	13.3
(12d)	(Not isolated; identified by mass spectrometry)								
(12e)	107—109 (EtOH)	1 680	$C_{15}H_{12}ClN_3O_5$	51.3	3.4	11.9	51.5	3.4	12.0
(12f)	122—124 (EtOH)	1 675	$C_{15}H_{12}ClN_3O_6$	49.0	3.3	11.4	49.2	3.3	11.5



(14) (15)



(16) (17)



(18) (19)

In our preliminary communication [1b] we referred to the formation of 4-arylamino-3-methoxycinnoline 1-oxides from other *N*-*o*-nitrobenzylideneanilines lacking the *o*-nitro-group in the amine-derived ring. In such cases, however, there is a different co-product and an additional mechanistic ambiguity; we shall discuss these reactions in full in a subsequent paper.

EXPERIMENTAL

' Petroleum ' refers to the fraction of b.p. 40—60°. I.r. spectra recorded are those of Nujol mulls. Chemical shifts are recorded relative to tetramethylsilane (internal reference).

Preparation of o-*Nitroanils.*—These were prepared by the standard methods described in Part IV.[14] Their properties are recorded in Table 6.

Reactions of o-*Nitroanils with Potassium Cyanide.*—(a) *Simple* o-*nitroanils* [(3) *and* (5)]. Potassium cyanide (0.65 g, 10 mmol) was added to a solution of the *o*-nitroanil (5 mmol) in dry methanol (10 ml) and the mixture was heated under reflux for 5 h, then cooled, diluted with water, and carefully acidified with concentrated hydrochloric acid. The precipitated 2-aryl-1-hydroxybenzimidazole was filtered off and recrystallised as indicated in Table 1. In one reaction (involving *N*-*p*-chlorobenzylidene-*o*-nitroaniline) the product isolated was a hydrochloride; in the remaining cases the free hydroxybenzimidazole was obtained.

(b) N-p-*Nitrobenzylidene*-o-*nitroaniline.* At the end of this reaction, carried out under the conditions described in (a), the methanol was distilled off and the residue chromatographed on silica gel. Elution with benzene gave *N*-*p*-nitrobenzoyl-*o*-nitroaniline (7) (30%), m.p. 219—221° (lit.,[15] 222—223°), and elution with methanol gave 1-hydroxy-2-*p*-nitrophenylbenzimidazole (30%), both identified by comparison with an authentic sample.

(c) N-o-*Nitrobenzylidene*-o-*nitroanilines* (9). A solution of the anil (5 mmol) and potassium cyanide (10 mmol) in methanol (100 ml) was heated under reflux for 3 h, then

[14] D. Johnston and D. M. Smith, *Org. Mass Spectrometry*, 1974, **9**, 789.

[15] P. Grammaticakis, *Bull. Soc. chim. France*, 1960, 1956.

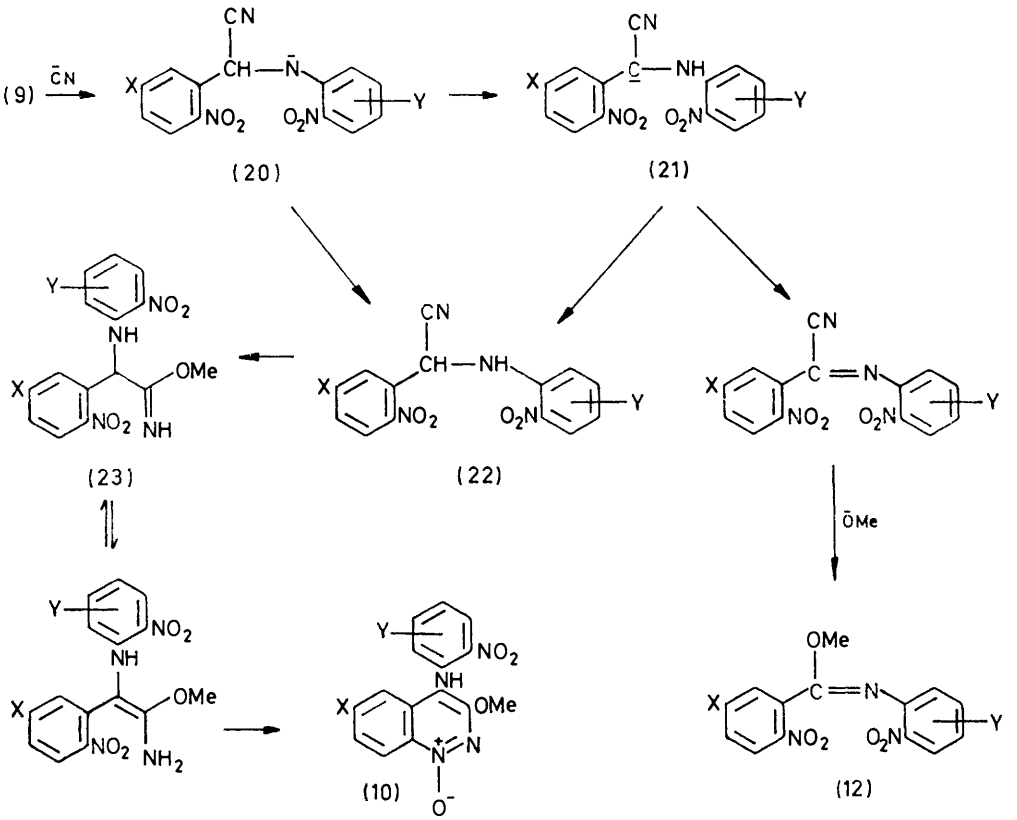
cooled, and the 3-*methoxy*-4-(o-*nitroarylamino*)*cinnoline* 1-*oxide* (10) was filtered off. The filtrate was diluted with water (*ca.* 400 ml) and extracted with chloroform; the extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel; elution with benzene gave the *methyl* N-(o-*nitroaryl*)-o-*nitrobenzimidate* (12).

In the reaction of *N*-(*o*-nitrobenzylidene)-6-methyl-2-nitroaniline, the cinnoline oxide [*viz.* (10c)] did not crystallise out of the reaction mixture. The entire mixture was diluted with water and extracted with chloroform, and the extract was chromatographed as described above to give the cinnoline 1-oxide (10c) [eluted by benzene–chloroform (3 : 1)].

The products were characterised as indicated in Tables 3—5.

(d) N-o-*Nitrobenzylidene*-o-*nitroaniline, in ethanol.* Under the conditions described in (c), but with ethanol replacing methanol, an ethanol-soluble mixture was obtained. The products were therefore isolated by dilution and extraction, and were separated by chromatography, as described above.

Ethyl N-(o-*nitrophenyl*)-o-*nitrobenzimidate* (12a; OEt for OMe), obtained in 16% yield, had m.p. 110—112° (from ethanol) (Found: C, 56.9; H, 4.1; N, 13.0. $C_{15}H_{13}N_3O_5$ requires C, 57.1; H, 4.2; N, 13.3%); $\nu_{max.}$ 1 680 cm^{-1} (C=N); δ($CDCl_3$) 1.76 (3 H, t, *J* 7 Hz, Me), 4.45 (2 H, q,



SCHEME 2

TABLE 6

o-Nitroanils (3), (5), and (9)

Compd.	M.p. (°C)	δ($CDCl_3$) (C*H*=N)	Formula	Found (%) C	H	N	Required (%) C	H	N
(3) Ar = *o*-BrC_6H_4	110—112	8.80	$C_{13}H_9BrN_2O_2$	50.7	2.9	9.0	51.1	2.95	9.1
o-ClC_6H_4	113—115	8.83	$C_{13}H_9ClN_2O_2$	59.6	3.6	10.6	59.9	3.45	10.75
o-MeO·C_6H_4	79—80	8.83	$C_{14}H_{12}N_2O_3$	65.4	4.9	10.9	65.6	4.7	10.9
p-ClC_6H_4	79—80	8.33	} See Part IV [14]						
p-MeO·C_6H_4	81—83	8.30							
p-MeC_6H_4	72—74	8.33							
p-O_2N·C_6H_4	132—134	8.49							
(5)	74—76	8.25	See Part II [4]						
(9) X = Y = H	181—182	8.90	} See Part IV [14]						
X = H, Y = 4′-Me	183—185	8.89							
X = H, Y = 6′-Me	145—147	8.72							
X = H, Y = 4′-OMe	165—167	8.90	$C_{14}H_{11}N_3O_5$	55.9	3.8	13.8	55.8	3.7	13.95
X = Cl, Y = 4′-Me	182—184	8.86	See Part IV [14]						
X = Cl, Y = 4′-OMe	164—166	8.88	$C_{14}H_{10}ClN_3O_5$	50.1	2.9	12.65	50.1	3.0	12.5

J 7 Hz, CH_2), 6.74—7.33 (3 H, m), 7.35—7.54 (3 H, m), and 7.76—8.16 (2 H, m).

3-*Ethoxy*-4-(o-*nitroanilino*)*cinnoline* 1-*oxide* (10a; OEt for OMe) (yield 11%) had m.p. 176—178° (from ethanol) (Found: C, 58.5; H, 4.3; N, 17.1. $C_{16}H_{14}N_4O_4$ requires C, 58.9; H, 4.3; N, 17.2%); $\nu_{max.}$ 3 300 cm^{-1} (N–H); $\lambda_{max.}(CHCl_3)$ 440 nm (ε 10 200); $\delta(CDCl_3)$ 1.33 (3 H, t, *J* 7 Hz), 4.52 (2 H, q, *J* 7 Hz), 6.53 (1 H, dd, *J* 8 and 2 Hz), 6.86 (1 H, dt, *J* 8 and 2 Hz), 7.34 (1 H, dt, *J* 8 and 2 Hz), 7.5—7.8 (3 H, m), 8.25 (1 H, dd, *J* 9 and 2 Hz), 8.55 (1 H, m), and 9.22br (1 H, s, NH); *m/e* 326 (M^+, 100%), 310 (4%), and 178 (6%).

Deoxygenation of 3-*Methoxy*-4-(o-*nitroanilino*)*cinnoline* 1-*oxide* (10a).—Phosphorus trichloride (0.3 ml) was added to a suspension of (10a) (0.15 g) in chloroform (5 ml) and the mixture was heated under reflux for 1 h, then cooled. Water was added, the aqueous layer was basified (2M-NaOH), and the organic product extracted with more chloroform. The chloroform solution was dried (Na_2SO_4) and evaporated, giving 3-*methoxy*-4-(o-*nitroanilino*)*cinnoline* (0.130 g, 90%), m.p. 198—200° (from ethanol) (Found: C, 60.6; H, 4.2; N, 18.7. $C_{15}H_{12}N_4O_3$ requires C, 60.8; H, 4.1; N, 18.9%); $\nu_{max.}$ 3 340 cm^{-1} (N–H); $\lambda_{max.}(CHCl_3)$ 409 nm (ε 10 800); $\delta(CDCl_3)$ 4.27 (3 H, s, OMe), 6.78 (1 H, dd, *J* 8 and 2 Hz), 7.02 (1 H, t, *J* 8 Hz), 7.26—7.88 (4 H, m), 8.24 (1 H, dd, *J* 8 and 2 Hz), 8.39 (1 H, dd, *J* 8 and 2 Hz), and 8.86br (1 H, s, NH); *m/e* 296 (M^+, 32%), 176 (12), 138 (15), and 136 (40).

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