Benzofurazan *N*-Oxides as Synthetic Precursors. Part 3.[1] Acid-catalysed Cyclisation of *NN*-Dialkyl-*N'*-(*o*-nitrophenyl)hydrazines [2]

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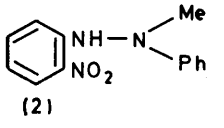
Acid-catalysed cyclisation of the title hydrazines with constant-boiling hydrochloric acid or hot polyphosphoric acid causes cyclisation in three ways: (a) by the most common pathway, to give *N*-(alkylamino)benzimidazoles (4); (b) to give benzotriazoles (5) and their *N*-oxides (5a): and (c) to give 2-alkyl-1,2,4-benzotriazinium-6-olates (6). These synthetically useful reactions have been rationalised mechanistically and their scope and limitations examined.

THE cyclisations of *NN*-dialkyl-*o*-nitroanilines [3] and *o*-nitrophenylhydrazines [4] as routes to benzimidazoles and benzotriazoles, respectively, are well documented. However, the related trisubstituted hydrazines (1) have been largely overlooked. Clemo and Lee [5] correctly reported the benzidine rearrangement of the *NN'*-diaryl-*N*-alkylhydrazine (2) in warm aqueous acid giving the biphenyl



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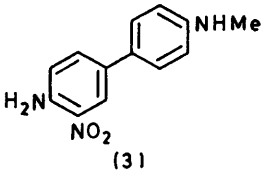


(3)

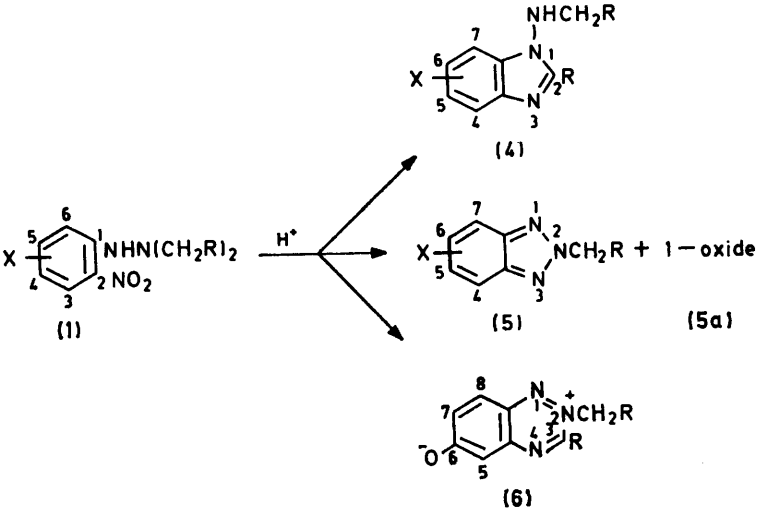
(3). We had available a wide variety of the *NN*-dialkyl analogues (1) derived from benzofurazan *N*-oxides,[6] in which this rearrangement is impossible, and have investigated their cyclisation potential.

The hydrazines (1) proved to be versatile in their cyclisation reactions, giving, by appropriate choice of substrate or conditions, *N*-aminobenzimidazoles (4), 2-alkylbenzotriazoles (5), or 2-alkyl-1,2,4-benzotriazinium-6-olates (6) (Scheme 1). For example, by treatment with hot, constant-boiling hydrochloric acid, a series of *NN*-dimethyl-*N'*-(*o*-nitrophenyl)hydrazines (1; R = H, X = H, 5-Cl, 4-CF_3, or 4-CO_2Et) gave good yields of the *N*-aminobenzimidazoles (4) (Table 1). That the parent (1; X = H) and the 5-chloro-derivative (1; X = 5-Cl) gave the same product (4; X = 6-Cl) is suggestive of an intermediate *N*-oxide. We have previously observed [7] such deoxygenative chlorination in treatment of benzimidazole *N*-oxides with hot hydrochloric acid. Treatment of the hydrazine (1; R = X = H) with hydrobromic or trifluoroacetic acid instead of hydrochloric acid gave the unsubstituted benzimidazole (4; X = R = H). The ester derivative (1; R = H, X = CO_2Et) naturally underwent hydrolysis during the cyclisation. *N*-Aminobenzimidazole formation did not occur with a

[1] Part 2, D. W. S. Latham, J. A. L. Herbert, O. Meth-Cohn, and H. Suschitzky, preceding paper.
[2] Preliminary communication, D. W. S. Latham, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Chem. Comm.*, 1973, 1302.
[3] O. Meth-Cohn and H. Suschitzky, *Adv. Heterocyclic Chem.*, 1972, **14**, 211.
[4] J. D. Loudon and G. Tennant, *Chem. Rev.*, 1972, **72**, 627.
[5] G. R. Clemo and T. B. Lee, *J. Chem. Soc.*, 1954, 2417.
[6] D. W. S. Latham, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1976, 2216.
[7] R. Fielden, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1973, 69 .

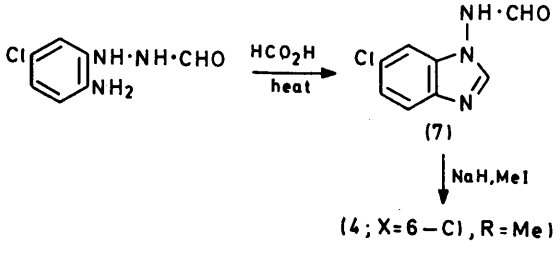
2,4-dinitrophenylhydrazine; instead 2-methyl-6-nitrobenzotriazole (5) together with its 1-oxide (5a) were produced. However, use of polyphosphoric acid (PPA) instead of hydrochloric acid did give a reasonable yield of 5-nitro-1-methylaminobenzimidazole (4).

N-aminobenzimidazoles (4) were obtained (Table 1) in various yields. Thus, the pyrrolidino-analogues (1; RR = $[CH_2]_2$) gave no cyclisation products at all, suggesting steric limitations in the necessary rearrangement, and the six- and seven-membered homologues (1;



SCHEME 1

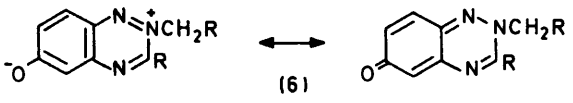
The structures of the products followed in particular from their spectra. The u.v. spectra showed a typical benzimidazole chromophore, containing the two diagnostic peaks (283 and 289 nm), and the i.r. spectra revealed one NH absorption. In the ^1H n.m.r. spectrum, the most useful feature was the coupling of the NH proton to the adjacent methyl group (not seen in every example), which was removed on addition of D_2O. 6-Chloro-1-methylaminobenzimidazole (4; R = X = H) was identical with material synthesised independently (Scheme 2).[8] The intermediate formamido-derivative



SCHEME 2

(7) displayed a typical u.v. spectrum (280 and 287 nm) and amidic NH (3 110 cm^{-1}) and carbonyl i.r. absorption (1 700 cm^{-1}), and was hydrolysed by acid to the corresponding *N*-aminobenzimidazole [$\nu_{max.}$ 3 320 and 3 180 cm^{-1} (NH_2)], which gave a benzylidene derivative with benzaldehyde. Thus, any possibility of triazine formation is ruled out. Attempted reduction of the formyl derivative (7) with lithium aluminium hydride gave 5-chlorobenzimidazole.

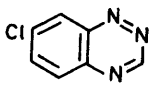
When this reaction was extended to hydrazines in which a heterocycle replaced the dimethyl amino-group (1; RR = $[CH_2]_{2-4}$ or $CH_2{\cdot}O{\cdot}CH_2$), the related tricyclic RR = $[CH_2]_3$ or $[CH_2]_4$) gave moderate yields of the corresponding benzimidazoles. The morpholino-derivatives (1; RR = $CH_2{\cdot}O{\cdot}CH_2$) were generally unreactive (in line with earlier observations in which a cyclisation sequence initiated by spiro-attack at the ring nitrogen atom generally failed [3]) though the 5-chloro-derivative (1; X = 5-Cl, RR = $CH_2{\cdot}O{\cdot}CH_2$) did yield the benzimidazole (4; X = 6-Cl, RR = $CH_2{\cdot}O{\cdot}CH_2$). The cyclisation again proceeded in the presence of various substituents, but once more was unsuccessful with the 2,4-dinitrophenylhydrazines (1; X = 4-NO_2). With hydrochloric acid or PPA as reagent only a low yield of the appropriate benzimidazole (4) was isolated, together with orange water-soluble solids to which we ascribe the quinonoid triazine structure (6). Both nitro-functions are lost during the reaction and the betaine character no doubt accounts for the water solubility and the disappearance of the orange colour on addition of mineral acid. The low carbonyl stretching frequency (1 625 cm^{-1}) is in accord with other quinone and pyridone systems.[9] Furthermore, the low field aromatic proton n.m.r. signals (τ 0.8—2.2) of the starting dinitro-compounds are replaced by high-field signals at τ 2.5—3.8. Similarly, the $^+N{\cdot}CH_2$ signal appears at τ 5.6—5.7,



more than 1 p.p.m. lower than the $N{\cdot}CH_2$ in the *N*-aminobenzimidazoles (τ 6.7—6.8) or the starting dinitro-compounds (τ 6.9—7.2).

[8] M. N. Sheng and A. R. Day, *J. Org. Chem.*, 1963, **28**, 736.
[9] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1960, p. 150.

Another variation in the reaction pathway was observed when *NN*-dimethyl-*N'*-(5-chloro-2-nitrophenyl)hydrazine (1; X = 5-Cl, R = Me) was treated with PPA. Surprisingly, only the pale yellow 7-chloro-1,2,4-benzotriazine (8) was isolated (27%).

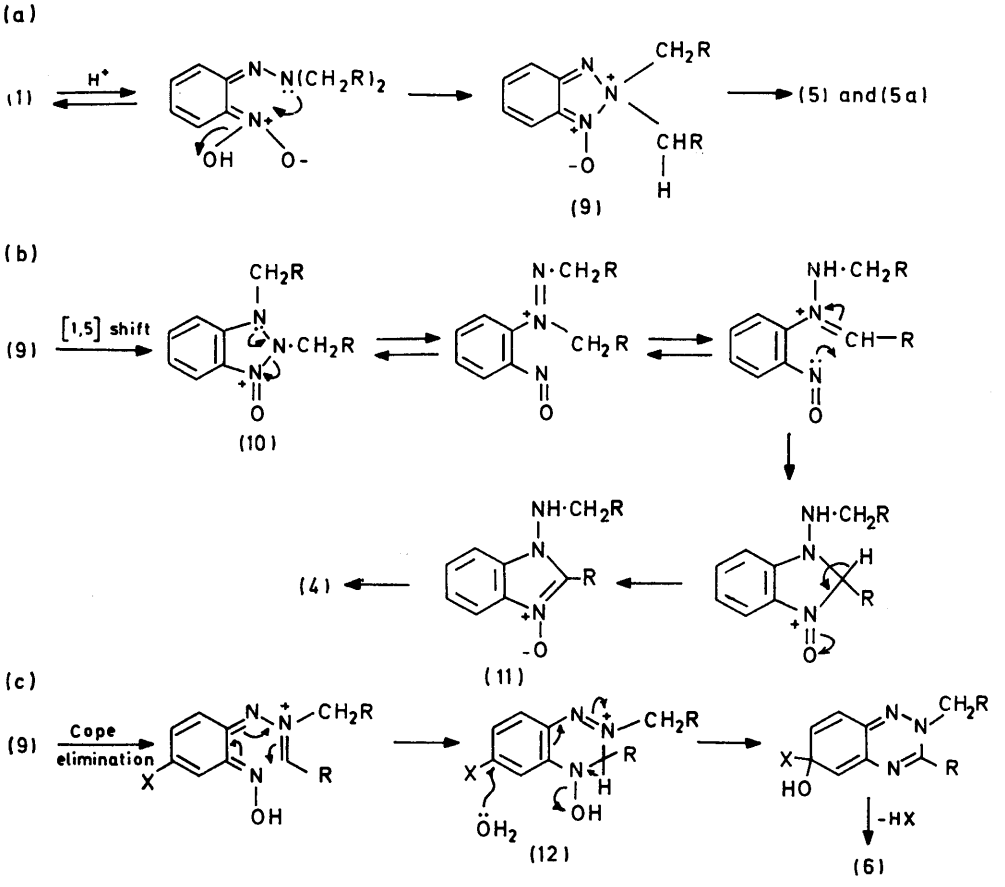


(8)

All these products may be rationalised by analogy with our previous examples[3] of the '*ortho*-tertiary-amino-effect' and are best viewed as variations upon one basic theme involving initially a non-aromatic benzotriazolium *N*-oxide (9) (Scheme 3). This intermediate derivative (9; RR = $[CH_2]_2$) as we have previously noted.[1] A ring-opening–ring-closure sequence converts the triazole *N*-oxide (10) into the benzimidazole'*N*-oxide (11) and thence into the aminobenzimidazole (4). The *N*-oxide is also able to undergo deoxygenative chlorination with hydrochloric acid as previously noted.

Finally (c) the triazolium salt (9) can undergo a Cope-type elimination followed by an electrocyclic rearrangement to yield the dihydro-1,2,4-triazine (12), a reasonable precursor of the triazine (8). Furthermore, by nucleophilic attack of water on the highly electrophilic 6-position of (12; X = NO_2) (activated by both the nitro and the diazonium entity) the quinonoid triazines (6) can be formed.

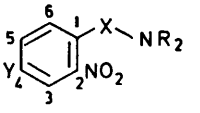
That the presence of the hydrazine NH group is



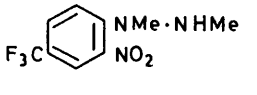
SCHEME 3

may react in one of three ways (a)—(c). In pathway (a) loss of an alkyl cation yields the benzotriazole *N*-oxide (5a) and/or the benzotriazole (5). Route (b) proceeds by a [1,5] sigmatropic shift of the offending alkyl group, is analogous to the thermal [1,5] shift of an alkyl group of 2,2-dialkyl-2*H*-benzimidazoles to give the more stable 1,2-dialkylbenzimidazoles.[10] The failure of the pyrrolidine derivatives to follow this pathway no doubt stems from the inherent instability of the [5.5] spiro-

essential for cyclisation is underlined by the failure to cyclise the analogues (13; X = NMe, CH_2, CO, or



(13)

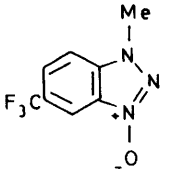


(14)

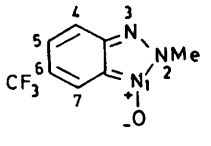
SO_2, RR = $[CH_2]_5$) in an analogous manner. Furthermore, whereas while the trimethylhydrazine (13; X = NMe, R = Me, Y = CF_3) was unchanged in boiling

[10] R. Garner, G. V. Garner, and H. Suschitzky, *J. Chem. Soc.* (*C*), 1970, 825.

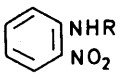
hydrochloric acid, the related dimethylhydrazine (14) did cyclise giving a benzotriazole *N*-oxide (15a or b) in



(15a)



(15b)



(16)

58% yield, rather than a benzimidazole. This cyclisation again is in accord with our proposed mechanisms [Scheme 3, pathway (a)]. The related *o*-nitroanilines (16; R = Ph, OMe, or cyclohexyl) were also unchanged under the usual conditions.

N, 16.9. $C_9H_{10}F_3N_3O_2$ requires C, 43.3; H, 4.1; N, 16.9%), M^+ 249, $\nu_{max.}$ (Nujol) 3 265 cm^{-1} (NH), τ ($CDCl_3$) 7.44 (d, NH*Me*, collapsed to singlet with D_2O), 6.86s (NMe), 6.58br (NH), 3.03 (d, 6-H, *J* 9 Hz), and 2.37 (m, 3- and 5-H).

NNN'-*Trimethyl*-N-(2-*nitro*-4-*trifluoromethylphenyl*)-*hydrazine* (13; X = NMe, R = Me, Y = CF_3).—To the dimethylhydrazine (14) (2.0 g) in dry dimethylformamide (50 ml) was added sodium hydride (1.0 g). When the effervescence had subsided methyl iodide (1.5 g) was added and the mixture stirred for 6 h and then poured into ice–water (300 ml). The mixture was extracted with toluene, washed with water (5 × 200 ml), dried, and evaporated. Chromatography on alumina (elution with toluene) gave the hydrazine (13) (1.2 g, 57%) as a yellow oil which showed no NH band in the i.r. spectrum; M^+ 263, τ ($CDCl_3$)

TABLE 1

Products from the acid-catalysed cyclisation of the hydrazines (1)

Hydrazine (1)			Products										
			Imidazole (4)			Triazole (5)			Triazine (6)			Others		
R or RR	X	Acid [time of heating (h)]	X	%	M.p. (°C)	X	%	M.p. (°C)	%	M.p. (°C)		%	M.p. (°C)
H	H	HBr [3]	H	37	226								
H	H	AcOH [3]	H	65	226								
H	H	HCl [3]	6-Cl	60	109								
H	5-Cl	HCl [4]	6-Cl	68	109	5-Cl *	2	137					
H	5-Cl	PPA									(8)	27	118—119
H	4-CF_3	HCl [3]	5-CF_3	50	131								
H	4-NO_2	HCl [5]				5-NO_2	16	189					
						5-NO_2 *	23	203					
H	4-NO_2	PPA [3]	5-NO_2	42	156	NO_2	†						
						5-NO_2 *	†						
H	4-CO_2Et	HCl [5]	5-CO_2H ‡	79	245—247								
$[CH_2]_2$	H	HCl [3]									Tar		
$[CH_2]_2$	4-CF_3	HCl [3]									Tar		
$[CH_2]_2$	4-NO_2	HCl [3]									Tar		
$[CH_2]_2$	4-NO_2	PPA [3]									Tar		
$[CH_2]_3$	H	HCl [3]	6-Cl	63	198—199								
$[CH_2]_3$	5-Cl	HCl [4]	6-Cl	23	198—199								
$[CH_2]_3$	4-CF_3	HCl [5]	5-CF_3	34	189								
$[CH_2]_3$	4-NO_2	HCl [8]	5-NO_2	6	224—226				17	240 (decomp.)			
$[CH_2]_3$	4-NO_2	PPA [4]	5-NO_2	50	224—226								
$[CH_2]_4$	5-Cl	HCl [2]	6-Cl	46	203—205								
$[CH_2]_4$	4-CF_3	HCl [5]	5-CF_3	22	148								
$[CH_2]_4$	4-NO_2	HCl [5]	5-NO_2	8	222				20	227—229			
$[CH_2]_4$	4-NO_2	PPA [6]	5-NO_2	10	222								
$CH_2{\cdot}O{\cdot}CH_2$	H	HCl [3]									Tar		
$CH_2{\cdot}O{\cdot}CH_2$	5-Cl	HCl [5]	6-Cl	36	215—217								
$CH_2{\cdot}O{\cdot}CH_2$	4-CF_3	HCl [3]									Tar		
$CH_2{\cdot}O{\cdot}CH_2$	4-NO_2	PPA [3]									Tar		

* *N*-Oxide (5a). † Isolated in small amounts. ‡ Converted into 5-CO_2Et, m.p. 135°.

EXPERIMENTAL

General conditions are as indicated in Part 1 [6] and 2.[1] The preparation of most of the hydrazines is described in Part 1.[6]

NN'-*Dimethyl*-N-(2-*nitro*-4-*trifluoromethylphenyl*)*hydrazine* (14).—1-Chloro-2-nitro-4-trifluoromethylbenzene (4.5 g) in dimethylformamide (30 ml) was treated with sodium carbonate (6.0 g) and *NN'*-dimethylhydrazine dihydrochloride (2.7 g), and the mixture was heated on a water-bath for 6 h. The cooled solution was poured into water (250 ml) and the yellow precipitate filtered off and recrystallised from ethanol to give *compound* (14) as yellow needles (4.0 g, 80%), m.p. 70° (Found: C, 43.7; H, 3.8; 7.60 (s, NMe_2), 7.13 (s, NMe), 2.63br (m, 5- and 6-H), and 2.34br (3-H).

N-(2-Nitrobenzyl)piperidine,[11] *N*-(2-nitrobenzoyl)piperidine,[12] 2-nitrodiphenylamine,[13] *N*-(2-nitrophenyl)cyclohexylamine,[14] and *N*-(2-nitrophenylsulphonyl)piperidine [15] were prepared by literature methods.

O-*Methyl*-N-(2-*nitrophenyl*)*hydroxylamine* (16; R = OMe).—1-Fluoro-2-nitrobenzene (1.4 g) in dimethylformamide (70 ml) was mixed with *O*-methylhydroxylamine hydrochloride (0.9 g) and sodium hydrogen carbonate (3.0 g). The mixture was heated on a water-bath for 7 h, cooled, and poured into water. Extraction with toluene

[11] E. Lellmann and H. Pekrun, *Annalen*, 1890, **259**, 40.
[12] A. P. N. Franchimont, W. van Ryn, and H. Friedman, *Rec. Trav. chim.*, 1907, **26**, 228.
[13] F. Ullmann and G. Nadai, *Ber.*, 1908, **41**, 1872.
[14] B. W. Ashton and H. Suschitzky, *J. Chem. Soc.*, 1957, 4559.
[15] O. Meth-Cohn, H. Suschitzky, and M. E. Sutton, *J. Chem. Soc.* (*C*), 1968, 923.

and washing with water (5 × 200 ml) gave a solution which, after drying and evaporation, yielded an oil. Elution through alumina with light petroleum–ethyl acetate gave compound (16) as orange plates, $\nu_{max.}$ (Nujol) 3 410 cm^{-1} (NH), M^+ 168, τ ($CDCl_3$) 6.11 (s, Me), 5.20 (s, NH), and 1.5—3.3 (m, aromatic).

and the product(s) were then eluted with appropriate solvents, and recrystallised (see Tables 1 and 2).

Method B. The hydrazine (2.0 g) and polyphosphoric acid (20 g) were heated at 77 or 100 °C until t.l.c. showed maximum consumption of starting material. The mixture was then poured into ice–water (100 ml) and carefully

TABLE 2

Properties of the benzimidazoles (4), benzotriazoles (5), and benzotriazines (6) and (8)

Compound			Found (%)				Required (%)			
No.	R or RR	X	C	H	N	Formula	C	H	N	τ ($CDCl_3$) {J/Hz}
(4)	H	6-Cl	52.3	4.2	23.5	$C_8H_8ClN_3$	52.0	4.5	23.1	6.93d {4} (Me), 1.94 (2-H), 2.25d {9} (4-H), 2.71dd {9, 2} (5-H), 2.47 {2} (7-H), 4.95br (NH)
(4)	H	5-CF_3	50.4	3.9	19.9	$C_9H_8F_3N_3$	50.2	3.8	19.5	6.91d {3} (Me), 1.84s (2- and 4-H), 2.34d {0.5} (6- and 7-H), 4.70br,q (NH)
(4)	H	5-NO_2	50.5	4.1	29.5	$C_8H_8N_4O_2$	50.0	4.2	29.2	6.97s (Me), 1.30s (2-H), 1.36d {2} (4-H), 1.71dd {9, 2} (6-H), 2.15d {9}, 3.10br (NH)
(4)	H	5-CO_2Et	60.0	5.7	19.1	$C_{11}H_{13}N_3O_2$	60.3	6.0	19.2	8.56t {8} (ester Me), 6.90d {5.5} (NMe), 5.56q {8} (CH_2), 1.40s (2-H), 1.83d {2} (4-H), 1.89dd {10, 2} (6-H), 2.42d {10} (7-H), 4.83br (NH)
(4)	$[CH_2]_3$	H	70.1	6.5	22.0	$C_{11}H_{13}ClN_3$	70.6	7.0	22.4	6.90m (NCH_2, $ArCH_2$), 8.15m (CH_2), 3.83br (NH), 2.3—2.9m (ArH)
(4)	$[CH_2]_3$	6-Cl	59.4	5.5	18.7	$C_{11}H_{12}ClN_3$	59.6	5.7	19.0	6.83m (NCH_2, $ArCH_2$), 8.10m (CH_2), 2.42d {8} (4-H), 2.81dd {8, 2} (5-H), 2.51d {2} (7-H), 5.49br,t (NH)
(4)	$[CH_2]_3$	5-CF_3	56.7	4.9	16.4	$C_{12}H_{12}F_3N_3$	56.5	4.7	16.5	6.80m (NCH_2, $ArCH_2$) 8.04m (CH_2), 2.02s (4-H), 2.44d {0.5} (6- and 7-H), 5.43br, t (NH)
(4)	$[CH_2]_3$	5-NO_2	56.7	5.4	23.6	$C_{11}H_{12}N_4O_2$	56.9	5.2	24.1	6.74m (NCH_2, $ArCH_2$), 8.04m (CH_2), 1.51d {2} (4-H), 1.80dd {9,2}, 2.37d {9} (7-H), 3.50br (NH)
(4)	$[CH_2]_4$	5-CF_3	60.9	5.5	17.7	$C_{12}H_{14}ClN_3$	61.2	6.0	17.8	6.85m (NCH_2, $ArCH_2$), 8.13m (CH_2), 2.45d {9} (4-H), 2.85dd {9, 2} (5-H), 2.52d {2} (7-H), 5.35br (NH)
(4)	$[CH_2]_4$	5-CF_3	58.0	4.8	15.9	$C_{13}H_{14}F_3N_3$	58.0	5.2	15.6	6.78m (NCH_2, $ArCH_2$), 8.18—8.73m (CH_2), 1.94s (4-H), 2.47s (6- and 7-H), 4.55br (NH)
(4)	$[CH_2]_4$	5-NO_2	59.0	5.4	22.8	$C_{12}H_{14}N_4O_2$	58.5	5.7	22.8	6.78m (NCH_2, $ArCH_2$), 8.12—8.65 (CH_2), 1.33d {2} (4-H), 1.73dd {9, 2} (6-H), 2.57d {9} (7-H), 4.70br (NH)
(4)	$CH_2{\cdot}O{\cdot}CH_2$	6-Cl	53.9	4.8	18.7	$C_{10}H_{12}ClN_3$	53.7	4.5	18.8	6.74m (NCH_2), 5.92t {7} (CH_2O), 5.03s ($ArCH_2$, CH_2O), 2.38d {9} (4-H), 2.78dd {9, 2} (5-H), 2.43d {2} (7-H), 4.05br(NH)
(5a)	H	5-Cl	45.3	3.1	22.5	$C_7H_6ClN_3O$	45.8	3.3	22.9	5.68s (Me), 2.70dd {9, 1.5} (6-H), 2.22d {9} (7-H), 2.24d {1.5} (4-H)
(5)	H	5-NO_2	46.9	3.7	31.3	$C_7H_6N_4O_2$	47.2	3.4	31.5	5.35s (Me), 2.02d {9} (7-H), 1.72dd {9, 2} (6-H), 1.12d {2} (4-H)
(5a)	H	5-NO_2	43.7	3.5	28.7	$C_7H_6N_4O_3$	43.3	3.1	28.9	5.61s (Me), 2.15d {9} (7-H), 1.73dd {9, 2} (6-H), 1.17d {2} (4-H)
(6)	$[CH_2]_3$		65.9	5.7	21.2	$C_{11}H_{11}N_3O$	65.7	5.5	20.9	5.72t {6} (NCH_2), 7.04t {6} (=C–CH_2), 7.90m (CH_2), 3.83d {2} (5-H), 3.03dd {10, 2} (7-H), 2.52d {10} (8-H)
(6)	$[CH_2]_4$		67.2	5.9	19.9	$C_{12}H_{13}N_3O$	67.0	6.1	19.5	5.57m (NCH_2), 7.00m (=C–CH_2), 8.08m (CH_2), 3.61d {2} (5-H), 2.96dd {10, 2} (7-H), 2.55d {10} (8-H)
(8)			50.8	2.7	25.6	$C_7H_4ClN_3$	50.8	2.4	25.4	1.94m (5- and 6-H), 1.40m (8-H), 1.04s (3-H)

Reactions of Hydrazines with Acids.—Method A. The nitrophenylhydrazine (2.0 g) in constant-boiling hydrochloric acid (100 ml) was heated under reflux until the u.v. absorption of the nitro-compound (*ca.* 420 nm) was minimal. The solution was evaporated to low bulk (*ca.* 10 ml) and water (20 ml) added, followed by sodium hydrogen carbonate solution (20%) until the mixture was alkaline. The mixture was extracted with chloroform (3 × 50 ml), the extract was dried ($MgSO_4$) and evaporated, and the residue was chromatographed on alumina. Elution with light petroleum–ethyl acetate removed starting material neutralised (with further addition of ice) with ammonia. The solution was extracted with chloroform and treated as in method A (see Tables 1 and 2).

Method C. 2-Nitro-*N*-piperidinoaniline (1; X = H, RR = $[CH_2]_3$) (1.0 g) in trifluoroacetic acid (50 ml) was treated as in method A. Elution with ethyl acetate gave 2,3,4,5-*tetrahydro*-1H-[1,2]*diazepino*[2,3-a]*benzimidazole* (4; X = H, RR = $[CH_2]_3$), which crystallised from ethyl acetate–light petroleum as white needles (0.4 g), m.p. 226° (Found: C, 70.1; H, 6.5; N, 22.4. $C_{11}H_{13}N_3$ requires C, 70.6; H, 7.0; N, 22.4%), M^+ 187, $\nu_{max.}$ (Nujol) 3 200 cm^{-1}

(NH), $\lambda_{max.}$ ($CHCl_3$) 282 and 288 nm, τ [$(CD_3)_2SO$–$CDCl_3$] 8.15 (m, $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$), 6.90 (m, $NH{\cdot}CH_2$ and $ArCH_2$), 3.83 (m, NH), and 2.3—2.9 (m, aromatic, AA'BB' system).

Method D. 2-Nitro-*N*-piperidinoaniline (1; X = H, RR = $[CH_2]_3$) (2.0 g) in aqueous hydrobromic acid (48%; 50 ml) was boiled and further treated as in method A, and gave the product recorded (Tables 1 and 2).

When *NN'*-dimethyl-*N'*-(2-nitro-4-trifluoromethylphenyl)hydrazine (14) (2.0 g) in constant-boiling hydrochloric acid was boiled for 11 h and worked up as in method A, a white product, 2- or 3-*methyl*-6-*trifluoromethylbenzotriazole* 1-*oxide* (15) (1.0 g, 58%), prisms (from ethyl acetate), m.p. 197°, was obtained (Found: C, 43.9; H, 2.9; N, 19.0. $C_8H_6F_3N_3O$ requires C, 44.2; H, 2.8; N, 19.3%), *m/e* 217 (M^+), 201 (M − O), and 173 (M − N_2O), τ ($CDCl_3$) 5.78 (Me), 2.10 (dd, *J* 10 and 1.5 Hz, 5-H), 1.86 (d, *J* 10 Hz, 4-H), and 1.77 (d, *J* 1.5 Hz, 7-H).

6-*Chloro*-1-*methylaminobenzamidazole* (4; X = 6-Cl, R = Me). (*a*) 5-Chloro-2-nitrophenylhydrazine (3.5 g) and formic acid (30 ml, 98%) were heated together for 1 h; the mixture was then evaporated to give N-(5-*chloro*-2-*nitrophenyl*)-N'-*formylhydrazine* as yellow needles (3.2 g, 81%) (from ethanol), m.p. 227° (Found: C, 38.9; H, 2.8; N, 19.7. $C_7H_6ClN_3O_3$ requires C, 39.0; H, 2.8; N, 19.5%), $\nu_{max.}$ (Nujol) 3 350 and 3 240 (NH), and 1 680 cm^{-1} (CO), τ [$CDCl_3$–$(CD_3)_2SO$] 3.10 (dd, *J* 9 and 2 Hz, 4-H), 2.75 (d, *J* 2 Hz, 6-H), 1.79 (d, *J* 9 Hz, 3-H), 1.68 (s, CHO), and 0.66br (NH).

(*b*) The above hydrazide (2.5 g) was hydrogenated in ethanol (120 ml) over palladium–charcoal (0.1 g; 10%), the filtered solution was evaporated to dryness, and formic acid (98%; 30 ml) was added to the residue. After boiling for 5 h the solution was evaporated and the residue recrystallised from ethanol–ethyl acetate to give 6-*chloro*-1-*formamidobenzimidazole* (7) (1.3 g, 58%), m.p. 240° (decomp.) (Found: C, 49.1; H, 3.3; N, 21.7. $C_8H_6ClN_3O$ requires C, 49.1; H, 3.1; N, 21.5%), $\nu_{max.}$ (Nujol) 3 120 (NH) and 1 700 cm^{-1} (CO), τ [$CDCl_3$–$(CD_3)_2SO$] 6.02br (NH), 2.65 (dd, *J* 9 and 2 Hz, 5-H), 2.47 (d, *J* 2 Hz, 7-H), 2.20 (d, *J* 9 Hz, 4-H), and 1.71 (s, 2-H).

(*c*) The benzimidazole (7) (0.6 g) in dry tetrahydrofuran (25 ml) was stirred with sodium hydride (0.4 g) and methyl iodide (0.5 g; added 15 min later). After 24 h water (10 ml) was added, followed by aqueous sodium hydroxide (10%; 5 ml), and the solution was stirred for 2 h. It was then extracted with chloroform (2 × 20 ml) and the extracts were washed with water, dried ($MgSO_4$), and evaporated. The residual white solid was recrystallised from light petroleum to give 6-chloro-1-methylaminobenzimidazole (0.36 g, 66%), m.p. 109°, identical with the product from acid-catalysed cyclisation of *N'*-(5-chloro-2-nitrophenyl)-*NN*-dimethylhydrazine (m.p., mixed m.p., and i.r. spectrum).

(*d*) 6-Chloro-1-formamidobenzimidazole (0.5 g) was heated in 2M-hydrochloric acid for 5 h and the cooled mixture was basified with 2M-sodium hydroxide and extracted with chloroform. The extract was dried and evaporated to yield an oil. Elution through alumina with ethyl acetate afforded a white solid giving needles (from ethyl acetate–light petroleum) of 1-*amino*-6-*chlorobenzimidazole* (0.3 g, 70%), m.p. 157° (Found: C, 50.3; H, 3.4; N, 25.0. $C_7H_6ClN_3$ requires C, 50.2; H, 3.6; N, 25.0%), $\nu_{max.}$ (Nujol) 3 320 and 3 180 cm^{-1} (NH_2), τ [$CDCl_3$–$(CD_3)_2SO$] 4.40 (m, NH_2), 2.77 (d) and 2.38 (2 H, d) (4-, 5-, and 7-H), and 1.96 (s, 2-H).

(*e*) The above amine (0.2 g) and benzaldehyde (1.0 ml) in ethanol (2 ml) containing 2 drops of hydrochloric acid (*d* 1.18) were heated for 15 min. When the mixture was cooled, 1-benzylideneamino-6-chlorobenzimidazole hydrochloride [needles from aqueous ethanol, m.p. 232° (decomp.)] was precipitated.

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