Metal Ions and Complexes in Organic Reactions. Part XIX.[1] Response of Some *N*-Substituted *o*-Nitrodiphenylamines to Cyclisation Procedures

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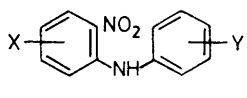
4-Chloro-4'-methyl-2-nitrodiphenylamine, the corresponding *N*-methyl- and *N*-acetyl-compounds, and *N*-acetyl-4-chloro-2'-methoxy-2-nitrodiphenylamine were compared in their susceptibility to cyclisation when heated (i) alone, (ii) with iron(II) oxalate, or (iii) with triethyl phosphite. The products were phenazine and benzimidazole derivatives and (in one case, with triethyl phosphite) an azepinobenzimidazole derivative. Aromatisation of *N*-acetyl-5,10-dihydrophenazine was examined. Results from these and preceding investigations of cyclisations through *o*-nitro-groups are summarised and are discussed in relation to suggested mechanisms. A note on the preparation of *o*-nitrodiarylamines is included.

THE preceding two papers [1,2] were concerned with polycyclic systems produced by heating suitably constituted nitro-compounds with iron(II) oxalate. The conversion of *o*-nitrodiarylamines (1) into phenazines (2)

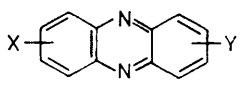
[1] Part XVIII, R. G. R. Bacon and S. D. Hamilton, preceding paper.

[2] R. G. R. Bacon and S. D. Hamilton, *J.C.S. Perkin I*, 1974, 1965.

is the prototype and most extensively investigated example of such cyclisations. According to one view [3] this process may involve generation of a nitrene, ring-closure with which gives an intermediate dihydrophenazine (3). Comparison has therefore been drawn [4] with the postulated involvement of nitrenes when deoxygenative cyclisation of nitro-compounds is effected with tervalent phosphorus species.[5] An alternative view of phenazine formation [6] is that water is eliminated in a polar type of condensation, giving an intermediate *N*-oxide (4). This mode of reaction is evident when transformations (1) ⟶ (2) are effected by catalysis with alkali; [7] a great variety of related polar-type additions to nitro-groups are known.[8,9]



(1)



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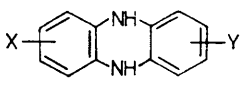

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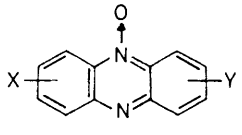


(4)

The role of iron(II) oxalate in phenazine formation [10a] remains obscure. The literature (*e.g.*, ref. 4) indicates that in some cases at least, cyclisation may occur, though in lower yield, in its absence. Introduced as the dihydrate, it loses water (at *ca.* 175°) and decomposes (at *ca.* 220°),[11] essentially to iron(II) oxide, as the temperature is raised to the region suitable for cyclisations (*ca.* 280° in our experiments). In the resulting transformations, iron(II) species might function as oxygen acceptors, or as heterogeneous catalysts, or, in conjunction with hydrogen donors in the system, they might cause reduction, *e.g.* to an amine, as occurs when iron(II) hydroxide is used with nitro-compounds in aqueous media.[12]

We have carried out a short investigation, with the structural and procedural variations shown in the Table. The parent nitro-amine (5) was known [10d] to be convertible into 2-chloro-8-methylphenazine (8); the nuclear substituents had possible value as indicators of rearrangement, such as may occur in cyclisations effected with tervalent phosphorus compounds.[5,13] Various modes of cyclisation were observed, but, in contrast to some systems examined earlier,[1,2] no amines or azo-compounds were detected among the products.

Heating with iron(II) oxalate gave cyclised products in 40—60% yield. The phenazine (8) resulted not only from the parent nitro-amine (5) but also, in minor amounts, with loss of an *N*-methyl and *N*-acetyl group respectively, from the nitro-amine derivatives (6) and (7). The major products from (6) and (7) (in *ca.* 4 : 1 and 6 : 1 ratio respectively) were the benzimidazoles resulting from cyclisation onto the *N*-substituent. Participation of *N*-methyl in reaction (6) ⟶ (9) recalls participation of (2-imidazolyl)methyl in previous cases,[1] whilst the deoxygenative coupling of COMe and NO_2 in reaction (7) ⟶ (10) is identical with that occurring in the known conversion of *o*-nitroacetanilide into 2-methylbenzimidazole.[10a]

Heating the nitro-amine (5) alone gave the phenazine (8) in almost half the yield attained with iron(II) oxalate, but no phenazine was obtained from the *N*-methyl derivative (6) and virtually none from the *N*-acetyl derivative (7). However, thermally induced production of the benzimidazole (9) from (6) was not greatly inferior to its production in the presence of iron(II) oxalate.

The reactions with triethyl phosphite were carried out in boiling cumene. We isolated no bicumyl which, in reported cases,[5,13] has been attributed to coupling of cumyl radicals resulting from hydrogen abstraction by triplet nitrenes. Phenazine production failed with the nitro-amine (5) and with its *N*-acetyl derivative (7), but it unexpectedly occurred as the minor reaction of the *N*-methyl compound (6); the major reaction was benzimidazole formation. Failure to obtain identifiable products from tervalent phosphorus compounds and *o*-nitrodiarylamines has been experienced elsewhere.[14,15] On the other hand *N*-acetyl-2′-methylthio-2-nitrodiphenylamine was reported [15] to give a phenazine (22%, with rearrangement) and a benzimidazole (3%). In our case the *N*-acetyl compound (7) furnished, in 2 : 1 ratio, the benzimidazole (10) and an azepinobenzimidazole (11), resulting from nitrogen insertion into the aromatic ring, which is considered to be characteristic of intermediate nitrenes; [4] this is also exemplified by production of an azepinoindole when an *o*-nitrodiphenylmethane derivative is heated with triethyl phosphite.[16]

[3] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149; *J. Chem. Soc.* (*C*), 1968, 119.

[4] 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970; see particularly P. A. S. Smith, 'Arylnitrenes,' pp. 99—162, and J. H. Boyer, 'Deoxygenation of Nitro and Nitroso Groups,' pp. 163—184.

[5] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.

[6] R. H. Smith and H. Suschitzky, *Tetrahedron*, 1961, **16**, 80; H. Suschitzky and M. E. Sutton, *Tetrahedron Letters*, 1967, 3933; G. V. Garner and H. Suschitzky, *ibid.*, 1971, 169.

[7] P. Cross, P. J. Williams, and R. E. Woodall, *J. Chem. Soc.* (*C*), 1971, 2085.

[8] A. T. Nielsen, 'Nitronic Acids and Esters,' in 'The Chemistry of the Nitro and Nitroso Groups,' ed. H. Feuer, Interscience, New York, 1969, Part I, pp. 349—486.

[9] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389; P. N. Preston and G. Tennant, *Chem. Rev.*, 1972, **72**, 627.

[10] (*a*) H. C. Waterman and D. L. Vivian, *J. Org. Chem.*, 1949, **14**, 289; (*b*) D. L. Vivian, G. Y. Greenberg, and J. L. Hartwell, *ibid.*, 1951, **16**, 1; (*c*) D. L. Vivian and J. L. Hartwell, *ibid.*, 1953, **18**, 1065; (*d*) D. L. Vivian, J. L. Hartwell, and H. C. Waterman, *ibid.*, 1954, **19**, 1641.

[11] R. A. Brown and S. C. Bevan, *J. Inorg. Nuclear Chem.*, 1966, **28**, 387.

[12] Reviewed by R. Schröter, in Houben–Weyl, 'Methoden der Organischen Chemie,' Thieme Verlag, Stuttgart, 4th edn., vol. 11/1, 1957, pp. 443—447.

[13] J. I. G. Cadogan and S. Kulik, *J. Chem. Soc.* (*C*), 1971, 2621.

[14] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.

[15] Y. Maki, T. Hosokami, and M. Suzuki, *Tetrahedron Letters*, 1971, 3509.

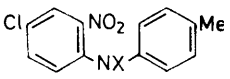
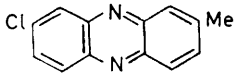
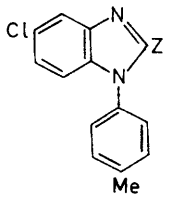
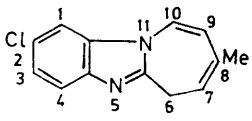
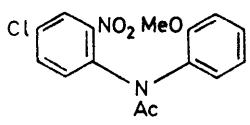
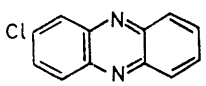
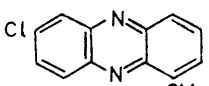
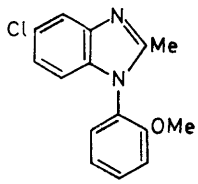
[16] J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim, and B. S. Tait, *J.C.S. Chem. Comm.*, 1972, 520.

The n.m.r. spectrum of (11) was consistent with either a 6*H*- or a 10*H*-structure, but the former assignment is preferred, since it accords with the presumed formation *via* an azanorcaradiene; also, the n.m.r. characteristics are similar to those described [17] for the azepinoindoles of analogously assigned structure obtained from *o*-nitro- [16] or *o*-azido-diphenylmethane derivatives.[17]

Experiments were also carried out with the *N*-acetyl nitro-amine (12), containing an *o*-methoxy-group on the other aromatic ring. The reactions with iron(II) oxalate and with triethyl phosphite were similar, being nearly equally divided between phenazine formation and the deoxygenative coupling of NO_2 with COMe which gives the benzimidazole (15). The phenazine produced with triethyl phosphite was entirely the 2-chloro-compound (13), due to elimination of the *o*-methoxy-group, which thus had a profound effect in reversing the course of reaction observed with the *N*-acetyl compound (7); *i.e.*, nuclear substitution succeeded and nuclear enlargement failed. A known case of *o*-methoxy-expulsion with triethyl phosphite is the conversion of 2,6-dimethoxyphenyl 2-nitrophenyl sulphide into 1-methoxyphenothiazine; [13] formaldehyde is believed to be formed. With iron(II) oxalate the resulting phenazine was mainly, likewise, the 2-chloro-compound, but a minor product was 2-chloro-6-methoxyphenazine (14), due to elimination of *o*-hydrogen; this limited retention of an *o*-methoxy-group was not observed in earlier examples.[2,10b]

There is no evidence indicating how, or at what stage in a cyclisation, an *N*-methyl or *N*-acetyl group is lost. Considering that reaction (7) ⟶ (8) might involve elimination of acetic acid instead of water, we tested the behaviour of *N*-acetyl-5,10-dihydrophenazine on heating with iron(II) oxalate at 280°; this gave a 40% yield of phenazine. When the oxidative component of a reaction system was simulated by incorporation of a nitro-compound (1-nitronaphthalene), as well as iron(II) oxalate, the yield of phenazine rose to 80%, and the isolation of some *N*-acetyl-1-naphthylamine showed that reduction of the nitro-group had also occurred.

Cyclisation of *N*-substituted *o*-nitrodiarylamines: (i) by heating alone (*ca.* 280°), (ii) by heating with ferrous oxalate (*ca.* 280°), and (iii) with triethyl phosphite in boiling cumene (*ca.* 152°)

Nitro-compound	Conditions	Yields (%) of cyclisation products			
					
(5) X = H (6) X = Me (7) X = Ac		(8)	(9) Z = H (10) Z = Me		(11)
(5)	(i)	21			
	(ii)	49			
	(iii)	0			
(6)	(i)	0	(9)	34	
	(ii)	11	(9)	46	
	(iii)	12	(9)	36	
(7)	(i)	Trace	(10)	Trace	0
	(ii)	5	(10)	32	0
	(iii)	0	(10)	20	11
					
(12)		(13)	(14)	(15)	
	(ii)	14	2	19	
	(iii)	25	Trace of isomer	22	

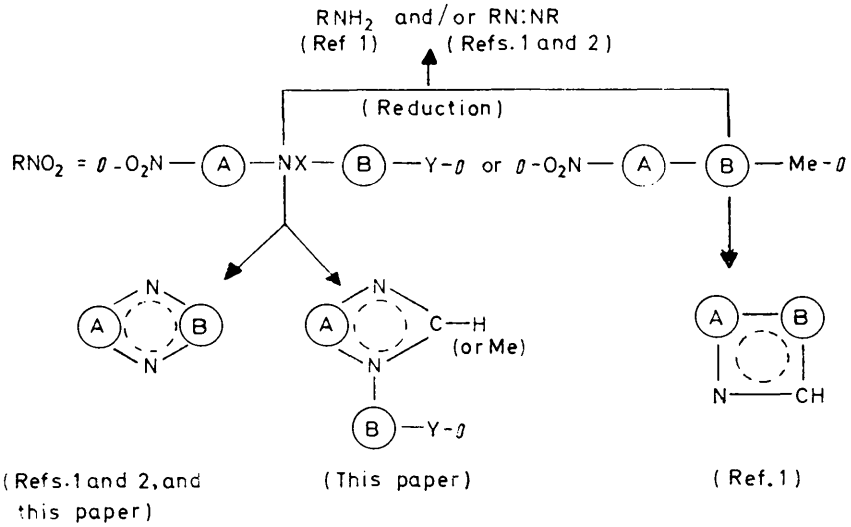
In summary, in the Scheme we bring together the modes of reaction reported here and in the preceding two papers [1,2] and we comment as follows.

(*a*) The reactions of nitrodiarylamines and related binuclear compounds shown in the Scheme are the result of oxidation, reduction, substitution, and elimination steps. Transformations may be possible under purely thermal conditions (*i.e.* may be independent of extraneous catalysts or oxygen acceptors) but,

[17] G. R. Cliff and G. Jones, *Chem. Comm.*, 1970, 1705; *J. Chem. Soc.* (*C*), 1971, 3418; G. R. Cliff, E. W. Collington, and G. Jones, *ibid.*, 1970, 1490.

when this is the case, some self-destrcttion of the substrate must occur.

(*b*) The role of iron(II) oxalate is open to various interpretations. It may improve yields by taking over the self-destructive reductive function of a substrate,



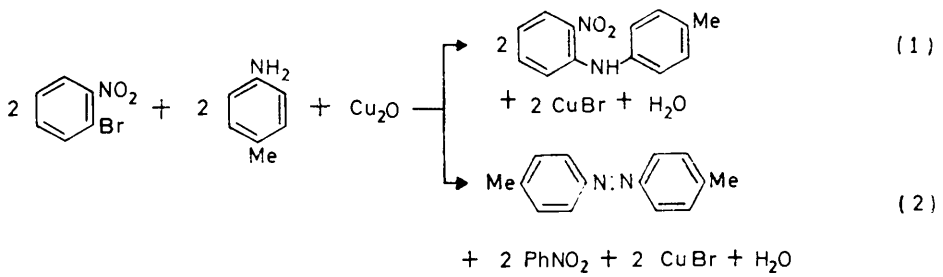
Summary of reactions, with iron(II) oxalate at *ca.* 280°, of *o*-nitro-substituted binuclear compounds, RNO_2 = *o*-O_2N–A–NX–B–Y-*o* or *o*-O_2N–A–B–Me-*o* [A and B = benzenoid or heterocyclic aromatic rings; X = H, Me, or Ac; eliminated substituent *o*-Y = H or OMe (or Me in one case [2])].

but transformations of some substrates do not occur in its absence.

(*c*) Both resemblances and differences are observed in the results of using triethyl phosphite in place of iron(II) oxalate. Insertion of nitrogen into a benzene ring (detected only with the phosphite) is characteristic of a nitrene mechanism, but there is no evidence that such intermediates are involved with iron(II) oxalate.

(*d*) A methyl or acetyl substituent X in a substrate Ar_2NX may provide a centre for cyclisation with NO_2, but cyclisation of NO_2 onto an aromatic nucleus may also occur, the substituent X being eliminated. It is not known whether such eliminations occur prior to, simultaneously with, or subsequent to the nuclear substitution step.

A Note on the Preparation of o-*Nitrodiarylamines.*—The nitro-amines required as intermediates are commonly prepared by nucleophilic substitution of *o*-nitroaryl halides by primary aromatic amines, a type of reaction which does not proceed particularly readily (*cf.* this paper and ref. 2). If copper(I)-catalysis is attempted, the result is likely to be worse rather than better, since arylamines are good hydrogen donors in copper-catalysed reductive substitution of the halides: [18] *e.g.* in a preparation of 4-methyl-2-nitrodiphenylamine, carried out in dimethylacetamide in the presence of copper(I) oxide, we achieved the desired nucleophilic substitution [equation (1)] in a yield of only 10%, owing to strong competition from the reductive substitution [equation (2)]. As well as nitrobenzene and 4,4′-dimethylazobenzene, 2,2′-dinitrobiphenyl was isolated; this could arise from



nitrophenyl radical intermediates in the hydrogen-transfer reaction [equation (2)].

EXPERIMENTAL

General Procedures.—M.p.s were determined on a Kofler block; n.m.r. spectra (unless otherwise stated) were obtained in deuteriochloroform at 60 MHz with a Varian A60 instrument, and mass spectra with an A.E.I. MS902 instrument.

The iron(II)-promoted reactions were carried out by the usual procedure [2] of making an intimate mixture of the

[18] R. G. R. Bacon and O. J. Stewart, *J. Chem. Soc.* (*C*), 1969, 301.

nitro-amine (5 mmol) and iron(II) oxalate dihydrate (10 mmol), adding lead shot (10 g), heating to 260—280°, and maintaining this temperature for 10—15 min. Products were extracted with dichloromethane and separated on a column of alumina (Peter Spence, type H), which had been deactivated with acetic acid as previously described.[1] ' Activated ' alumina in certain preparations refers to the untreated absorbent.

The phosphite-promoted reactions were carried out by heating a solution of the nitro-amine (5 mmol) and an excess of triethyl phosphite (20 mmol) in refluxing cumene (50 ml) for 8 h under nitrogen. Volatile liquids were removed under reduced pressure and the residual oil was chromatographed on alumina.

Cyclisation of 4-*Chloro*-4'-*methyl*-2-*nitrodiphenylamine* (5).—2,5-Dichloronitrobenzene (40 mmol), *p*-toluidine (50 mmol), and anhydrous sodium acetate (50 mmol) were ground together and heated at 190° for 30 h. Extraction of the product with dichloromethane and elution of the extract with light petroleum on activated alumina yielded unchanged dichloronitrobenzene (17 mmol), followed by 4-chloro-4'-methyl-2-nitrodiphenylamine (5) (5·3 g, 50%), m.p. 122° (lit.,[10d] 120—122°), *m/e* 264/262 (M^+), τ 0·5—0·6br (s, NH), 1·77 (d, 3-H), 2·5—3·0 (m, 6 nuclear H), and 7·6 (s, Me) ($J_{3.5}$ 2·0 Hz).

(*a*) The nitro-amine was heated with iron(II) oxalate and the products were separated on alumina. Elution with light petroleum gave unchanged nitro-amine (8%), and light petroleum–ether (10 : 1) eluted 2-chloro-8-methylphenazine (8) (0·56 g, 49%), m.p. 162—164° (lit.,[10d] 163·5—164·5°), *m/e* 230/228 (M^+), τ 1·85 (d, 1-H), 1·9 (d, 4-H), 1·94 (d, 6-H), 2·1br (s, 9-H), 2·35 (q, 3-H), 2·39 (q, 7-H), and 7·39 (d, Me) ($J_{1.3}$ 2·0, $J_{3.4}$ 8·8, $J_{6.7}$ 9·0, $J_{7.9}$ 2·0, and $J_{9.Me}$ 1·0 Hz).

(*b*) The nitro-amine (5 mmol) was heated alone for 15 min at 270—300° and the product examined as in (*a*). Nitro-amine (40%) was recovered, followed by 2-chloro-8-methylphenazine (0·24 g, 21%), identical with the sample described in (*a*).

(*c*) Heating the nitro-amine with triethyl phosphite gave no identifiable products.

Cyclisation of 4-*Chloro*-4',N-*dimethyl*-2-*nitrodiphenylamine* (6).—4-Chloro-4'-methyl-2-nitrodiphenylamine (20 mmol) was added with stirring to a suspension of powdered potassium hydroxide (70 mmol) in acetone (20 ml). The mixture was briefly brought to the b.p., cooled slightly and stirred, while dimethyl sulphate (50 mmol) was added over 1 h; the colour changed from purple through brown to red. Acetone was distilled off and the residual oil was washed with aqueous ammonia, then with water, and purified on alumina. Light petroleum–ether (19 : 1) eluted red 4-*chloro*-4',N-*dimethyl*-2-*nitrodiphenylamine* (6) (4·4 g, 79%), m.p. 92° (Found: C, 60·6; H, 4·7; Cl, 13·0; N, 10·1. $C_{14}H_{13}ClN_2O_2$ requires C, 60·8; H, 4·7; Cl, 12·8; N, 10·1%), *m/e* 278/276 (M^+), τ 2·22 (d, 3-H), 2·51 (q, 5-H), 2·77 (d, 6-H), 2·96 (d, 2'- and 6'-H), 3·31 (d, 3'- and 5'-H), 6·74 (s, NMe), and 7·74 (s, Me) ($J_{3.5}$ 2·4, $J_{5.6}$ 8·6, and $J_{2'.3'}$ and $J_{5'.6'}$ 8·8 Hz).

(*a*) The *N*-methyl-nitro-amine was heated with iron(II) oxalate, and the product chromatographed. Light petroleum eluted unchanged material (8%) and light petroleum–ether (7 : 1) eluted 2-chloro-8-methylphenazine (0·13 g, 11%). Ether then eluted 5-*chloro*-1-p-*tolylbenzimidazole* (9) (0·56 g, 46%), m.p. 115° (Found: C, 69·3; H, 4·4; Cl, 14·5; N, 11·6. $C_{14}H_{11}ClN_2$ requires C, 69·3; H, 4·6; Cl, 14·6; N, 11·5%), *m/e* 244/242 (M^+), τ 1·87 (s, 2-H), 2·1 (d, 4-H), 2·6 (s, all other nuclear H), and 7·53 (s, Me) ($J_{4.6}$ 2·0 Hz).

(*b*) The *N*-methyl-nitro-amine (5 mmol) was heated alone for 15 min at 270—300° and the black residue was extracted with dichloromethane and the extract chromatographed. This yielded unchanged material (2%) and 5-chloro-1-*p*-tolylbenzimidazole (0·41 g, 34%), identical with the sample described in (*a*); no 2-chloro-8-methylphenazine was detected.

(*c*) Heating with triethyl phosphite afforded a brown oil, which was chromatographed to yield unchanged *N*-methyl-nitro-amine (20%), 2-chloro-8-methylphenazine (0·14 g, 12%), and 5-chloro-1-*p*-tolylbenzimidazole (0·44 g, 36%).

Cyclisation of N-*Acetyl*-4-*chloro*-4'-*methyl*-2-*nitrodiphenylamine* (7).—A mixture of 4-chloro-4'-methyl-2-nitrodiphenylamine (4 g), zinc chloride (2 g), and acetic anhydride (12 ml) was heated at 60—80° for 2 h. Addition to ice, extraction with chloroform, and chromatography on activated alumina afforded, in almost quantitative yield, the pale yellow N-*acetyl derivative* (7), m.p. 90° (Found: C, 59·2; H, 4·0; Cl, 11·7; N, 9·3. $C_{15}H_{13}ClN_2O_3$ requires C, 59·1; H, 4·3; Cl, 11·6; N, 9·2%), τ 2·05 (d, 3-H), 2·4—3·0 (m, all other nuclear H), 7·6 (s, Me), and 7·96 (s, COMe) ($J_{3.5}$ 2·2 Hz).

(*a*) The *N*-acetyl-nitro-amine was heated with iron(II) oxalate and the product chromatographed. Elution with light petroleum–ether (9 : 1) gave 2-chloro-9-methylphenazine (0·057 g, 5%), and light petroleum–ether (5 : 1) gave 5-*chloro*-2-*methyl*-1-p-*tolylbenzimidazole* (10) (0·41 g, 32%), m.p. 107° (Found: C, 70·2; H, 5·1; Cl, 13·8; N, 11·0. $C_{15}H_{13}ClN_2$ requires C, 70·3; H, 5·1; Cl, 13·8; N, 10·9%), *m/e* 258/256 (M^+), τ 2·3 (d, 4-H), 2·5—3·1 (m, all other nuclear H), and 7·53 (2 Me) ($J_{4.6}$ 2·0 Hz). Continued elution with light petroleum–ether (3 : 1) gave unchanged *N*-acetyl-nitro-amine (6%).

(*b*) The *N*-acetyl compound (5 mmol) was heated alone for 15 min at 270—300°. Chromatography successively furnished trace amounts of 4-chloro-4'-methyl-2-nitrodiphenylamine, 2-chloro-8-methylphenazine, and 5-chloro-2-methyl-1-*p*-tolylbenzimidazole, each spectroscopically identical with the samples described above. Unchanged *N*-acetyl compound (82%) was then eluted.

(*c*) Heating with triethyl phosphite gave an oil; chromatographic separation with light petroleum gave crystalline 2-*chloro*-8-*methyl*-6H-*azepino*[1,2-a]*benzimidazole* (11) (0·13 g, 11%), m.p. 148° (Found: C, 67·5; H, 4·7; Cl, 15·2; N, 12·2. $C_{13}H_{11}ClN_2$ requires C, 67·7; H, 4·8; Cl, 15·4; N, 12·1%), *m/e* 232/230 (M^+), 231/229 (M − H), and 217/215 (M − Me), $\nu_{max.}$ 1470, 1395, 800, and 780 cm^{-1}, τ (at 100 MHz; assignments given for the 6*H*-structure) 2·41 (d, 4-H), 2·62 (d, 1-H), 2·79 (q, 3-H), 2·96 (d, 10-H), 3·97 (d, 9-H), 4·34br (t, 7-H), 6·53 (d, 6-H_2), and 8·14 (d, Me) ($J_{1.3}$ 1·8, $J_{3,4}$ 8·3, $J_{9,10}$ 9·0, $J_{6,7}$ 6·4, and $J_{7.Me}$ 1·1 Hz; the splitting pattern was confirmed by spin–spin decoupling). Elution was continued with light petroleum–ether (4 : 1), which gave 5-chloro-2-methyl-1-*p*-tolylbenzimidazole (0·26 g, 20%), followed by unchanged *N*-acetyl-compound (20%).

Cyclisation of N-*Acetyl*-4-*chloro*-2'-*methoxy*-2-*nitrodiphenylamine* (12).—2,5-Dichloronitrobenzene (40 mmol), *o*-anisidine (80 mmol), and anhydrous sodium acetate (40 mmol) were heated together for 48 h at 180°, and the product was extracted and chromatographed on activated alumina. Light petroleum eluted unchanged dichloronitrobenzene (12%) and light petroleum–ether (9 : 1) furnished 4-chloro-2'-methoxy-2-nitrodiphenylamine (8·1 g,

72%), m.p. 105° (lit.,[19] 100—101°), *m/e* 280/278 (M^+). The amine (20 mmol) was heated with zinc chloride (2 g) and acetic anhydride (20 ml) for 30 h at 80°. Isolation and purification with light petroleum–ether (1 : 1) on alumina furnished the N-*acetyl derivative* (12) as an oil, which when triturated with methanol solidified to pale yellow crystals (4·6 g, 74%), m.p. 89° (Found: C, 56·1; H, 4·1; Cl, 11·0; N, 8·6. $C_{15}H_{13}ClN_2O_4$ requires C, 56·2; H, 4·1; Cl, 11·0; N, 8·7%), *m/e* 322/320 (M^+) and 280/278 ($M - CH_2CO$), τ 2·2 (d, 3-H), 2·2—3·1 (m, all other nuclear H), 6·02 (s, OMe), and 8·02 (s, COMe) ($J_{3,5}$ 2·2 Hz).

(*a*) The *N*-acetyl derivative was heated with iron(II) oxalate and the product chromatographed. Elution with light petroleum gave 2-chlorophenazine (13) (0·15 g, 14%); this was identical in m.p. and spectroscopic properties with a sample prepared by heating 4-chloro-2-nitrodiphenylamine with iron(II) oxalate.[10a,c] Elution with light petroleum–ether (9 : 1) then gave 2-chloro-6-methoxyphenazine (14) (0·025 g, 2%), m.p. 164—166° (lit.,[20] 164—165°; lit.,[21] 165—166°), *m/e* 246/244 (M^+), $\nu_{max.}$ 1275, 1105, and 815 cm^{-1}, τ 1·5—2·9 (m, all nuclear H) and 5·83 (s, OMe). Elution with light petroleum–ether (1 : 1) gave yellowish crystals of *5-chloro-1-o-methoxyphenyl-2-methylbenzimidazole* (15) (0·24 g, 19%), m.p. 109° (Found: C, 66·0; H, 5·0; Cl, 12·9; N, 10·4. $C_{15}H_{13}ClN_2O$ requires C, 66·0; H, 4·8; Cl, 13·0; N, 10·3%), *m/e* 274/272 (M^+), τ 2·2 (d, 4-H), 2·3—3·1 (m, all other nuclear H), 6·3 (s, OMe), and 7·61 (s, Me) ($J_{4,6}$ 2·2 Hz). Further elution gave unchanged *N*-acetyl-nitro-amine (10%) and tars.

(*b*) The *N*-acetyl derivative was heated with triethyl phosphite and the oily product chromatographed. Petroleum eluted 2-chlorophenazine (0·27 g, 25%), identical with the sample described in (*a*). Light petroleum–ether (7 : 1) furnished a trace of a yellow solid, m.p. 165—168°, apparently an isomer of chloromethoxyphenazine, *m/e* 246/244 (M^+) and 203/201 (? M — COMe), $\nu_{max.}$ 1480, 1430, and 1300 cm^{-1}. Elution with light petroleum–ether (1 : 1) then gave 5-chloro-1-*o*-methoxyphenyl-2-methylbenzimidazole (0·3 g, 22%), identical with the sample described in (*a*); this was followed by unchanged *N*-acetyl-nitro-amine (15%), triethyl phosphate, and tars.

Aromatisation of N-Acetyl-5,10-dihydrophenazine.—(*a*) The *N*-acetyl compound was prepared [22] by adding zinc powder (2·0 g) with stirring to phenazine (10 mmol) in acetic anhydride (8 ml) and acetic acid (2·4 ml), and filtering the grey mixture after 36 h. The filtrate contained unchanged phenazine; the solid residue, when extracted with acetone in a Soxhlet apparatus, yielded *N*-acetyl-5,10-dihydrophenazine (1·7 g, 76%).

(*b*) Analogously to an earlier phenazine preparation,[23] a solution of *N*-acetyl-*N*-*o*-nitrophenylaniline in diethylene glycol diethyl ether was heated (24 h) under reflux and the product chromatographed to yield unchanged material, unidentified oils, phenazine (5%), and *N*-acetyl-5,10-dihydrophenazine (10%), identical in m.p. and spectroscopic properties with the product obtained in (*a*).

(*c*) The *N*-acetyl compound (5 mmol) was mixed with iron(II) oxalate (10 mmol) and lead shot (10 g) and the mixture heated at 270—300° for 30 min. Some darkening of the powder, loss of water, and appearance of a yellow sublimate were noted. Extraction of the mixture with dichloromethane gave phenazine (0·36 g, 40%), eluted with light petroleum–ether (9 : 1), and unchanged *N*-acetyl compound (17%), eluted with ether; a further 38% of the latter was recovered by acetone extraction of the remaining crude product.

(*d*) Procedure (*c*) was modified by incorporation of 1-nitronaphthalene (5 mmol) in the reaction mixture. Chromatography gave unchanged nitronaphthalene (5%) and phenazine (0·71 g, 79%), both eluted by light petroleum–ether (9 : 1); ether then eluted *N*-acetyl-1-naphthylamine (9%), identical with a sample prepared from 1-naphthylamine.

Effect of Copper(I) in a Preparation of 4-Methyl-2′-nitrodiphenylamine.—Copper(I) oxide (5 mmol) was added to a solution of *o*-bromonitrobenzene (10 mmol) and *p*-toluidine (20 mmol) in dimethylacetamide (30 ml) and the mixture was stirred under reflux, in an atmosphere of nitrogen, for 18 h, filtered, poured into water, extracted with dichloromethane, and the extract chromatographed on activated alumina. Light petroleum eluted nitrobenzene, identified spectroscopically, followed by orange crystals of 4,4′-dimethylazobenzene, m.p. 144° (lit.,[24] 144°), *m/e* 210 (M^+), 119 ($N_2C_6H_4Me$), and 91 (C_6H_4Me), τ 2·17 (d, H *ortho* to N_2), 2·73 (d, H *ortho* to Me), and 7·6 (s, Me) (J 8·4 Hz). Further elution with light petroleum gave an unidentified red oil, followed by 4-methyl-2′-nitrodiphenylamine (0·23 g, 10%), m.p. 69° (lit.,[10d] 69—70°), *m/e* 228 (M^+). Further elution gave 2,2′-dinitrobiphenyl, identical in m.p. and spectroscopic properties with an authentic sample.

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