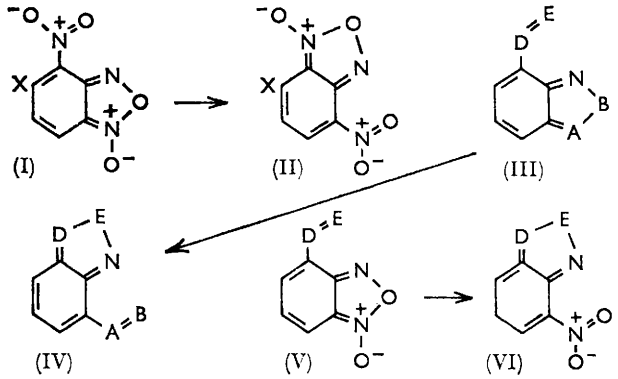
Heterocyclic Rearrangements. Part V.[1] Rearrangement of 4-Arylazo- and 4-Nitroso-benzofuroxans: New Syntheses of the Benzotriazole and Benzofurazan Ring Systems[2]

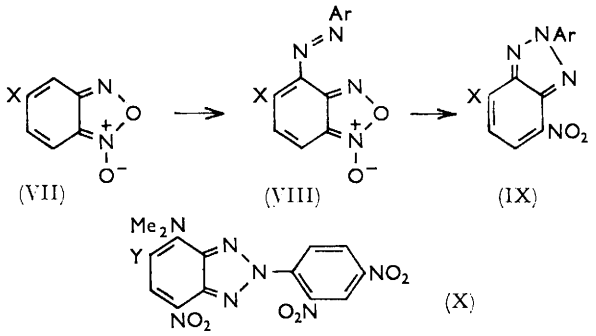
By A. J. Boulton, P. B. Ghosh, and A. R. Katritzky

4-*p*-Anisylazo-5-nitrobenzofuroxan rearranges spontaneously to 2-*p*-anisyl-4,7-dinitrobenzotriazole, whose structure is proved by n.m.r. spectroscopy. 5-Dimethylamino-4-nitrosobenzofuroxan rearranges spontaneously to 4-dimethylamino-7-nitrobenzofurazan, whose structure was proved by independent synthesis. The preparation of some derivatives of 4-aminobenzofuroxan is reported.

DURING work on nitrobenzofuroxans,[3] two of us postulated and realised the smooth interconversion of 4-nitrobenzofuroxans (I ⟶ II).[4] Considering this to be a case of the new class of heterocyclic rearrangement generalised by (III ⟶ IV), we sought further examples,

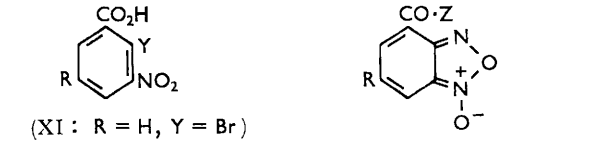


and now record the rearrangement of 4-arylazo- and 4-nitroso-benzofuroxans (V ⟶ VI, D=E is N=NAr and N=O); the succeeding Paper[5] is concerned with the rearrangement of 4-carbonyl- and 4-ketimino-benzofuroxans (V ⟶ VI, D=E is C=O and C=N.)



Rearrangement of 4-Azobenzofuroxans.—Azo-coupling of 5-substituted benzofuroxans. Our first approach (VII ⟶ VIII ⟶ IX) lay in the azo-coupling of benzofurans carrying an activating substituent in the 5-position. 5-Methoxy- and 5-chloro-4-methoxy-benzofuroxan did not couple even with the reactive *p*-nitro- and 2,4-dinitro-benzenediazonium sulphates: contrast the successful coupling of anisole.[6] Although we prepared 5-amino- and 5-hydroxy-benzofuroxan,[7] they were too unstable for use in coupling. 5-*NN*-Dimethylaminobenzofuroxan (VII; X = NMe_2) and its 6-chloro-analogue[7] did not couple with normal diazonium salts, probably because of steric hindrance. However, the reaction was successful with 2,4-dinitrobenzenediazonium sulphate; we formulate the products as the benzotriazoles (X; Y = H or Cl) on the basis of their thermal stability and spectra. The infrared spectrum showed absorption at 1605, 1580, 1556, and 1500 $cm.^{-1}$. High-intensity peaks were present in the electronic spectrum at 327, 390, and 470 mμ; the n.m.r. spectra (taken in $AsCl_3$) were not fully interpreted but appeared consistent with the assigned structures. However, although these results agree with structures of type (X), they do not rule out the unrearranged structures. Because of the difficulty of an unambiguous proof of structures (X), further approaches were initiated.

Attempted preparation of 4-aminobenzofuroxans. Our second approach envisaged 4-aminobenzofuroxans as



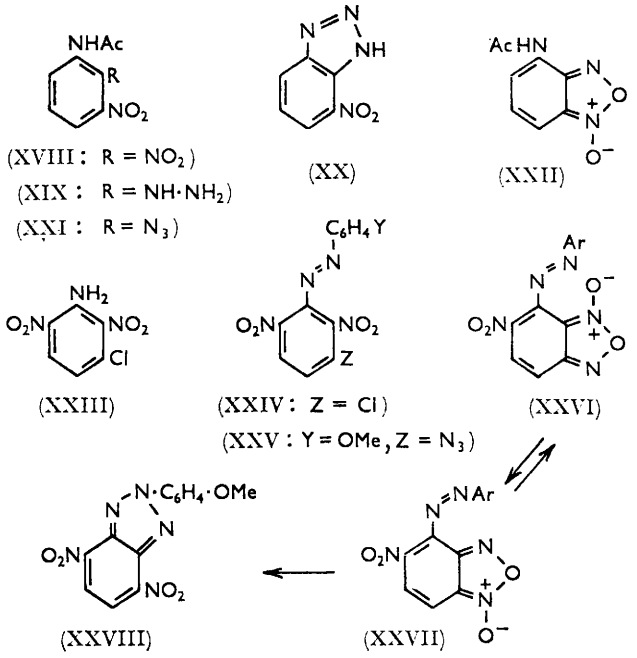
(XI: R = H, Y = Br)
(XII: R = H, Y = NH_2)
(XIII: R = H, Y = N_3)
(XVI: R = Me, Y = NH_2)

(XIV: R = H, Z = OMe)
(XV: R = H, Z = NH_2)
(XVII: R = Me, Z = OH)

intermediates, and we made several attempts to prepare them. 2-Bromo-3-nitrobenzoic acid (XI) with alcoholic ammonia gave the 2-amino-analogue (XII) which was converted into the azide (XIII). This azido-acid (XIII) did not lose nitrogen smoothly, decomposing only above 200°. However, its methyl ester (XIII) gave the benzofuroxan ester (XIV) which was converted into the amide (XV). Attempted Hofmann degradation of (XV) failed to give a well-defined product.

[1] Part IV, A. J. Boulton, A. C. Gripper Gray, and A. R. Katritzky, *J. Chem. Soc.*, 1965, 5958.
[2] Preliminary communication: A. J. Boulton, P. B. Ghosh, and A. R. Katritzky, *Angew. Chem.*, 1964, **76**, 816; *Angew. Chem., Internat. Edn.*, 1964, **3**, 693.
[3] R. K. Harris and A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.*, 1963, 197.
[4] A. J. Boulton and A. R. Katritzky, *Proc. Chem. Soc.*, 1962, 257; *Rev. Chim. Acad. R.P.R.*, 1962, **7**, 691.
[5] A. J. Boulton, P. B. Ghosh, and A. R. Katritzky, following Paper.
[6] K. H. Meyer, A. Irschick, and H. Schlösser, *Ber.*, 1914, **47**, 1741.
[7] A. J. Boulton, P. B. Ghosh, and A. R. Katritzky, *J. Chem. Soc.* (*C*), 1966, 971.

2-Amino-5-methyl-3-nitrobenzoic acid (XVI) was converted successively into the 2-azido-analogue and the benzofuroxan acid (XVII), although the last was not obtained analytically pure, possibly owing to decarboxylation. In view of the previous failure, Hofmann degradation was not attempted.



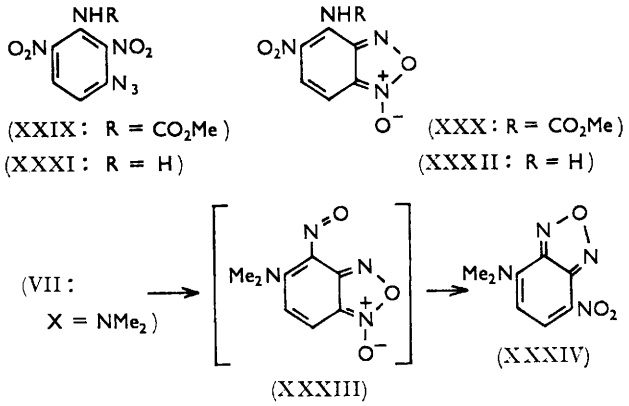
2,3-Dinitroacetanilide [8] (XVIII) could be hydrogenated to a nitro-aminoacetanilide, m. p. 182—183°, whose orientation has not been settled. Alcoholic ammonia with (XVIII) gave mainly 2,3-dinitroaniline, whereas attempted reduction with hydrazine formed the hydrazino-compound (XIX), whose orientation was proved by conversion by oxidation with chlorine into 4-nitrobenzotriazole (XX). However, reaction of 2,3-dinitroacetanilide with sodium azide in dimethyl sulphoxide gave the monoazido-derivative (XXI) which on pyrolysis yielded 4-acetamidobenzofuroxan (XXII).

Attempts to hydrolyse 4-acetamidobenzofuroxan to the 4-amino-analogue failed, and we conclude that 4-aminobenzofuroxans are unstable, just as are the 5-aminobenzofuroxans.[5] However, electron-withdrawing groups evidently confer stability, as shown by 4-amino-5-nitrobenzofuroxan, described below.

4-Azobenzofuroxans by furoxan ring synthesis. We finally decided to synthesise by ring-closure a 4-arylazobenzofuroxan which on rearrangement would yield a symmetrical benzotriazole, the symmetry of which (and thus its distinction from the unsymmetrically substituted benzofuroxan) could be demonstrated by n.m.r. *m*-Chloroaniline was converted in several stages into 3-chloro-2,6-dinitroaniline (XXIII) which was diazotised and coupled with dimethylaniline and anisole to yield the azo-compounds (XXIV; Y = NMe_2 and OMe). The methoxy-derivative (XXIV; Y = OMe) (unlike its dimethylamino-analogue) reacted smoothly with sodium azide in dimethyl sulphoxide or dimethylformamide to give the azide (XXV). The n.m.r. spectrum of the azide (XXV) in arsenic trichloride solution (insufficiently soluble in other solvents), showed for the *p*-methoxyphenyl group a simplified A_2B_2 spectrum which appeared as an AB quartet (area 4) (τ_A 2·08; τ_B 2·96; J = 9·0 c./sec.), for the *ortho*-benzenoid protons, an AB quartet (area 2) (τ_A 2·21; τ_B 2·68; J = 9·0 c./sec.), and for the OCH_3 group a singlet at 6·06 (area 3) (Figure 1). The ultraviolet spectrum had bands at $\lambda_{max.}$ 253 (ε 16,500) and 390 mμ (ε 23,000).

On pyrolysis at 155—160°, the azide (XXV) lost nitrogen and the charred reaction mixture afforded a colourless product which we formulate as 2-*p*-methoxyphenyl-4,7-dinitrobenzotriazole (XXVIII). The n.m.r. spectrum (in $AsCl_3$) (Figure 2) again has the simplified A_2B_2 structure (τ_A 2·08; τ_B 2·86; J = 9·0 c./sec.) and the OCH_3 singlet (τ 6·05) for the anisyl group, but now the signal for the remaining two ring protons appeared as a sharp singlet (τ 2·21). This singlet is good evidence for the symmetrical structure (XXVIII), formed by two successive rearrangements (XXVI ⟶ XXVII) (cf. ref. 3) and (XXVII ⟶ XXVIII). The electronic absorption spectrum ($\lambda_{max.}$ 242 and 292·5 mμ, ε 10,050 and 23,000) also eliminates structures such as (XXVI) or (XXVII) which contain an azo-group.

4-Amino-5-nitrobenzofuroxan.— 4-Methoxycarbonamido-5-nitrobenzofuroxan (XXX) was prepared from 1-chloro-3-methoxycarbonamido-2,4-dinitrobenzene *via* the corresponding azide (XXIX). The urethane (XXX) resisted attempted hydrolysis with sulphuric acid at 100° to 4-amino-5-nitrobenzofuroxan (XXXII). However, the last compound was successfully prepared from the chloro-aniline (XXIII) *via* the azide (XXXI). An attempt to use the method of partial deuteration (cf. ref. 9) to determine the tautomeric structure of 4-amino-5-nitrobenzofuroxan failed owing to its insufficient solubility in suitable solvents.



Rearrangements of 4-Nitrosobenzofuroxans.—5-*NN*-Dimethylaminobenzofuroxan (VII; X = NMe_2) was nitrosated in aqueous ethanol to yield a red product to which was assigned the benzofurazan structure (XXXIV), evidently formed by spontaneous rearrangement of the

[8] L. H. Welsh, *J. Amer. Chem. Soc.*, 1941, **63**, 3276.

intermediate (XXXIII), on the following evidence. It was thermally stable to above its m. p. of 215°. The infrared spectrum had peaks at 1615 cm.$^{-1}$ (benzofuroxan or benzofurazan) and 1570 and 1330 cm.$^{-1}$ (NO_2 group: these bands are absent from the spectrum of 5-*NN*-dimethylaminobenzofuroxan) and 1370 cm.$^{-1}$. This evidence strongly supports the rearranged structure (XXXIV).

the chemical shifts of the 4- and 6-protons were almost identical ($\tau_A = 2{\cdot}63$, $\tau_B = \tau_{B'} = 2{\cdot}83$, $J_{AB} = J_{AB'} = 8{\cdot}0$ c./sec.); this would not be expected were the positions of the nitro- and dimethylamino-groups reversed. Attempts to diazotise the diamine gave only the nitroso-compound (XXXVII), evidently a result of the strong activation of the 6-position. Phenyliodosodiacetate usually converts an *o*-nitroaniline into a mixture of the

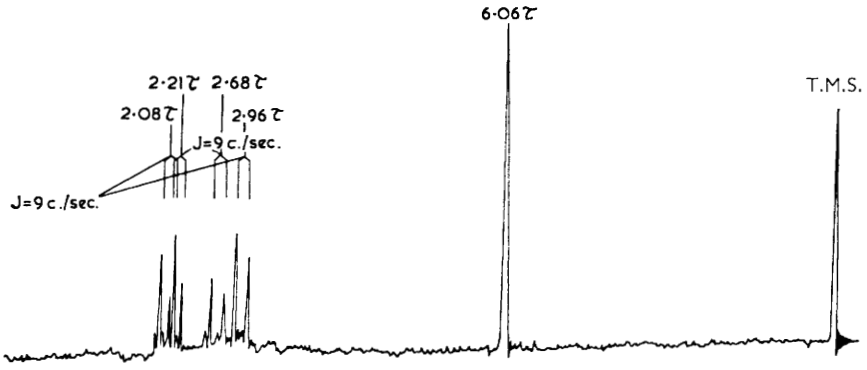


FIGURE 1 N.m.r. spectrum of the azide (XXV) in $AsCl_3$

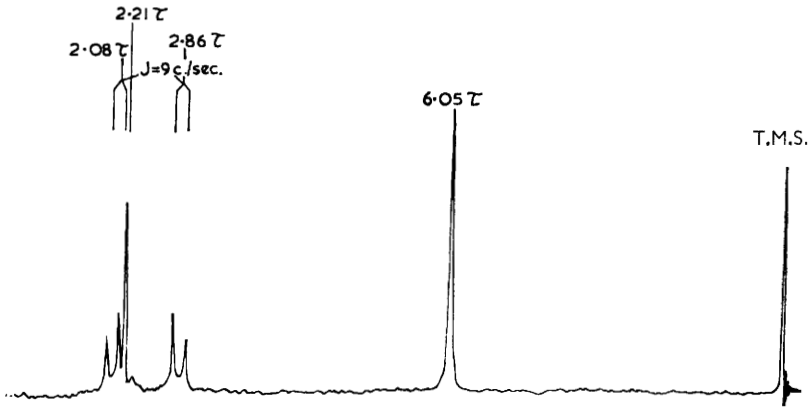
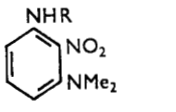
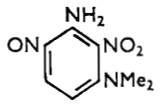


FIGURE 2 N.m.r. spectrum of 2-*p*-methoxyphenyl-4,7-dinitrobenzotriazole (XXVIII) in $AsCl_3$

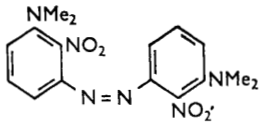
The 4-dimethylamino-7-nitrobenzofurazan structure (XXXIV) was confirmed by independent synthesis. The first attempt was aimed at 4-dimethylaminobenzofuroxan, which seemed a promising intermediate. 2,3-Dinitroacetanilide (XVIII) with aqueous-ethanolic dimethylamine gave 3-dimethylamino-2-nitroacetanilide



(XXXV: R = Ac)
(XXXVI: R = H)



(XXXVII)



(XXXVIII)

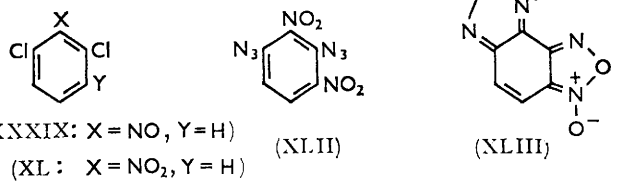
(XXXV), which was hydrolysed to the diamine (XXXVI), whose structure was proved by n.m.r.:

azobenzene and the benzofuroxan,[10] but with the diamine (XXXVI) it yielded only the azo-compound (XXXVIII).

Attention was turned to the preparation of 4-chlorobenzofurazan as an intermediate. It was first envisaged that this intermediate would be made *via* 4-chlorobenzofuroxan. 2,6-Dichloroaniline (commercial) was oxidised by peracetic acid (cf. ref. 11) to 1-nitroso-2,6-dichlorobenzene (XXXIX). This was oxidised by 50% nitric acid to 1-nitro-2,6-dichlorobenzene (XL) (previously obtained[12] by a seven-stage synthesis from *p*-nitroaniline); use of 100% nitric acid for the oxidation led to simultaneous nitration to form 2,4-dichloro-1,3-dinitrobenzene (XLI). Attempted replacement of a chlorine atom in the mononitro-compound by azide or ammonia failed, probably because the nitro-group is

[9] A. J. Boulton and A. R. Katritzky, *Tetrahedron*, 1961, **12**, 51.
[10] K. H. Pausacker and J. G. Scroggie, *Austral. J. Chem.*, 1958, **11**, 487.
[11] R. R. Holmes and R. P. Bayer, *J. Amer. Chem. Soc.*, 1960, **82**, 3454.
[12] A. F. Holleman, *Rec. Trav. chim.*, 1904, **23**, 365.

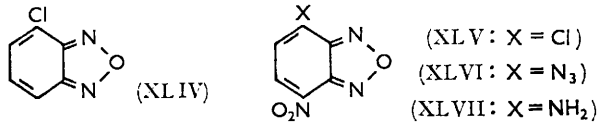
forced out of conjugation by the two *ortho* substituents. However, the dinitro-derivative (XLI) with sodium azide in dimethyl sulphoxide gave the diazide (XLII) which readily lost two molecules of nitrogen to give furoxanobenzofuroxan (XLIII) (cf. ref. 13).



(XXXIX: X = NO, Y = H)
(XL: X = NO_2, Y = H)
(XLI: X = Y = NO_2)

(XLII)

(XLIII)



(XLIV)

(XLV: X = Cl)
(XLVI: X = N_3)
(XLVII: X = NH_2)

Another possible precursor of 4-chlorobenzofuroxan, 6-chloro-2-nitroaniline, is conveniently [14] prepared by the action of ammonia on 2,3-dichloro-1-nitrobenzene: however, available commercial supplies of the latter proved to be mainly the 3,4-isomer. Further, the oxidation of 6-chloro-2-nitroaniline to 4-chlorobenzofuroxan by phenyliodosodiacetate in our hands gave far lower yields than those previously claimed.[15]

In view of these difficulties, we developed a new synthesis [16] of benzofurazans. 4-Chlorobenzofurazan (XLIV) [17] was nitrated to the 7-nitro derivative (XLV).

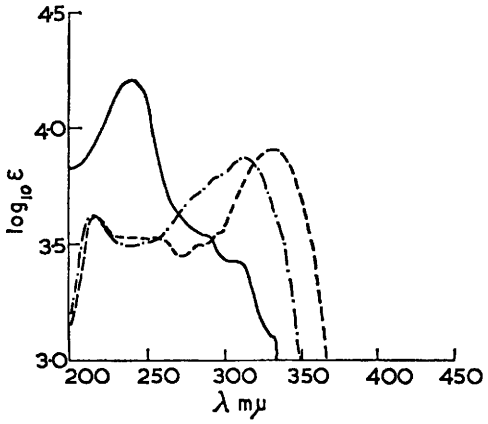


FIGURE 3 Ultraviolet spectra in cyclohexane of 4-chloro-7-nitrobenzofurazan (XLV) – – –, 5-nitrobenzofurazan ——, 4-nitrobenzofurazan — · — · —

The orientation was proved (*a*) by the n.m.r. spectrum which disclosed an AB pattern ($\tau_A = 1{\cdot}3$, $\tau_B = 2{\cdot}0$; $J_{AB} = 8$ c./sec.); this J can only be due to *ortho*-coupling and thus eliminates nitration in the 6-position; (*b*) by the ultraviolet spectrum, which was similar to that of 4-nitrobenzofurazan but significantly different from that of the 5-nitro-isomer (Figure 3); and (*c*) by reaction with sodium azide. The latter gave the azide (XLVI) which was thermolysed in toluene with extraction of hydrogen from the solvent to yield the 4-amino-7-nitrobenzofurazan (XLVII). (An analogy [18] is the conversion of 2-azidoquinoline 1-oxide into the 2-amino-analogue on heating in benzene.) Had the nitration occurred in the 5-position, the *o*-nitro-azide formed would have ring-closed to give furazanobenzofuroxan.[1] 4-Chloro-7-nitrobenzofurazan was converted by dimethylamine into 4-dimethylamino-7-nitrobenzofurazan (XXXIV), identical with the compound obtained from the rearrangement (XXXIII ⟶ XXXIV).

EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope apparatus. Infrared spectra were measured on a Perkin-Elmer 237 spectrometer, ultraviolet spectra on Perkin-Elmer 137 recording and Unicam S.P. 500 manual spectrometers, and n.m.r. spectra on Perkin-Elmer 40 and 60 Mc./sec. instruments. Light petroleum had b. p. 60—80°.

5-Methoxybenzofuroxan,[19] m. p. 117—118° (lit.,[19] 118°), and 5-chloro-4-methoxybenzofuroxan,[20,21] m. p. 80—81° (lit.,[21] 80·6—82·0°), were prepared by established methods.

Attempted Coupling of the Above Benzofuroxans with Diazonium Salts.—Benzenediazonium sulphate and *p*-nitrobenzenediazonium sulphate were prepared by standard methods. 2,4-Dinitrobenzenediazonium sulphate was prepared by use of nitrosylsulphuric acid.[22,23] The diazonium salt solution was added to an alcoholic solution of the benzofuroxan ether, and the mixture kept at 35—40° for several hours. No colour change was observed and in each case the starting methoxybenzofuroxan was obtained on dilution with water. The preparations of 5-amino-, 5-hydroxy-, 5-*NN*-dimethylamino-, an 6-chloro-5-NN-dimethylaminobenzofuroxan have been described previously.

Attempted Coupling of 5-NN-*Dimethylamino- and* 6-*Chloro*-5-NN-*dimethylamino-benzofuroxan with Benzenediazonium Sulphate and* p-*Nitrobenzenediazonium Sulphate.*—The above procedure was employed but no coupling product was obtained.

Coupling of (*a*) 5-NN-*Dimethylaminobenzofuroxan and* (*b*) 6-*Chloro*-5-NN-*dimethylamino-benzofuroxan with* 2,4-*Dinitrobenzenediazonium Sulphate.*— 2,4-Dinitrobenzenediazonium sulphate (0·01 mole) in *ca.* 20% sulphuric acid (100 ml.) was added with shaking to the dimethylamino-compound (0·01 mole) in alcohol (50 ml.). A red colour was produced almost immediately which intensified on warming the solution to 45°. The crimson precipitate which separated showed no sign of change up to its m. p. of (*a*) 280° and (*b*) 210°. Product (*a*), 4-*dimethylamino*-2-(2,4-*dinitrophenyl*)-7-*nitrobenzotriazole* (X; Y = H) (95%) separated from dimethylformamide as red needles, m. p.

[13] A. S. Bailey and J. R. Case, *Tetrahedron*, 1958, **3**, 113.
[14] A. F. H. Lobry de Bruyn, *Rec. Trav. chim.*, 1917, **36**, 138.
[15] L. K. Dyall and K. H. Pausacker, *Austral. J. Chem.*, 1958, **11**, 491.
[16] A. J. Boulton, P. B. Ghosh, and A. R. Katritzky, *Tetrahedron Letters*, 1966, 2887.
[17] D. Dal Monte and E. Sandri, *Ann. Chim.* (*Italy*), 1963, **53**, 1697.
[18] S. Kamiya, *J. Pharm. Soc. Japan*, 1961, **81**, 1743.
[19] R. J. Gaughran, J. P. Picard, and J. V. R. Kaufman, *J. Amer. Chem. Soc.*, 1954, **76**, 2233.
[20] F. B. Mallory and S. P. Varimbi, *J. Org. Chem.*, 1965, **28**, 1656.
[21] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, 1912, **101**, 2452.
[22] A. Claus and R. Wallbaum, *J. prakt. Chem.*, 1897, II, **56**, 48; A. Claus and C. Beyson, *Annalen*, 1891, **266**, 224.
[23] H. A. J. Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4531; *Rec. Trav. chim.*, 1935, **54**, 97.

287° (decomp.) (Found: C, 44·7; H, 3·1; N, 26·5. $C_{14}H_{11}N_7O_6$ requires C, 44·9; H, 3·0; N, 26·3%). Product (*b*), 5-*chloro*-4-*dimethylamino*-2-(2,4-*dinitrophenyl*)-7-*nitrobenzotriazole* (X; Y = Cl) separated from dimethylformamide as red needles, m. p. 223—225° (Found: C, 41·3; H, 2·7. $C_{14}H_{10}ClN_7O_6$ requires C, 41·1; H, 2·5%).

2-*Bromo*-3-*nitrobenzoic Acid* (XI).—Prepared from 3-nitrophthalic acid,[24] m. p. 207—212° (lit.,[24] m. p. 215—218°) by the published [25] method, this had m. p. 185—187° (lit.,[25] 185—187°).

2-*Amino*-3-*nitrobenzoic Acid* (XII).—The previous compound (XI) (25 g.) was heated in a sealed tube with alcohol (50 ml.) and aqueous ammonia (*d* 0·88, 100 ml.) for 3½ hr. at 145—150°. Neutralisation of the ammonium salt of 2-amino-3-nitrobenzoic acid with glacial acetic acid gave, after washing and drying, material pure enough for the next stage (16·3 g., 88%), m. p. 203—204° (lit.,[26] 205°).

2-*Azido*-3-*nitrobenzoic Acid* (XIII).—To the above amine (XII) (15·2 g.) in glacial acetic acid (100 ml.) and 98% sulphuric acid (35 ml.) was added nitrosylsulphuric acid [from sodium nitrite (6 g.) and 98% sulphuric acid (15 ml.) at 0°] with stirring. After ½ hr. the solution was added to crushed ice (200 g.), and the resulting clear solution was treated, with vigorous shaking, with sodium azide (10 g.) in water (50 ml.). The precipitate was washed with water (100 ml.) and crystallised from ethanol, yielding the azide (13·0 g., 75%) as pale yellow needles, m. p. 202° (decomp.) (Found: C, 40·7; H, 2·0; N, 27·2. $C_7H_4N_4O_4$ requires C, 40·4; H, 1·9; N, 26·9%); $\nu_{max.}$ 2140, 2170 (N_3), 1700 (C=O), 1530, 1330 cm.$^{-1}$ (NO_2).

Refluxing the above azide in xylene, *o*-dichlorobenzene, or tetralin gave a brown solid which could not be purified sufficiently for analysis.

Methyl 2-*Azido*-3-*nitrobenzoate*.—The azido-acid (XIII) (3 g.) was refluxed in methanol (50 ml.) containing 98% sulphuric acid (0·5 ml.) for 3½ hr. The cooled solution was diluted with water (50 ml.) and extracted with ether. The ether extracts were washed with 10% sodium hydroxide (10 ml.) and dried (Na_2SO_4) and the solvent was distilled off. Crystallisation from methanol afforded the *methyl ester* (0·5 g., 16%) as needles, m. p. 82—83° (Found: C, 43·4; H, 2·8; N, 25·4. $C_8H_6N_4O_4$ requires C, 43·3; H, 2·7; N, 25·2%); $\nu_{max.}$ 2160, 2180 (N_3), 1730 (C=O), 1530, 1340 cm.$^{-1}$ (NO_2). Neutralisation of the alkaline washings gave unchanged acid (2·0 g.).

4-*Methoxycarbonylbenzofuroxan* (XIV).—The azido-ester (0·5 g.) was refluxed in xylene (25 ml.) for 3 hr. Reduction of the volume of the solvent to about 10 ml., followed by the addition of light petroleum (15 ml.), gave on cooling a white solid. Recrystallisation from ethyl acetate–hexane (1 : 1) (charcoal) gave the *methyl ester* (0·35 g., 80%) as small white needles, m. p. 145—146° (Found: C, 49·6; H, 3·0; N, 14·6. $C_8H_6N_2O_4$ requires C, 49·5; H, 3·1; N, 14·4%); $\nu_{max.}$ 1730 (C=O), 1620, 1590, 1550 cm.$^{-1}$ (benzofuroxan).

Benzofuroxan-4-*carboxyamide* (XV).—The above methyl ester (0·5 g.) was refluxed for 1 hr. with alcohol (20 ml.) and aqueous ammonia (*d* 0·88; 20 ml.). Dilution with water (50 ml.) gave a yellow solid, which on crystallisation from ethanol (charcoal) afforded the *amide* (0·25 g., 53%) as yellow prisms, m. p. 180·5—181° (Found: C, 47·1; H, 3·0; N, 23·7. $C_7H_5N_3O_3$ requires C, 46·9; H, 2·8; N, 23·5%); $\nu_{max.}$ 3380, 3160 (NH_2), 1660 (C=O), 1620, 1590, 1550 cm.$^{-1}$ (benzofuroxan).

Treatment of the amide (XV) with an aqueous alkaline solution of sodium hypobromite [prepared from bromine (0·1 ml.) and sodium hydroxide (0·5 g.) in water (10 ml.)] for 12 hr. at 20° gave no well defined product but a small amount of a dark brown solid which resisted attempts at purification.

2-*Amino*-5-*methyl*-3-*nitrobenzoic Acid* (XVI).—This was prepared from 5-methylisatin as described by Cassebaum,[27] and had m. p. 250—253° (lit.,[27] 252—253°).

2-*Azido*-5-*methyl*-3-*nitrobenzoic Acid*.—Compound (XVI) (17 g.) was diazotised by addition to a stirred mixture of sodium nitrite (7 g.) in 98% sulphuric acid (100 ml.) at 0°. After 30 minutes' stirring, orthophosphoric acid (50 ml.) was run in, the temperature being allowed to rise to 30°. After a further hour's stirring the solution was poured on crushed ice (300 g.) and the resulting clear solution treated with sodium azide (25 g.) in water (100 ml.). The yellow solid which separated was crystallised from ethyl acetate–light petroleum (2 : 1) (charcoal), giving yellow needles of the *azide* (18·1 g., 92%), m. p. 151—152° (decomp.) (Found: C, 43·4; H, 2·9; N, 25·4. $C_8H_6N_4O_4$ requires C, 43·2; H, 2·7; N, 25·2%); $\nu_{max.}$ 2180 (N_3), 1730 (C=O), 1540, 1340 cm.$^{-1}$ (NO_2).

6-*Methylbenzofuroxan*-4-*carboxylic Acid* (XVII).—The above azide (4 g.) was refluxed for 2 hr. in *o*-dichlorobenzene (50 ml.). To the black solution a small amount of alumina and charcoal were added, and refluxing was continued for a further 15 min. after which the solution was filtered, and the process twice repeated. Reduction of the volume to about 10 ml. and addition of light petroleum (15 ml.) gave a yellow precipitate. Recrystallisation (twice) from ethyl acetate–light petroleum (2 : 1) gave the *acid* (1·5 g., 37%) as a yellow powder, m. p. 207—210° (Found: C, 50·3; H, 3·5. $C_8H_6N_2O_4$ requires C, 49·5; H, 3·1%); $\nu_{max.}$ 1690 (C=O), 1620, 1590, 1550 cm.$^{-1}$ (benzofuroxan).

2,3-*Dinitroacetanilide* (XVIII).—Nitration of *m*-nitroacetanilide gave a mixture of isomers which were readily separated by Welsh's method.[8] The 2,3-dinitro-isomer had m. p. 188—189° (lit.,[8] m. p. 189·5—190°).

Hydrogenation of 2,3-*Dinitroacetanilide*.—The dinitro-compound (2·25 g., 0·01 mole) in absolute ethanol (250 ml.), containing Pd on $BaSO_4$ (10%, 2·0 g.), was hydrogenated at room temperature at a pressure of 45 lb. in.$^{-2}$. Removal of the catalyst by filtration and of the solvent by distillation (reduced pressure) gave an orange crystalline mass (1·9 g.), consisting of a mixture of red and yellow crystals. These were separated by chromatography on neutral alumina (Woelm). The yellow constituent crystallised from ethyl acetate–light petroleum (1 : 1) as pale yellow plates, m. p. 182—183° (Found: C, 49·0; H, 4·5; N, 21·7. $C_8H_9N_3O_3$ requires C, 49·2; H, 4·6; N, 21·5%); $\nu_{max.}$ 3440, 3340 (NH_2), 3310 (NH), 1670 (C=O), 1530, 1330 cm.$^{-1}$ (NO_2). The red component was not examined but was probably a diamine.

Action of Alcoholic Ammonia on 2,3-*Dinitroacetanilide*.—The dinitro-compound (10 g.), ethanol (100 ml.), and aqueous ammonia (*d* 0·88; 100 ml.) were heated in a sealed tube at 110° for 1½ hr. Removal of the solvents under reduced pressure yielded a dark yellow residue. Crystall-

[24] P. J. Culhane, *Org. Synth.*, Coll. Vol. I, 1941, 125.
[25] F. C. Whitmore, P. J. Culhane, and H. T. Neher, *Org. Synth.*, Coll. Vol. I, 1941, 56.
[26] A. F. Holleman and B. R. De Bruyn, *Rev. Trav. chim.*, 1901, **20**, 209.
[27] H. von Cassebaum, *J. prakt. Chem.*, 1964, **23**, 302.

isation from aqueous ethanol (1 : 2) (charcoal) gave a mixture of white and yellow needles which were separated by chromatography (silica gel–$CHCl_3$). The yellow component, m. p. 125°, was 2,3-dinitroaniline, the white, m. p. 189°, was starting material.

2-Acetamido-6-nitrophenylhydrazine (XIX).—The dinitro-compound (XVIII) (10 g.) in ethanol (250 ml.) was treated with stirring with hydrazine hydrate (10 ml.) in ethanol (25 ml.). The mixture was boiled for 10 min. under reflux, and the solvent was then evaporated off at reduced pressure to yield red crystals. Crystallisation from ethanol (charcoal) gave the *hydrazine* (8 g., 87%) as red needles, m. p. 166—168° (decomp.) (Found: C, 45·6; H, 5·0; N, 26·3. $C_8H_{10}N_4O_3$ requires C, 45·7; H, 4·8; N, 26·6%); $\nu_{max.}$ 3420, 3350 (NH_2), 3280 (NH), 1660 (C=O), 1515, 1315 cm.$^{-1}$ (NO_2).

4-Nitrobenzotriazole (XX).—Chlorine was bubbled through a solution of 2-acetamido-6-nitrophenylhydrazine (1 g.) in ethanol (250 ml.), cooled in ice, until the red colour was discharged (*ca.* 3—5 min.). Removal of the solvent under reduced pressure left a pale yellow residue which crystallised from aqueous alcohol (3 : 1) as pale yellow microprisms (80%), m. p. 235—236° (lit.,[28] 236—237°) (Found: C, 43·8; H, 2·7; N, 34·0. Calc. for $C_6H_4N_4O_2$: C, 43·9; H, 2·5; N, 34·2%).

3-Azido-2-nitroacetanilide (XXI).—2,3-Dinitroacetanilide (23·7 g.) was added with shaking to a solution of sodium azide (6·5 g.) in dimethyl sulphoxide (150 ml.) at *ca.* 90°. After standing for a further 10 min. at this temperature the dark red solution was diluted with water (500 ml.), and the dark yellow solid which separated was crystallised from aqueous ethanol (1 : 10) (charcoal) to give the *azide* (20 g., 87%) as yellow needles, m. p. 113—114° (Found: C, 43·5; H, 3·1; N, 31·6. $C_8H_7N_5O_3$ requires C, 43·4; H, 3·2; N, 31·7%); $\nu_{max.}$ 3350 (NH), 2140 (N_3), 1690 (C=O), 1530, 1330 cm.$^{-1}$ (NO_2).

4-Acetamidobenzofuroxan (XXII).—The above azide (5 g.) was refluxed for 1 hr. in glacial acetic acid (30 ml.), and the resulting dark brown solution boiled twice with charcoal. Dilution of the now yellow solution with water (50 ml.) containing a few drops of sodium hydroxide solution produced a pale yellow solid. Crystallisation from aqueous ethanol (1 : 1), then twice from ethyl acetate–hexane (1 : 2) gave the *acetamido-compound* (0·75 g., 18%) as a yellow powder, m. p. 162—163° (Found: C, 49·6; H, 3·8; N, 21·9. $C_8H_7N_3O_3$ requires C, 49·7; H, 3·6; N, 21·7%); $\nu_{max.}$ 3360 (NH), 1685 (C=O), 1625, 1590, 1560 cm.$^{-1}$ (benzofuroxan).

Attempted Hydrolysis of 4-Acetamidobenzofuroxan.—The acetamido-compound (XXII) (0·1 g.) in ethanol (25 ml.)–2N-hydrochloric acid (25 ml.) was heated to 100° for 30 min. Evaporation of the solvent under vacuum yielded a brown solid, unidentified owing to shortage of material.

3-Chloro-1-methoxycarbonamido-2,6-dinitrobenzene.— The 3-chloro-*N*-methoxycarbonylaniline [29] was nitrated by a modification of De Monchy's [29] procedure. The chloro-urethane (60 g.) was added to stirred nitric acid (*d* 1·5; 300 ml.) cooled in ice, at such a rate that the temperature did not exceed 15°. When addition was complete (*ca.* 1 hr.) stirring and temperature were maintained for 30 min. and then the mixture was poured on ice (1000 g.). The pale yellow precipitate (85 g.) was washed free from acid and air-dried. Boiling with chloroform (200 ml.) and rapid cooling to −10° gave crystals mainly of the 2,6-dinitro-isomer. A second crystallisation from chloroform gave pure material (17·5 g.), m. p. 189—190° (lit.,[29] 188°); $\nu_{max.}$ 3350 (NH), 1740 (C=O), 1510, 1525, 1340 (NO_2), 1390 cm.$^{-1}$ (CH_3).

3-Chloro-2,6-dinitroaniline (XXIV).—The dinitro-urethane prepared as above (10 g.) was heated for 1 hr. at 135° with 98% sulphuric acid (50 ml.). Addition to crushed ice (200 g.) gave, after crystallisation from ethanol (charcoal), 3-chloro-2,6-dinitroaniline as yellow needles (7 g., 89%), m. p. 108—110° (lit.,[29] 112°); $\nu_{max.}$ 3460, 3350 (NH_2), 1560, 1540, 1315 cm.$^{-1}$ (NO_2).

Coupling of 3-Chloro-2,6-dinitrobenzenediazonium Sulphate with NN-Dimethylaniline, and with Anisole.—The dinitroaniline (XXIV) (7 g.) was diazotised by dissolving in glacial acetic acid (50 ml.) and adding to ice-cold nitrosylsulphuric acid, prepared from sodium nitrite (2·5 g.) and 98% sulphuric acid (50 ml.). After 30 minutes' stirring the mixture was poured into ice–water (300 ml.) and urea was added to destroy excess of nitrous acid. The addition of this solution to *NN*-dimethylaniline (3·4 g.) in ethanol (50 ml.) instantly produced a violet colour. Ice (200 g.) and sodium chloride (20 g.) were added, and vigorous shaking caused precipitation of a fine black solid. Two crystallisations from ethanol afforded the *azo-compound* (XXIV; Y = NMe_2) (6·5 g., 60%) as small leaflets, black by reflected light, purple by transmitted, m. p. 201—204° (Found: C, 48·4; H, 4·2; N, 19·6. $C_{14}H_{12}ClN_5O_4$ requires C, 48·1; H, 3·4; N, 20·0%). Anisole (1·5 g.) in ethanol (5 ml.) was added to the diazotised amino-compound (XXIII) (3 g.). A red colour was produced, and an orange solid separated on dilution with water (50 ml.) after 15 minutes' stirring. Crystallisation from acetone gave the *azo-compound* (XXIV; Y = OMe) (1·2 g., 25%) as orange needles, m. p. 160—160·5° (Found: C, 46·4; H, 3·3; N, 16·5. $C_{13}H_9ClN_4O_5$ requires C, 46·5; H, 2·7; N, 16·7%).

3-Azido-4'-methoxy-2,6-dinitroazobenzene (XXV).—The above compound (XXIV; Y = OCH_3) (0·7 g.) was heated in dimethyl sulphoxide (15 ml.) containing sodium azide (0·3 g.). After 5 min. at 100° the temperature was raised to 120° for 1 min. Dilution with water (35 ml.) precipitated an orange solid. The *azo-azide* (XXV) (0·64 g., 90%) crystallised from acetone (charcoal) as orange needles, m. p. 143—145° (decomp.) (Found: C, 45·8; H, 2·7; N, 28·8. $C_{13}H_9N_7O_5$ requires C, 45·5; H, 2·6; N, 28·6%); $\nu_{max.}$ 2130 (N_3), 1550, 1510, 1340, 1310 cm.$^{-1}$ (NO_2).

2-p-Methoxyphenyl-4,7-Dinitrobenzotriazole (XXVIII).—The above azide (0·5 g.) was heated in diglyme (25 ml.) at 155—160° for 20 min. Dilution with water (50 ml.) afforded a brown precipitate which was redissolved in acetone and chromatographed on alumina. The *benzotriazole* (XXVIII) (0·1 g., 23%) crystallised from acetone as needles, m. p. 271—272° (Found: N, 22·2. $C_{13}H_9N_5O_5$ requires N, 22·2%); $\nu_{max.}$ 1520, 1340 cm.$^{-1}$ (NO_2).

3-Methoxycarbonamido-2,4-dinitrophenyl Azide (XXIX).—1-Chloro-3-methoxycarbonamido-2,4-dinitrobenzene (1 g.) was heated to 115° in dimethylformamide (25 ml.) containing sodium azide (0·5 g.) and water (2 ml.) for 15 min. Addition of water (25 ml.) gave the *azide* (XXIX) (0·7 g., 60%) as yellow needles, m. p. 133—135° (decomp.) from ethanol (Found: C, 34·5; H, 3·0; N, 29·6. $C_8H_6N_6O_6$ requires C, 34·1; H, 2·2; N, 29·8%); $\nu_{max.}$ 3365 (NH), 2165 (N_3), 1745 (C=O), 1540, 1510, 1340, 1305 cm.$^{-1}$ (NO_2).

4-Methoxycarbonamido-5-nitrobenzofuroxan (XXX).—The above compound (XXIX) (0·5 g.) was refluxed in xylene

[28] N. Miller and E. Wagner, *J. Amer. Chem. Soc.*, 1954, **76**, 1847.
[29] M. M. De Monchy, *Rec. Trav. chim.*, 1934, **53**, 141.

(25 ml.) for 15 min. Removal of the solvent under reduced pressure and crystallisation of the residue from ethyl acetate gave the *benzofuroxan* (XXX) (0·25 g., 55%) as yellow prisms, m. p. 195—197° (Found: C, 37·8; H, 2·8; N, 22·1. $C_8H_6N_4O_6$ requires C, 37·8; H, 2·4; N, 22·0%); $\nu_{max.}$ 3315 (NH), 1740 (C=O), 1640, 1590 (benzofuroxan), 1520, 1330 cm.$^{-1}$ (NO_2).

Attempted Hydrolysis of Urethane (XXX).—The urethane was recovered after treatment with: (*a*) hydrogen chloride in ethanol for 15 hr. at 20°, (*b*) concentrated sulphuric acid for ½ hr. at 100°.

3-*Azido*-2,6-*dinitroaniline* (XXXI).— 3-Chloro-2,6-dinitroaniline (XXIII) (3 g.) in dimethylformamide (25 ml.) was treated with sodium azide (1 g.) in water (10 ml.) and heated to 100° for 5 min. Dilution with water (50 ml.) gave a brown precipitate which after two recrystallisations from aqueous acetone (1 : 1) (charcoal) gave 3-*azido*-2,6-*dinitroaniline* (XXXI) (1·5 g., 45%) as pale yellow needles, (decomp. *ca.* 110°) (Found: C, 32·3; H, 2·2; N, 37·7. $C_6H_4N_6O_4$ requires C, 32·3; H, 1·8; N, 37·5%); $\nu_{max.}$ 3460, 3360 (NH_2), 2160 (N_3), 1570, 1535, 1330, 1305 cm.$^{-1}$ (NO_2).

4-*Amino*-5-*nitrobenzofuroxan* (XXXII).—3-Azido-2,6-dinitroaniline (XXXI) (1·5 g.) was refluxed for 20 min. in toluene (25 ml.). Addition of light petroleum (10 ml.), followed by cooling, precipitated a maroon solid which crystallised from ethyl acetate (charcoal) to give the *benzofuroxan* (XXXII) (0·85 g., 65%) as orange needles, m. p. 250° (decomp.) (Found: C, 37·0; H, 4·1; N, 28·1. $C_6H_4N_4O_4$ requires C, 36·8; H, 2·0; N, 28·5%); $\nu_{max.}$ 3360, 3200 cm.$^{-1}$ (NH_2).

Nitrosation of 5-NN-*dimethylaminobenzofuroxan*.—5-*NN*-Dimethylaminobenzofuroxan (1·79 g., 0·01 mole) was dissolved in ethanol (50 ml.) by warming, rapidly cooled to 0°, and treated with nitrous acid [sodium nitrite (0·7 g.) and hydrochloric acid (10%, 15 ml.)]. The orange solid which separated had m. p. 210—212°, and showed no sign of change up to this temperature. Crystallisation (twice) from acetone gave 4-NN-*dimethylamino*-7-*nitrobenzofurazan* (XXXIV) (1·5 g., 75%) as orange-red needles, m. p. 215—216° (Found: C, 46·1; H, 4·0; N, 25·9. $C_8H_8N_4O_3$ requires C, 46·2; H, 3·9; N, 26·0%); $\nu_{max.}$ 1620 (benzofurazan), 1570, 1330 cm.$^{-1}$ (NO_2).

3-NN-*Dimethylamino*-2-*nitroacetanilide* (XXXV).—2,3-Dinitroacetanilide (22·5 g.) and dimethylamine (100 ml., 40% aqueous solution) were refluxed for 1 hr. in ethanol (100 ml.). Dilution with hot water (500 ml.) gave a deep red solution from which orange crystals separated on cooling. Recrystallisation from aqueous ethanol (4 : 1) gave the *acetanilide* (XXXV) (15 g., 67%) as pale yellow needles, m. p. 127° (Found: C, 53·8; H, 5·9; N, 18·8. $C_{10}H_{13}N_3O_3$ requires C, 53·8; H, 5·8; N, 18·8%); $\nu_{max.}$ 3200 (NH), 1660, (C=O), 1570, 1340 cm.$^{-1}$ (NO_2).

3-*Amino*-NN-*dimethyl*-2-*nitroaniline* (XXXVI).—The above acetanilide (XXXV) (4·46 g.) was hydrolysed to the free base by refluxing in ethanol (50 ml.) and 50% aqueous sodium hydroxide (25 ml.) for 1½ hr. Dilution with water (100 ml.) followed by extraction with ether (3 × 50 ml.) and removal of the solvent by distillation left the *diamine* as a red oil, which was redissolved in ethyl acetate–light petroleum (1 : 1) and kept for 14 days at 0°. The diamine separated as dark red crystalline clusters. Recrystallisation (3 times) from hexane gave the product (2·5 g., 69%) as crimson prisms, m. p. 54—55° (Found: C, 52·8; H, 6·5; N, 23·0. $C_8H_{11}N_3O_2$ requires C, 53·0; H, 6·1; N, 23·2%); $\nu_{max.}$ 3500, 3380 cm.$^{-1}$ (NH_2).

Attempted Diazotisation of 3-*Amino*-NN-*dimethyl*-2-*nitroaniline*.—Attempts to diazotise the diamine in (*a*) conc. hydrochloric acid, (*b*) by the general procedure of Hodgson and Walker,[30] (*c*) by the method of Schoutissen [23] (using nitrosylsulphuric and phosphoric acids) gave in each case a yellow-green (by reflected light) solid which was crystallised (twice) from ethyl acetate to give the *nitroso-compound* (XXXVII) (80%) as blue-black needles, m. p. 149·5—150° (Found: C, 45·9; H, 5·1; N, 26·4. $C_8H_{10}N_4O_3$ requires C, 45·7; H, 4·8; N, 26·6%).

Attempted Oxidation of 3-*Amino*-NN-*dimethyl*-2-*nitroaniline with Phenyliodosodiacetate*.—Oxidation of the diamine in benzene with phenyliodosodiacetate according to the general procedure of Dyall and Pausacker [15] gave a dark brown solid which was chromatographed on alumina. The only product identified from this mixture (apart from starting material) was 2,2′-*dinitro*-3,3′-*bisdimethylamino*-*azobenzene* (XXXVIII), which crystallised from benzene as red prisms, m. p. 218—219° (Found: C, 53·9; H, 5·0. $C_{16}H_{16}N_6O_4$ requires C, 53·9; H, 4·4%).

2,6-*Dichloronitrosobenzene* (XXXIX).—2,6-Dichloroaniline (32·3 g.) was oxidised with peracetic acid–glacial acetic acid as described by Holmes and Bayer.[11] The nitroso-compound crystallised as plates (30 g., 86%), m. p. 170—171° (lit.,[11] 175·5—176°), from glacial acetic acid.

2,6-*Dichloronitrobenzene* (XL).—The nitroso-compound (XXXIX) (10 g.) was boiled for 20 min. with 50% nitric acid (100 ml.), with vigorous stirring. Dilution with ice–water (150 ml.) gave after 1 hour's standing an off-white solid, which crystallised from aqueous ethanol (1 : 2) (charcoal) as white needles (9 g., 82·5%), m. p. 70° (lit.,[12] 70°) (Found: C, 37·8; H, 2·2; N, 7·4. Calc. for $C_6H_3NO_2Cl_2$: C, 37·5; H, 1·6; N, 7·3%); $\nu_{max.}$ 1550, 1380 cm.$^{-1}$ (NO_2).

2,4-*Dichloro*-1,3-*dinitrobenzene* (XLI).—2,6-Dichloronitrosobenzene (XXXIX) (1·5 g.) was added with shaking to nitric acid (*d* 1·5; 10 ml.) at 20°. When addition was complete the temperature was slowly raised to 100° on a steam-bath. When the evolution of oxides of nitrogen had ceased (*ca.* 20 min.) the solution was poured on crushed ice (100 g.) and kept for 30 min. at 0°. The solid which separated crystallised from ethanol as needles (2·0 g., 98%), m. p. 67·5—68° (lit.,[31] 68·0°) (Found: C, 30·1; H, 1·6; N, 11·6. Calc. for $C_6H_2Cl_2N_2O_4$: C, 30·2; H, 0·9; N, 11·8%); $\nu_{max.}$ 1550, 1560, 1350, 1360 cm.$^{-1}$ (NO_2); n.m.r. (acetone solvent): $\tau_A = 1{\cdot}93$, $\tau_B = 1{\cdot}6$, $J_{AB} = 8{\cdot}8$ c./sec.

1,3-*Diazido*-2,4-*dinitrobenzene* (XLII).—2,4-Dichloro-1,3-dinitrobenzene (XLI) (1·9 g.) was heated with sodium azide (1·0 g.) in dimethyl sulphoxide (50 ml.) for 3 hr. at 70°. Dilution with water (100 ml.) gave a yellow oil which solidified on standing. Recrystallisation (charcoal) from methanol gave the *diazido-compound* (XLII) (1·0 g., 50%) as pale yellow prisms, m. p. 95·5—96° (decomp.) (Found: N, 44·6. $C_6H_2N_8O_4$ requires N, 44·8%); $\nu_{max.}$ 2150 (N_3), 1540, 1520, 1335 cm.$^{-1}$ (NO_2).

Furoxanobenzofuroxan (XLIII).—The above diazide (1·0 g.) was refluxed for 1 hr. in xylene (50 ml.). Removal of the solvent under reduced pressure gave a yellow oil which semi-solidified on standing at 0° for several hours. Separation of the crystals by filtration gave the furoxanobenzofuroxan (0·2 g., 26%), m. p. 90° (lit.,[1] 93°), identical (mixed m. p.) with a sample made by a different route (see ref. 1).

1,3-*Diamino*-2,4-*dinitrobenzene*.—The dinitro-compound (XLI) (5·5 g.) in ethanol (100 ml.) saturated with ammonia,

[30] H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 1933, 1620.
[31] A. T. Dann, *J. Chem. Soc.*, 1929, 2461.

was heated in a sealed tube for 2 hr. at 120°. Removal of the solvent by distillation yielded a yellow residue of the diamine which crystallised from acetone as needles (90%), m. p. 260° (lit.,[32] 260°).

Oxidation of 6-Chloro-2-nitroaniline with Phenyliodosodiacetate.—The nitroaniline [14] (3 g.) was oxidised with phenyliodosodiacetate in benzene as described by Dyall and Pausacker.[15] Chromatography of the material obtained after removal of the solvent gave the desired 4-chlorobenzofuroxan (0·2 g., 7%), m. p. 77—78° (lit.,[15] 77—77·5°) and starting material (2·0 g.).

4-Chlorobenzofurazan from 2,6-Dichloronitrosobenzene.—2,6-Dichloronitrosobenzene (XXXIX) (14·0 g.) in dimethyl sulphoxide (150 ml.) containing sodium azide (7·0 g.) was heated with shaking to 100°. Effervescence began at about this temperature and cooling was necessary to moderate the reaction. When effervescence had ceased the temperature was raised to 120° for 1 min. Dilution with water (200 ml.) gave a precipitate which crystallised from aqueous ethanol (5 : 1) as needles. Sublimation (100°/50 mm. Hg) gave 4-chlorobenzofurazan (XLIV) (11·5 g., 93%), m. p. 83—84° (lit.,[17] 83—84°) (Found: C, 47·0; H, 2·9; N, 18·0. Calc. for $C_6H_3ClN_2O$: C, 46·8; H, 2·0; N, 18·1%).

4-Chloro-7-nitrobenzofurazan (XLV).—4-Chlorobenzofurazan (3·86 g., 0·025 mole) was dissolved in 98% sulphuric acid (30 ml.) and sodium nitrate (2·5 g.) in 50% sulphuric acid (10 ml.) was added dropwise with stirring, to maintain a temperature of 60°. When addition was complete the temperature was raised to 85° for a further 30 min. The orange solid obtained after pouring on crushed ice (250 g.) crystallised from aqueous ethanol (1 : 1) to give pale yellow needles of the *nitro-compound* (XLV) (3·5 g., 70%) which after sublimation had m. p. 96·5—97° (Found: C, 36·3; H, 2·0; N, 20·9. $C_6H_2ClN_3O_3$ requires C, 36·2; H, 1·0; N, 21·2%); $\nu_{max.}$ 1530, 1340 cm.$^{-1}$ (NO_2).

[32] J. J. Blanksma, *Rec. Trav. chim.*, 1908, **27**, 52.
[33] P. Drost, *Annalen*, 1899, **307**, 49.

4-Nitrobenzofurazan.—Prepared according to the literature method,[33] it had m. p. 97—98° (lit.,[33] 98°).

5-Nitrobenzofurazan.—Prepared by the literature method [34] it had m. p. 63—64° (lit.,[34] 64·6—65·4°).

4-Azido-7-nitrobenzofurazan (XLVI).—4-Chloro-7-nitrobenzofurazan (0·5 g.) in dimethyl sulphoxide (10 ml.) containing sodium azide (0·3 g.) was heated on a steam-bath for 5 min. at 100°. Dilution with water (40 ml.) and crystallisation of the precipitate from aqueous ethanol (1 : 1) (charcoal) gave yellow needles of *4-azido-7-nitrobenzofurazan* (0·4 g., 77%), m. p. 84—85° (decomp.) (Found: C, 35·0; H, 1·5; N, 41·0. $C_6H_2N_6O_3$ requires C, 35·0; H, 1·0; N, 40·7%); $\nu_{max.}$ 2160 (N_3) 1640 (benzofurazan), 1530, 1330 cm.$^{-1}$ (NO_2).

4-Amino-7-nitrobenzofurazan (XLVII).—The above azide (1 g.) was refluxed for ½ hr. in toluene (50 ml.). Addition of light petroleum (10 ml.) to the hot solution gave on cooling a brown solid. Sublimation (120°/0·5 mm. Hg) gave *4-amino-7-nitrobenzofurazan* (0·2 g., 43%) as orange microprisms, m. p. 237° (decomp.) (Found: C, 40·5; H, 2·4; N, 31·2. $C_6H_4N_4O_3$ requires C, 40·1; H, 2·2; N, 31·1%); $\nu_{max.}$ 3450, 3350, (NH_2), 1660 (NH_2), 1630 (benzofurazan), 1570, 1320 cm.$^{-1}$ (NO_2). The mother-liquors yielded unchanged azide on evaporation.

4-NN-Dimethylamino-7-nitrobenzofurazan (XXXIV).—4-Chloro-7-nitrobenzofurazan (XLV) (0·2 g.) in ethanol (10 ml.) was treated with 40% aqueous dimethylamine (5 ml.). The orange-red precipitate that immediately formed was crystallised from acetone as orange-red needles (0·2 g., 96%), m. p. 215—216°, identical (m. p., mixed m. p., u.v., i.r.) with the product from the nitrosation of 5-*NN*-dimethylaminobenzofuroxan.

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[34] F. B. Mallory and S. P. Varimbi, *J. Org. Chem.*, 1963, **28**, 1661.