Syntheses of Heterocyclic Compounds. Part XXV.[1] Action of Acid on *NN*-Disubstituted *o*-Nitroanilines: Benzimidazole *N*-Oxide Formation and Nitro-group Rearrangements

By **Rae Fielden, Otto Meth-Cohn,** and **Hans Suschitzky,*** Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancashire

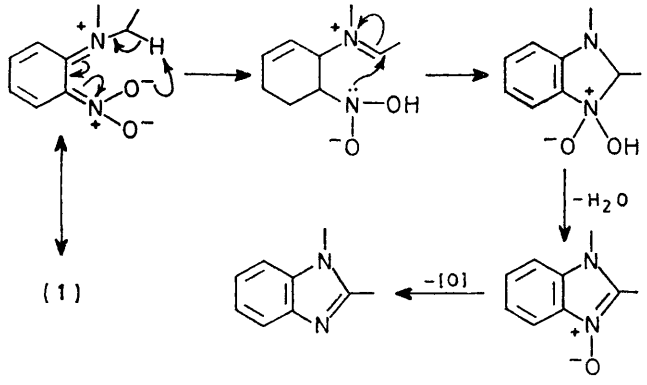
A variety of *NN*-disubstituted *o*-nitroanilines are shown to give benzimidazole *N*-oxides, often in high yield, when heated in mineral acid solution. The product is accompanied by small amounts of the denitrated parent compound and *p*-nitro- and 2,4-dinitro-derivatives. Irradiation of acidic solutions of *NN*-disubstituted *o*-nitroanilines similarly yields either the corresponding benzimidazole *N*-oxide or the benzimidazole by different mechanisms and with no concomitant rearrangement of nitro-groups. Synthetic and mechanistic implications are discussed.

THE ready, and often unusual, reactions of *NN*-disubstituted *ortho*-substituted anilines have been reviewed.[2] They include numerous examples of unexpected reactions involving the *o*-nitro-group, often with benzimidazole formation caused by the action of heat or reduction. To rationalise these cyclisations we have

[1] Part XXIV, G. V. Garner, D. B. Mobbs, H. Suschitzky, and J. S. Millership, *J. Chem. Soc.*, 1971, 3693.

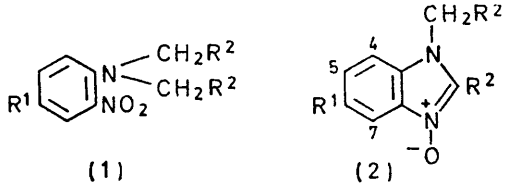
[2] O. Meth-Cohn and H. Suschitzky, *Adv. Heterocyclic Chem.*, 1972, **14**, 211.

proposed the intermediacy of the corresponding benzimidazole *N*-oxides (*e.g.* Scheme 1). An alternative mechanism involving hydride ion transfer may also be envisaged.



SCHEME 1

These *N*-oxides are exceptional in that they are not available by direct oxidation of the parent heterocycle.[3] We have now found an efficient synthesis of these compounds from readily accessible nitro-compounds. The method is particularly suitable for making annulated derivatives of benzimidazole *N*-oxides[4] and involves the acid-catalysed cyclisation of *NN*-disubstituted *o*-nitroanilines (1), which proceeds broadly as shown in Scheme 1, probably *via* an *O*-protonated species. For instance, when an *o*-nitroaniline (1) is boiled in hydrochloric acid a high yield of the *N*-oxide (2) (or its



(1) (2)

	R^1	R^2R^2		R^1	R^2R^2		R^1	R^2
a	H	$[CH_2]_2$	j	NO_2	$CH_2{\cdot}O{\cdot}CH_2$	r	H	H
b	Cl	$[CH_2]_2$	k	H	$[CH_2]_4$	s	H	Me
c	NO_2	$[CH_2]_2$	l	Cl	$[CH_2]_4$	t	Cl	Et
d	CO_2H	$[CH_2]_2$	m	NO_2	$[CH_2]_4$			
e	CF_3	$[CH_2]_2$	n	Cl	$[CH_2]_5$			
f	H	$[CH_2]_3$	o	Cl	$[CH_2]_6$			
g	Cl	$[CH_2]_3$	p	H	$[CH_2]_{10}$			
h	NO_2	$[CH_2]_3$	q	Cl	$[CH_2]_{10}$			
i	H	$CH_2{\cdot}O{\cdot}CH_2$						

hydrochloride) may be isolated together with readily removed by-products. The results are summarised in Table 1. Higher temperatures considerably reduced the reaction time (see Table 1) and the kinetics of the reaction in the case of (1k) revealed pseudo-first-order behaviour. Results were satisfactory with various substituents in the aromatic ring and also with dialkylamino- (except dimethyl—see later) or cyclic amino-groups *ortho* to the nitro-group. However, the thirteen-membered heterocycles (1p and q) gave solely the ω-chlorododecylamino-compounds (3a and b) in high

[3] A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic *N*-Oxides,' Academic Press, London and New York, 1971, p. 101.

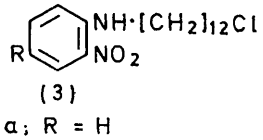
TABLE 1

Products from the action of hot acid on the *NN*-disubstituted *o*-nitroanilines (1)

			Yield (%)				
Compound	Temp. (°C)	Time (h)	Unchanged (1)	(2)	(3)	(4)	(5)
(1a)	110	20	18·5	51		2·5	5·0
(1b)	110	20		70			28
(1c)	110	20	46·5	32			
(1d)	110	2	24	61			
(1e) *	110	1	63	33			
(1f)	110	20	89	Trace			
(1f)	160	7	10	61			
(1g)	110	72		27			59
(1h)	110	20	80	20		Trace	
(1i)	110	20	68	26		1	
(1i)	150	12	66	30			
(1j)	110	20	87	13		Trace	
(1k)	110	1		12			
	110	2		16			
	110	4		25			
	110	8		38			
	110	20	14·5	61		4	15
	110	40		74			
(1l)	110	48		62			21
(1m)	110	20	80	16			
(1m)	150	12	19	76			
(1n)	110	72	0	61			15
(1o)	110	72	35	52			5
(1p)	110	24			90		
(1q)	110	24			90		
(1r) †	110	8	75			3·5	
(1s)	110	8	75			2·5	
(1s)	150	12	10	47			
(1t)	110	48	0	56			32

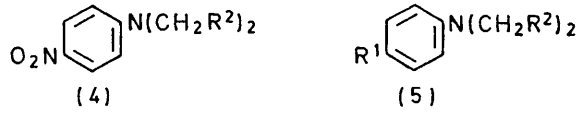
* Trace of (2d) also isolated. † *N*-Methyl-*p*-nitroaniline (2%) also isolated.

yield. It appears that the large ring size precludes proton abstraction from the α-position, and ring fission to relieve steric strain is favoured.



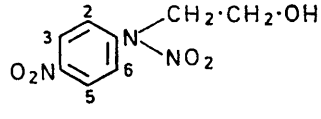
(3)

a; R = H
b; R = Cl



(4) (5)

[R^1 and R^2 as in (1) and (2)]

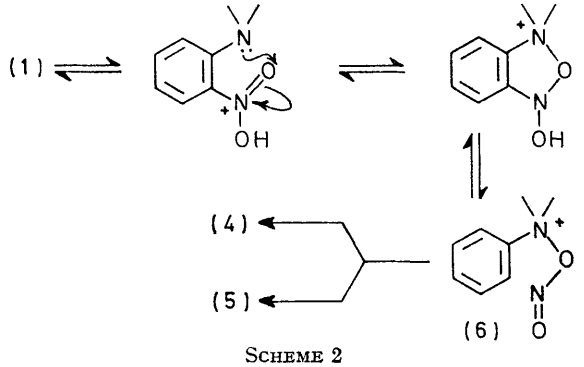


(7)

The *N*-oxide is accompanied by minor by-products arising from the rearrangement or loss of the nitro-group. Thus, many of the *o*-nitro-compounds (1) gave the *para*-isomers (4) and the denitrated products (5) as

[4] Preliminary communication, R. Fielden, O. Meth-Cohn, and H. Suschitzky, *Chem. Comm.*, 1969, 772.

shown in Table 1 together with unchanged material. The extent of denitration is increased if a scavenger such as *o*-phenylenediamine or phenol is added. However, ' crossing ' experiments revealed that the products due to nitro-group rearrangement are formed intramolecularly and not by denitration followed by renitration. Thus a mixture of *o*-nitrophenylmorpholine (1i) and phenylpyrrolidine (5a) gave only *p*-nitrophenylmorpholine (4i) and phenylpyrrolidine on heating in hydrochloric acid, and *o*-nitrophenylpyrrolidine (1a) mixed with phenylmorpholine (5i) again gave no crossed products but only *p*-nitrophenylpyrrolidine (4a) and phenylmorpholine as by-products. That the rearrangement was irreversible was shown by the fact that the *p*-nitro-compounds remain unchanged under the reaction conditions. Obviously, the *ortho*-(disubstituted amino)-group is essential to bring about the removal of the nitro-group, possibly as shown in Scheme 2. The

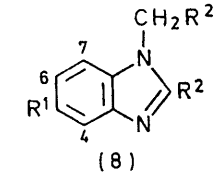


SCHEME 2

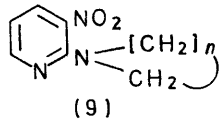
nitroso-oxy-amine salt (6) is reminiscent of the intermediate proposed by Hughes [5] to account for the acid-catalysed nitramine rearrangement. The fact that dimethylaniline *N*-oxide reacts with nitrosating agents to give predominantly *o*- and *p*-nitrodimethylaniline [6] appears to be relevant to our mechanism.

In order to test the intermediacy of the nitroso-oxy-amine (6) we treated various *N*-oxides with freshly prepared nitrosyl chloride. At −20°, *p*-nitrophenylpiperidine *N*-oxide gave only the hydrochloride, but in the presence of potassium carbonate an almost quantitative yield of 2,4-dinitrophenylpiperidine was obtained. *p*-Nitrophenylmorpholine *N*-oxide gave a mixture of the 2,4-dinitro-compound (85%) and 2-(*N*-nitro-*p*-nitroanilino)ethanol (7) (15%). These products speak strongly for the *N*-nitrite intermediate, which may rearrange to the 2,4-dinitrophenylmorpholine or eliminate (presumably ethylene) from the morpholine ring to give the *N*-nitro-compound (7). It is significant that *NN*-dimethyl-*o*-nitroaniline (1r) with hot acid gave *NN*-dimethyl-*p*-nitroaniline (4r) and *N*-methyl-*p*-nitroaniline. The latter product is readily explained on the basis of an *N*-nitroso-oxy-intermediate which acts analogously to an *N*-oxide causing demethylation by a Polonovski-type reaction.[7] Further support for the involvement of an *N*-nitrite in these reactions derives from the action of nitrosyl chloride on *N*-phenylmorpholine *N*-oxide in the presence of potassium carbonate. Extraction of the reaction mixture with ether after addition of water gave a mixture of *o*- (36%) and *p*-nitrophenylmorpholine (10%). The remaining colourless aqueous alkaline solution was evaporated to low bulk and acidified; a brown gas was evolved and the solution became yellow. From this solution were isolated 2,4-dinitrophenylmorpholine (23%) and 2-(2,4-dinitroanilino)ethanol (12%). It is evident that both these compounds were formed after acidification, not unreasonably by acid-catalysed rearrangement of an *N*-nitrite. Treatment of *N*-phenylmorpholine with nitrosyl chloride again gave products suggestive of *N*-nitration followed by rearrangement, namely 2-(*N*-nitro-*p*-nitroanilino)ethanol (7) (68%), together with *o*-nitro- (8%), *p*-nitro- (4%), and 2,4-dinitro-phenylmorpholine (7%). Moreover, recent evidence [8] that *N*-nitration is a significant step in *C*-nitration of aromatic amines appears to bear out our own observations.

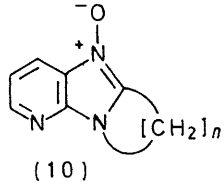
In view of the interesting results from the action of heat on the *NN*-disubstituted *o*-nitroanilines (1) under acidic conditions, we undertook a related photochemical study. The photolability of *o*-nitro-aromatic compounds has long been known.[9] In many cases, the products are nitroso-compounds formed by oxygen transfer from the nitro-group. Thus, *o*-nitrobenzaldehyde yields *o*-nitrosobenzoic acid, and *N*-(*o*-nitrophenyl)-α-amino-acids



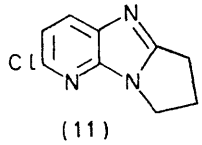
(8)
[R¹ and R² as in (1)]



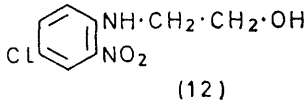
(9)
a; *n* = 3
b; *n* = 4



(10)
a; *n* = 3
b; *n* = 4



(11)



(12)

at pH ⩾ 6 yield *o*-nitrosoaniline and aldehydes which interact at pH 2—5 to give benzimidazole *N*-oxides. We have observed that *NN*-disubstituted *o*-nitroanilines react slowly in sunlight, in the solid state or in solution,

[5] E. D. Hughes and C. K. Ingold, *Quart. Rev.*, 1952, **6**, 34.
[6] D. V. Banthorpe and J. A. Thomas, *J. Chem. Soc.*, 1965, 1749, 1758.
[7] O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc.*, 1963, 4666.
[8] J. H. Ridd and E. F. V. Scriven, *J.C.S. Chem. Comm.*, 1972, 641.
[9] A. Schönberg, G. O. Schenk, and O. A. Neumüller, ' Preparative Organic Photochemistry,' Springer-Verlag, Berlin, 1968, p. 266.

when a medium-pressure mercury lamp is employed. However, in aqueous acidic methanol * solution, the reaction proceeded within 20—80 h with high yields (and in most cases no by-products) of either the benzimidazole (8) or its *N*-oxide (2) (Table 2). These two

TABLE 2

Benzimidazole *N*-oxides (2) and benzimidazoles (8) by irradiation of *o*-nitroanilines (1) in aqueous methanolic hydrochloric acid

		Yield (%)				
Compound	Time (h)	Unchanged (1)	(2)	(8)	M.p. of (8) (°C)	Lit.[11] m.p. (°C)
(1a)	48	12	78	0		
(1b)	54	86	13	0		
(1f)	66	2	0	83	102	102
(1i)	80	23	55 [a]	0		
(1k)	24	12	0	81	126	125
(1l)	24	13	79	0		
(1p)	24	12	0	86	111 [b]	
(1q)	24	71	0	23	129 [c]	

[a] Also 2-(4-chloro-2-nitroanilino)ethanol (17%) as yellow prisms (from benzene), m.p. 110° (lit.,[21] 108°). [b] *Needles* from light petroleum (Found: C, 80·2; H, 9·8; N, 10·4%; M^+, 270. $C_{18}H_{26}N_2$ requires C, 79·9; H, 9·7; N, 10·4%; *M*, 270), τ($CDCl_3$) 5·90 (t, *J* 7·0 Hz, N·CH_2), 7·08 (t, *J* 7·0 Hz, C·CH_2), 7·79—8·88 (m, $[CH_2]_8$), 2·09—2·37 (m, H-4), and 2·61—2·82 (m, H-5, -6, -7). [c] *Needles* from light petroleum (Found: C, 70·9; H, 8·4; N, 9·0%; M^+ 304/306. $C_{18}H_{25}ClN_2$ requires C, 70·9; H, 8·3; N, 9·2%; *M*, 304/306), τ($CDCl_3$) 5·87 (t, *J* 7·0 Hz, N·CH_2), 7·06 (t, 7·0 Hz, C·CH_2), 7·74—8·92 (m, $[CH_2]_8$), 2·22 (s, H-4), and 2·73 (s, H-6 and -7).

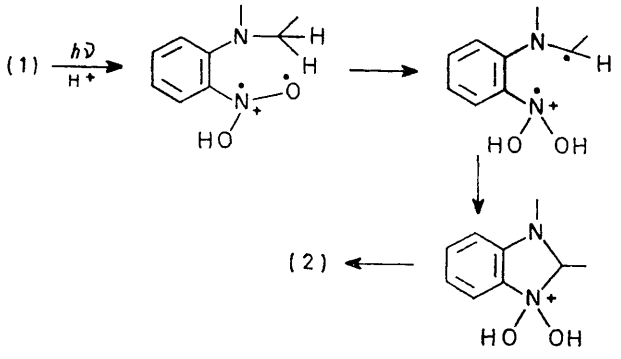
products must be formed by independent routes since they never occurred in admixture and the *N*-oxides were unchanged after irradiation in acidic methanol solution. The possibility that the *N*-oxide was formed first and was deoxygenated by interaction with excited nitro-compound [10] was also considered. However, when *o*-nitrophenylperhydroazepine (1k), which yields only hexahydroazepino[1,2-*a*]benzimidazole (8k) on photolysis, was irradiated in the presence of hexahydroazepino[1,2-*a*]benzimidazole *N*-oxide (2k), the amount of *N*-oxide remained unchanged and that of benzimidazole was the same as expected from an independent reaction. The reaction is equally applicable to the pyridine derivatives (9a and b), yielding the corresponding pyridoimidazole *N*-oxides (10a and b). In the former case the chloro-substituted pyridoimidazole (11) was a by-product which is also produced by the irradiation of the *N*-oxide in aqueous methanolic hydrochloric acid. This type of reaction will be considered in detail in a later paper.

There seems to be a delicate balance between the two pathways leading respectively to a benzimidazole and to its *N*-oxide. Two factors appear to determine the course of the reaction, namely the basicity of the tertiary nitrogen atom and the size of the *N*-substituents. Thus, with the *o*-nitroanilines the small pyrrolidino- (1a) and less basic morpholino- (1i) nitro-compounds gave the *N*-oxide. The piperidino- and the hexa- and the dodeca-methylene compounds (1f, k, and p) all gave

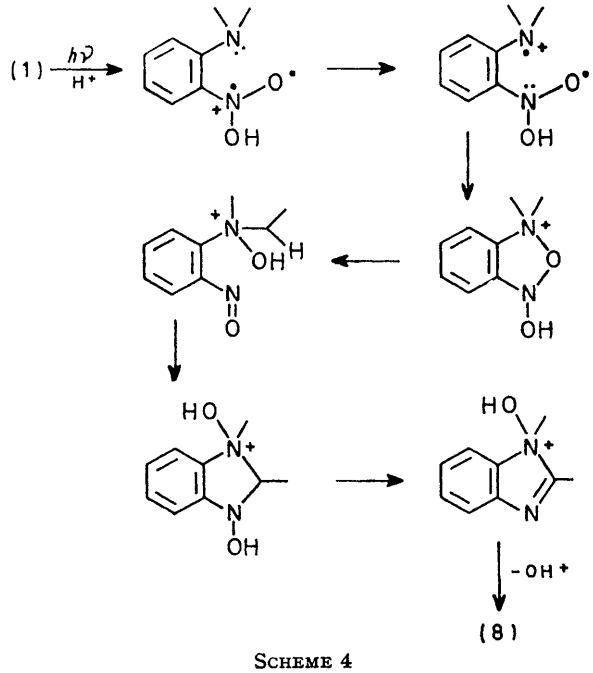
* AnalaR methanol is essential for these reactions. Other grades cause deoxygenation of the product *N*-oxides under the influence of u.v. light, presumably because of aldehyde impurities.

benzimidazoles. However, compounds containing an electron-withdrawing substituent such as chlorine gave the *N*-oxide in the case of the five- and the seven-membered nitrophenyl heterocycles (1b and l) but the larger thirteen-membered ring-system (1q) still gave the benzimidazole. The presence of a 4-nitro-substituent gave rise to intractable products presumably because of the photolability of this group. The pyridine derivatives (9a and b) gave *N*-oxides [78 and 16% yields, respectively after 40 h; 75% (9b) recovered] in accord with the foregoing ideas.

These results may be rationalised by analogy with the routes proposed for other photoreactions of *o*-nitro-compounds as outlined (Scheme 3). The photo-excitation of the nitro-group can lead by way of a diradical to the *N*-oxides (2) according to Scheme 3. However,



SCHEME 3



SCHEME 4

larger or more basic heterocycles in the starting material may lead to attack at the tertiary nitrogen atom in the

[10] R. S. Davidson, S. Korkut, and P. R. Steiner, *Chem. Comm.*, 1971, 1052.

[11] L. Ruzicka, M. Kobelt, O. Haflinger, and V. Prelog, *Helv. Chim. Acta*, 1949, **32**, 544.

former case because of the preferred orthogonality of the hetero- and aromatic rings (Scheme 4). This sequence is in part analogous to the oxygen transfer photoreactions of nitro-compounds already mentioned.

In the photolysis of *o*-nitrophenylmorpholine, a small amount of 2-(4-chloro-2-nitroanilino)ethanol (12) was isolated together with the benzimidazole *N*-oxide. This product probably arises by Orton rearrangement of a 2-(chloroamino)ethanol produced in turn by photocleavage of the morpholine ring. *o*-Nitrophenylmorpholine is not cleaved in the thermal acid-catalysed cyclisation, and no chlorination occurs when 2-(*o*-nitroanilino)ethanol is irradiated in hydrochloric acid.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 137 or 337 instrument, n.m.r. spectra on a Varian A60A or HA100, and mass spectra on an A.E.I. MS12 instrument. Light petroleum was the fraction of b.p. 60—80° unless otherwise stated. Alumina type H (Hopkin and Williams) was used for chromatography. Hepta-, octa-, and dodeca-methyleneamine were prepared by the literature method.[11]

Preparation of NN-*Disubstituted* o-*Nitroanilines* (1).—Literature methods [12-20] were used to obtain most of these compounds. The amines (1n, o, q, and t) were prepared as follows: a mixture of 2,5-dichloronitrobenzene (0·1 mol), the appropriate base (0·1 mol), and sodium hydrogen carbonate (0·1 mol) was heated in ethanol (30 ml) for 72 h, filtered, and evaporated. The orange product was distilled *in vacuo* to give (i) *N*-(4-chloro-2-nitrophenyl)heptamethyleneamine (1n), m.p. 82° (Found: C, 58·2; H, 6·1. $C_{13}H_{17}ClN_2O_2$ requires C, 58·1; H, 6·6%); (ii) *N*-(4-chloro-2-nitrophenyl)octamethyleneamine (1o), m.p. 88° (Found: C, 59·0; H, 6·4. $C_{14}H_{19}ClN_2O_2$ requires C, 59·5; H, 6·8%); (iii) *N*-(4-chloro-2-nitrophenyl)dodecamethyleneamine (1g), m.p. 36° (Found: C, 63·5; H, 7·6. $C_{18}H_{27}ClN_2O_2$ requires C, 63·8; H, 8·0%); (iv) *N*-(4-chloro-2-nitrophenyl)dipropylamine (1t), b.p. 142° at 0·5 mmHg (Found: C, 56·1; H, 6·7. $C_{12}H_{17}ClN_2O_2$ requires C, 56·1; H, 6·7%).

N-(2-*Nitrophenyl*)*dodecamethyleneamine* (1p).—*o*-Fluoronitrobenzene (0·1 mol) and dodecamethyleneamine (0·1 mol) in ethanol (30 ml) were heated under reflux for 12 h and the orange *nitro-compound* (1p) obtained on evaporation was distilled *in vacuo*; b.p. 228° at 0·5 mmHg (Found: C, 69·7; H, 9·6. $C_{18}H_{28}N_2O_2$ requires C, 70·0; H, 9·3%).

Thermal Cyclisation of NN-*Disubstituted* o-*Nitroanilines* (1).—(i) The appropriate nitro-compound (1) (3 g) was heated under reflux in constant-boiling aqueous hydrochloric acid for periods shown in Table 1. The solvent was removed *in vacuo* leaving a dark brown gum which was worked up by one of the following methods. (A) The gum was treated with water (100 ml) and extracted with chloroform (3 × 100 ml). Evaporation of the extract left a tacky residue from which were isolated by column chromatography on alumina, (*a*) the amine (5) (light petroleum), (*b*) the starting material (1) (benzene), (*c*) the nitro-compound (4) (benzene). The aqueous layer was evaporated to yield the *N*-oxide hydrochloride (2) as a buff solid which was purified by recrystallisation from methanol–ether. (B) The gum was dissolved in water (50 ml), basified with saturated sodium hydrogen carbonate solution, and extracted with chloroform (6 × 100 ml) to give after evaporation a brown solid. Chromatography as in (A) gave the by-products followed by the *N*-oxide (2) (chloroform), which was recrystallised from ethyl acetate.

(ii) The appropriate nitro-compound (2 g) in hydrochloric acid (25 ml; *d* 1·18) was heated in a Carius tube and the mixture worked up as in (i).

Preparation of the N-*Oxides of* N-(4-*Nitrophenyl*)*morpholine*, N-(4-*Nitrophenyl*)*piperidine*, *and* N-*Phenylmorpholine*.—The amine (2·0 g) was heated on a steam-bath with formic acid (12 ml; 98%) and hydrogen peroxide (6 ml; 30%) for 15 min. Water (40 ml) was added; the mixture was neutralised with ammonia and extracted with chloroform (4 × 20 ml) to give (i) N-(4-*nitrophenyl*)*morpholine* N-*oxide* (1·4 g, 65%), m.p. 148°, as pale yellow plates (from ethyl acetate–chloroform) (Found: C, 53·3; H, 5·1; N, 12·0. $C_{10}H_{12}N_2O_4$ requires C, 53·6; H, 5·4; N, 12·5%); (ii) N-(4-*nitrophenyl*)*piperidine* N-*oxide* (75%), m.p. 125°, as light yellow crystals (from ethyl acetate) (Found: C, 59·3; H, 5·9; N, 12·8. $C_{11}H_{14}N_2O_3$ requires C, 59·5; H, 6·3; N, 12·6%); (iii) N-*phenylmorpholine* N-*oxide* (76%), m.p. 160° as a cream powder (from ethyl acetate) (Found: C, 67·3; H, 7·3; N, 7·5. $C_{10}H_{13}NO_2$ requires C, 67·0; H, 7·3; N, 7·8%).

Reaction of N-*Oxides with Nitrosyl Chloride*.—(i) To a solution of *N*-(4-nitrophenyl)piperidine *N*-oxide (1 g) in chloroform (20 ml) at −20° was added nitrosyl chloride (1 ml) in one portion. The precipitated salt gave the starting material (1·0 g) on basification.

(ii) Reaction (i) was repeated in the presence of anhydrous potassium carbonate (10 g) and the mixture was stirred for 4 h. Water (50 ml) was added and the organic layer was dried ($MgSO_4$) and evaporated to give 2,4-dinitrophenylpiperidine (1h) (1·0 g, 95%).

(iii) *N*-(4-Nitrophenyl)morpholine *N*-oxide (1 g) was subjected to the conditions in (ii) and gave, after chromatography on alumina with benzene, *N*-(2,4-dinitrophenyl)-morpholine (1j) (0·84 g, 80%) followed by 2-(N-*nitro*-4-*nitroanilino*)*ethanol* (7) (0·15 g, 15%), m.p. 107—108° (Found: C, 42·3; H, 4·1; N, 18·4. $C_8H_9N_3O_5$ requires C, 42·3; H, 4·0; N, 18·5%), τ [$(CD_3)_2CO$] 1·54 (d, *J* 9·0 Hz, H-3 and H-5), 1·91 (d, *J* 9·0 Hz, H-2 and H-6), 5·73 (q, *J* 5·5 Hz, O·CH_2), 6·1—6·42 (m, N·CH_2), and 7·08 (s, OH).

(iv) *N*-Phenylmorpholine *N*-oxide (1 g) was treated as in (ii). Chromatography on alumina gave *N*-(2-nitrophenyl)morpholine (1i) (0·37 g, 30%) and *N*-(4-nitrophenyl)morpholine (0·1 g, 8%). The colourless aqueous phase was acidified (4N-hydrochloric acid); it became yellow. Extraction with chloroform gave a yellow solid which was chromatographed to give *N*-(2,4-dinitrophenyl)-morpholine (1j) (0·25 g) and 2-(2,4-dinitroanilino)ethanol (0·12 g) as yellow prisms (from aqueous ethanol), m.p. 89° (lit.,[21] m.p. 90°).

(v) Phenylmorpholine (1 g) was similarly treated with nitrosyl chloride. Chromatography on alumina gave *N*-(2-nitrophenyl)morpholine (8%), *N*-(4-nitrophenyl)morpholine

[12] K. H. Saunders, *J. Chem. Soc.*, 1955, 3275.
[13] M. A. Phillips, *J. Chem. Soc.*, 1929, 2820.
[14] M. D. Nair and R. Adams, *J. Amer. Chem. Soc.*, 1961, **83**, 3518.
[15] N. Tuttle, *J. Amer. Chem. Soc.*, 1923, **45**, 1906.
[16] H. Suschitzky and M. E. Sutton, *Tetrahedron Letters*, 1967, 3933.
[17] E. Lellmann and W. Geller, *Ber.*, 1888, **21**, 2281.
[18] R. H. Harradence and F. Lions, *J. Proc. Roy. Soc. N.S.W.*, 1937, **70**, 406.
[19] H. Markwald and E. Chain, Ger.P. 119,785/1901.
[20] G. Weissenberger, *Monatsh.*, 1912, **33**, 830.
[21] K. F. Waldkötter, *Rec. Trav. chim.*, 1937, **57**, 1294.

TABLE 3

Properties of the benzimidazole *N*-oxides (2)

Compound	M.p. (°C)	Found (%) C	H	N	Required (%) C	H	N	τ Values (*J*/Hz) Solvent	N–CH_2	C–CH_2	Other alkyl	4-H	5-H	6-H	7-H
(2a), HCl	224	57·0	5·2	13·2	57·0	5·3	13·3	$CF_3{\cdot}CO_2D$	5·87t (7·0)	6·82t (7·0)	7·38qu † (7·0)	2·62			2·86m
(2b)	182	57·3	4·1	13·0	57·5	4·4	13·4	$CDCl_3$	5·74t (7·0)	6·63t (7·0)	7·15qu (7·0)	2·10d (2·5)	2·64		2·73m
(2c), HCl	212	47·0	4·2	16·1	47·0	3·9	16·4	D_2O	5·42t (7·0)	6·40t (7·0)	7·10qu (7·0)	1·31d (2·0)		1·55dd (9·5 and 2·0)	2·08d (9·5)
(2d)	255—260														
(2e)	196·8														
(2f), HCl,H_2O	202—204	54·7	5·7	11·4	54·4	6·2	11·5	D_2O	5·68br, t (5·5)	6·73br,t (5·5)	7·70—8·00m	2·24			2·37m
(2g)	131	54·6	5·0	11·5	54·9	5·4	11·6	$CDCl_3$	5·85br,t (5·5)	6·80br,t (5·5)	7·74—8·20m	2·10d (1·5)	2·61		2·73m
(2h), HCl	228	48·7	4·8	15·3	49·0	4·5	15·6	D_2O	5·56br,t (5·5)	6·65br,t (5·5)	7·63—8·04m	1·29d (2·0)		1·52dd (9·5 and 2·0)	2·02d (9·5)
(2i), HCl	201	52·8	4·9	12·0	53·0	4·9	12·4	D_2O	5·58s	4·62s	5·58s	2·17			2·31m
(2j), HCl	215—218	43·9	3·7	14·4	44·2	3·7	15·5	$CF_3{\cdot}CO_2D$	5·73s	4·92s	5·73s	1·51d		1·78dd (9·5 and 2·0)	2·38d (9·5)
(2k), HCl	212	59·9	6·2	12·2	60·4	6·3	11·7	D_2O	5·38—5·63m	6·48—6·75m	7·95—6·75m	2·28			2·41m
(2l), $2H_2O$	129	53·3	5·8	10·3	52·9	6·3	10·3	$CDCl_3$	5·66—5·87m	6·48—6·72m	7·92—8·24m	2·01—2·08m	2·62		2·71m
(2m)	188	58·3	5·3	16·7	58·3	5·3	17·0	D_2O	5·28—6·67m	6·38—6·67m	7·82—8·25m	1·38d (2·0)		1·59dd (9·5 and 2·0)	2·02d (9·5)
(2n), H_2O	125	57·6	6·1	10·1	58·1	5·6	10·4	$CDCl_3$	5·47—5·75m	6·51—6·96m	7·78—8·95m	1·97—2·06m	2·52		2·64m
(2o), H_2O	110	59·3	6·2	9·1	59·7	6·7	9·8	$CDCl_3$	5·56t (6·0)	6·69br,t (6·0)	7·71—9·08m	1·97—2·06m	2·55		2·64m
(2s)	240	56·1	6·2	13·0	56·4	6·2	13·2	D_2O	5·60t (7·5)	7·19s	8·60t (7·5) 8·16qu (7·5)CH_3	2·19			2·56m
(2t), H_2O	101	56·0	6·6	11·0	56·2	6·7	10·9	$CDCl_3$	5·83t (7·5)	6·81q (7·5)	9·01t (7·5) Me 8·57t (7·5) Me	1·94—2·02m	2·58		2·65m

† qu = Quintet.

TABLE 4

Properties of other products in Table 1

Compound	M.p. (b.p./mmHg) (°C)	Found (%) C	H	N	Required (%) C	H	N	Lit. m.p. (b.p./mmHg) (°C)
(4a)	170							167—168 [a]
(5a)	(90—95/1)							(124/14) [b]
(5b)	85	66·2	6·4	7·9	65·8	6·7	7·7	85 [c]
(5g)	69	67·1	7·1	7·2	67·5	7·2	7·2	208 [d]
(4h)	106							103—105 [a]
(4i)	53							52 [e]
(4j)	148—149							149—150 [f]
(4k)	80—81							74—76 [g]
(5k)	(114—118/1)							(146—148/12) [h]
(5l)	(239/1·5)	68·3	7·3		68·8	7·7		
(5n)	(186/0·4)	70·0	8·2		69·8	8·1		
(5o)	(142/0·5)	68·8	8·1		68·1	8·6		
(3a)	41	63·8	8·5	8·2	63·4	8·6	8·2	
(3b)	55	57·2	7·9	7·4	57·6	7·5	7·5	
(4r)	161—162							163 [i]
(5t)	39							39 [j]

[a] J. E. Luvalle, D. B. Glass, and A. Weissberger, *J. Amer. Chem. Soc.*, 1948, **70**, 2223. [b] J. von Braun and G. Lemke, *Ber.*, 1922, **55B**, 3536. [c] B. Burger, Ger.P., 812,552/1951. [d] M. Scholz and E. Wassermann, *Ber.*, 1907, **40**, 852. [e] R. E. Rindfusz and V. L. Harnack, *J. Amer. Chem. Soc.*, 1930, **42**, 1725. [f] Ref. 18. [g] M. S. Raasch, U.S.P. 2,612,500/1952. [h] H. J. Nitzschke and H. Budha, *Chem. Ber.*, 1955, **88**, 264. [i] H. Ley and G. Pfeiffer, *Ber.*, 1921, **54**, 363. [j] E. Schmidt and H. Fischer, *Ber.*, 1920, **53**, 1537.

(4%), *N*-(2,4-dinitrophenyl)morpholine (7%), and 2-(*N*-nitro-4-nitroanilino)ethanol (68%).

Crossing Experiments.—(i) *N*-(2-Nitrophenyl)pyrrolidine (5 g) and phenylmorpholine (1 g) were heated under reflux in hydrochloric acid (50 ml; *d* 1·18) for 24 h. After 1 h, t.l.c. (alumina) revealed that *N*-(4-nitrophenyl)pyrrolidine was also present. T.l.c. showed no significant change after 24 h, and no nitrophenylmorpholines were detected.

(ii) A similar experiment with *N*-(2-nitrophenyl)morpholine (5 g) and *N*-phenylpyrrolidine (1 g) showed *N*-(4-nitrophenyl)morpholine present (t.l.c.) but no nitrophenylpyrrolidines.

Irradiation of the NN-*Disubstituted* o-*Nitroanilines.*—A solution of the nitro-compound (3 g) in AnalaR methanol (250 ml) and hydrochloric acid (50 ml; *d* 1·18) was deaerated by bubbling nitrogen for 15 min. The solution was then irradiated under nitrogen with a 200 W Hanovia medium-pressure mercury lamp in a Pyrex cooling jacket. The reaction was monitored by u.v. spectroscopy. When it was complete the mixture was evaporated to dryness and the residue dissolved in water (100 ml). The solution was further worked up by one of two methods. (i) It was neutralised with saturated sodium hydrogen carbonate solution and extracted with chloroform (6 × 100 ml). The organic layer was dried ($MgSO_4$) and evaporated and the residue chromatographed on alumina. Light petroleum eluted starting material and ethyl acetate removed the benzimidazole (8); chloroform eluted the *N*-oxide (2). (ii) The aqueous solution was extracted with chloroform (3 × 60 ml) and the extract was chromatographed as in (i). A sample (0·5 ml) of the aqueous phase was neutralised with aqueous sodium hydrogen carbonate. If a precipitate was formed, the whole solution was similarly treated and the product filtered off. If not, the aqueous phase was evaporated to dryness and the residue recrystallised from ether–methanol. The results of the photolyses are recorded in Table 2.

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