Proximity Effects in Diaryl Derivatives. Part III.[1,2] The Formation of Phenazines and Dibenzothiadiazepines by Reduction of 2,2′-Dinitrodiaryl Sulphides, Sulphoxides, and Sulphones

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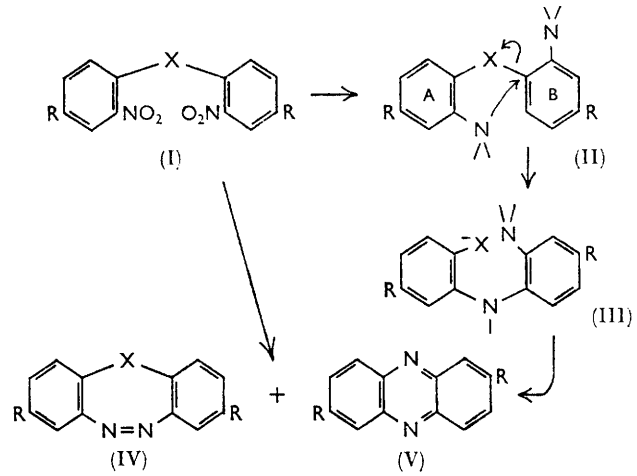
Reduction of 2,2′-dinitrodiaryl sulphides, sulphoxides, and sulphones with zinc and sodium hydroxide in aqueous dioxan afforded phenazines (V), dibenzo[*b*,*f*][1,4,5]thiadiazepines (IV; X = S or SO_2), dibenzo[*b*,*f*][1,4,5]-thiadiazepine *N*-oxides, and other products. Phenazines arise by intramolecular nucleophilic rearrangement of a partially reduced species, followed by loss of the sulphur-containing group. Studies of the reduction of 2-amino-2′-nitrodiphenyl sulphone and of dibenzothiadiazepine derivatives show that these compounds are not intermediates in the formation of phenazines.

In previous Parts[1,2] we showed that reduction of 2,2′-dinitrodiaryl ethers (I; X = O) with lithium aluminium hydride or with zinc and sodium hydroxide gave dibenz[*b*,*f*][1,4,5]oxadiazepines (IV; X = O) and phenazines (V) as principal products. Phenazines are formed presumably by intramolecular nucleophilic (Smiles) rearrangement of a partly reduced species, followed by loss of the oxygen substituent, as represented in the general Scheme 1 (X = O).



Scheme 1

Suitable *ortho*-substituted diaryl sulphones, sulphoxides, and sulphides also undergo the Smiles rearrangement,[3] and we have extended our enquiry to the corresponding 2,2′-dinitro-derivatives, in the expectation that reduction under alkaline conditions would also give phenazines. Phenazines have not been isolated from such reactions hitherto. For instance, reduction of 4,4′-dichloro-2,2′-dinitrodiphenyl sulphone (I; X = SO_2, R = Cl) with hydrazine and Raney nickel furnished the dibenzo[*b*,*f*][1,4,5]thiadiazepine trioxide (XVI; R = Cl)[4] and reaction of 2,2′-dinitrodiphenyl sulphide with lithium aluminium hydride gave dibenzo[*b*,*f*][1,4,5]thiadiazepine (IV; X = S, R = H).[5]

Our reductions were accomplished with zinc dust (10 mols.) and sodium hydroxide (30 mols.) in aqueous dioxan at 20° and at reflux. The non-acidic products were separated by chromatography, and in some cases the acidic fractions were also examined. The results are summarised in Table 1. The three *o*,*o*′-dinitrodiaryl sulphones (I; X = SO_2, R = H, Cl, and Me) afforded the respective phenazines (V; R = H, Cl, and Me) in yields of 10—25% and the one sulphoxide (I; X = SO, R = Cl) that was studied behaved similarly. Reduction of 2,2′-dinitrodiphenyl sulphide gave only a trace of phenazine, but 2,7-dichlorophenazine (V; R = Cl) was obtained in 6% yield from the diaryl sulphide (I; X = S, R = Cl). Since the reduction products were difficult to separate quantitatively, the yields given in Table 1 are only approximate. Nevertheless, certain general trends can be observed, and it is clear, for example, that phenazines are formed more readily from sulphones and sulphoxides than from sulphides. This supports the suggestion that an intramolecular nucleophilic rearrangement, (II) ⟶ (III), is involved in the formation of phenazines, because the same order of reactivity is observed in the Smiles rearrangement.[3] Further, within both the sulphone and sulphide series, the presence of chloro-substituents promotes the production of phenazines, presumably by providing extra activation at the site of nucleophilic attack. Again this provides a parallel with the Smiles rearrangement. Galbraith and Smiles[6] thus showed that a 4′-chloro-substituent [in ring B, cf. (II)] increased the rate of rearrangement of 2-hydroxy-2′-nitrodiphenyl sulphones. The effect of a 4-chloro-substituent [ring A, cf. (II)] is more difficult to predict, but there is some evidence that electron-attracting groups in ring A promote the rearrangement of amino-derivatives, for example, 2-acetamido-2′-nitrodiphenyl sulphides.[7]

In one reduction of 2,2′-dinitrodiphenyl sulphone, the acidic fraction was treated with methyl iodide, and two products were separated by chromatography. One compound was the methyl sulphone (VIII; R = NO_2), which has been prepared previously[7] by similar methylation of the sulphinate (VII; R = NO_2) derived by rearrangement of 2-amino-2′-nitrodiphenyl sulphone (VI). The other product of methylation, $C_{13}H_{14}N_2O_2S$, $\nu_{max.}$

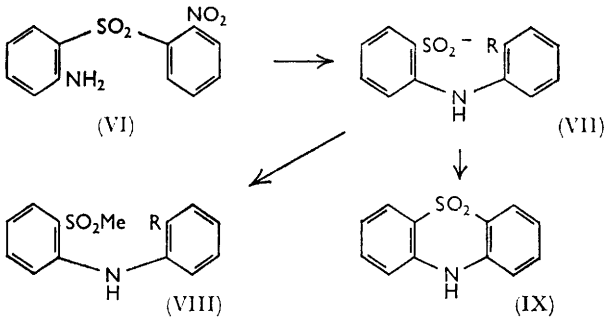
[1] Part I, M. F. Grundon, B. T. Johnston, and A. S. Wasfi, *J. Chem. Soc.*, 1963, 1436.
[2] Part II, M. F. Grundon and A. S. Wasfi, *J. Chem. Soc.*, 1963, 1982.
[3] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, pp. 362—371.
[4] H. H. Szmant and R. Infante, *J. Org. Chem.*, 1961, **26**, 4173.
[5] N. L. Allinger and G. A. Youngdale, *J. Amer. Chem. Soc.*, 1962, **84**, 1020.
[6] F. Galbraith and S. Smiles, *J. Chem. Soc.*, 1935, 1234.
[7] W. J. Evans and S. Smiles, *J. Chem. Soc.*, 1935, 181.

TABLE 1

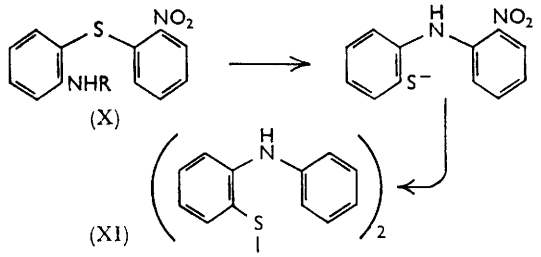
Reduction of 2,2′-dinitrodiaryl sulphones and sulphides with zinc and sodium hydroxide in aqueous dioxan

Reactant	Temp.	Time (hr.)	Yield (%) of phenazine (V)	Yield (%) of diazepines (IV)	Yield (%) of diazepine 5-oxides (XVI) or (XIX)
(I; X = SO_2, R = H)	20°	2	18	6	0
(I; X = SO_2, R = H)	100	0·5	14	0	<1
(I; X = SO_2, R = H)	100	13	16	2	0
(I; X = SO_2, R = Cl)	20	2	25	0	0
(I; X = SO_2, R = Cl)	100	0·5	12	0	0
(I; X = SO_2, R = Me)	100	1·5	11	9	0
(I; X = SO_2, R = Me)	20	2	10	0	<1
(I; X = S, R = H)	20	2	0	6—13	12
(I; X = S, R = H)	100	3	<1	0	0
(I; X = S, R = Cl)	20	7	6	0	0
(I; X = S, R = Cl)	100	2	0	0	0

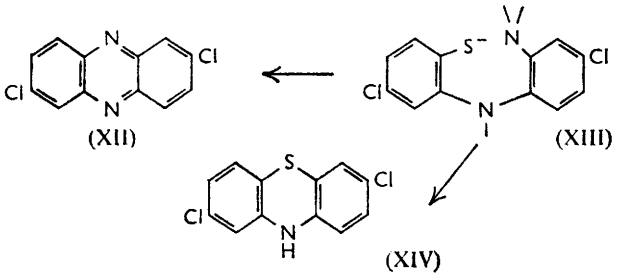
3400 and 3350 cm.$^{-1}$ (NH_2), is probably the corresponding primary aromatic amine (VIII; R = NH_2). The reduction products present in the alkaline solution before methylation are presumably the sulphinates (VII; R = NO_2 and NH_2). A minor product of the reduction of 2,2′-dinitrodiphenyl sulphide with zinc and alkali proved to be the disulphide (XI). Clearly this is derived by rearrangement of a nitrodiaryl sulphide (X), followed by oxidation during work-up of the resultant thio-



phenoxide. The three by-products are not necessarily intermediates in the formation of phenazines from 2,2′-dinitrodiaryl sulphones or sulphides, but their identification indicates that Smiles rearrangements do occur under the conditions employed.



From the reduction of 4,4′-dichloro-2,2′-dinitrodiphenyl sulphide at 20° only 2,7-dichlorophenazine (XII) was obtained, whereas at 100° 2,7-dichlorophenothiazine (XIV) was isolated. Both products must arise by cyclisation of a rearranged intermediate (XIII), and it appears that the displacement of the nitrogen substituent becomes important only at an elevated temperature. In accord with this consideration, Farrington [8] isolated the phenothiazine (XIV) from reaction of 4,4′-dichloro-2,2′-dinitrodiphenyl sulphide with hydrazine in boiling aqueous alkali.



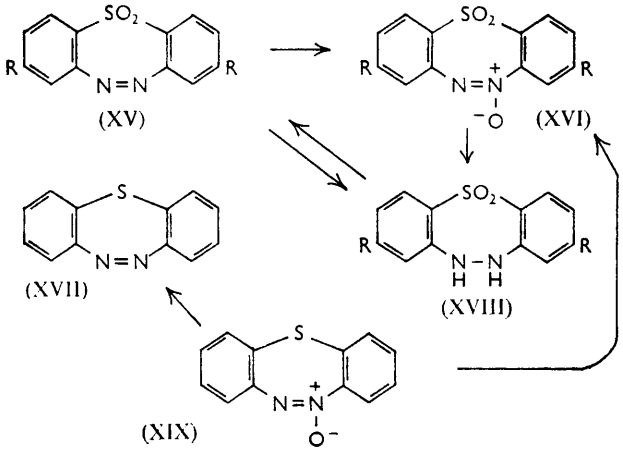
The next objective was to identify species (II) capable of rearrangement under the conditions of our reactions. 2-Amino-2′-nitro-derivatives were possible candidates, and one such compound, 2-amino-2′-nitrodiphenyl sulphide (X; R = H) was isolated from the reduction of 2,2′-dinitrodiphenyl sulphide with zinc and alkali. However, in the sulphide series, the amino-nitro-derivatives are unlikely to be intermediates in the formation of phenazines, since they are reported to resist rearrangement with aqueous alkali even at 100°.[7] Furthermore, we find that 2-amino-2′-nitrodiphenyl sulphone (VI) is unaffected by alkali at 20°; after the addition of zinc, 2,2′-diaminodiphenyl sulphone and other products are formed, but no phenazine. With zinc and sodium hydroxide in refluxing aqueous dioxan, the sulphone gave phenothiazine 5,5-dioxide (IX) (61%), and this product was obtained almost quantitatively in the absence of zinc. The phenothiazine derivative could arise either by direct displacement of the nitro-group, or by replacement, (VII; R = NO_2) ⟶ (IX), after rearrangement. We prefer the latter alternative, since Evans and Smiles [7] observed rearrangement of the sulphone (VI) to the sulphinate (VII; R = NO_2) under less vigorous conditions. Again, phenazine was not formed in these reactions, and we conclude that 2-amino-2′-nitrodiaryl sulphones are not intermediates in the conversion of the 2,2′-dinitrosulphones into phenazines. An investigation of other reduction products (II) is described in the following Paper.

Dibenzo[*b*,*f*][1,4,5]thiadiazepine derivatives as well as phenazines were isolated from reduction of 2,2′-dinitro-

[8] K. J. Farrington, *Austral. J. Chem.*, 1959, **12**, 196.

diaryl sulphones and sulphides (I) (Table 1). The structures of the dibenzothiadiazepine 11,11-dioxides (XV; R = H and Me) were indicated by their characteristic ultraviolet absorption and by oxidation with peroxyacetic acid to the trioxides (XVI; R = H and Me). Reduction with tin and hydrochloric acid afforded the colourless dihydro-derivatives (XVIII; R = H and Me), which were also prepared by a similar reduction of the trioxides (XVI; R = H and Me). The dihydro-derivatives were oxidised to the azo-compounds (XV; R = H and Me) by sodium hypobromite, but in contrast to 5,6-dihydrodibenzo[*b*,*f*][1,4,5]triazepine,[1] they were stable in air. Dibenzothiadiazepine 11,11-dioxides and 5,11,11-trioxides have been prepared previously by other methods.[4,9] Szmant and Chow[10] reported the isolation of two dioxides (XV; R = H), m. p. 174 and 131—132°, and two trioxides (XVI; R = H), m. p. 251—252 and 250—251°, and assigned boat and chair conformations to the compounds. This seems inherently unlikely, and Allinger and Youngdale[11] showed that the material, m. p. 131—132°, was a mixture of the dioxide, m. p. 174°, and 2,2′-diaminodiphenyl sulphone. We have obtained only one dioxide, m. p. 172—173°, and only one trioxide, m. p. 255—257°.

Reduction of 2,2′-dinitrodiphenyl sulphide with zinc and alkali gave dibenzo[*b*,*f*][1,4,5]thiadiazepine (XVII), $\lambda_{max.}$ 426 mμ, which has been prepared previously[5] by a similar method, and it was accompanied by a less coloured compound, $C_{12}H_8N_2OS$, which showed no absorption maximum above 318 mμ. This is the thiadiazepine 5-oxide (XIX), since it was reduced with zinc and sodium hydroxide or with alkaline sodium arsenite to the azo-derivative (XVII), and was oxidised by peroxyacetic acid to the trioxide (XVI; R = H).



Dichlorothiadiazepines were not isolated from the reduction of the 2,2′-dinitro derivative (I; X = SO_2, R = Cl), and in other cases less thiadiazepines were obtained from reactions conducted at elevated temperatures (Table 1). This suggested that thiadiazepines might be a source of phenazines, and to test this hypothesis we decided to study the reduction of certain thiadiazepine dioxides and trioxides. For this purpose a more efficient synthesis of the thiadiazepines was required. Oxidation of 2,2′-diaminodiaryl sulphones with phenyl iodosodiacetate, a procedure introduced by Szmant and his collaborators,[4,9] proved to be satisfactory, and afforded the dioxides (XV; R = H, Cl, and Me) in yields of 25—55%. The dichloro-derivative was characterised as described above for other thiadiazepine dioxides, and it was converted into the trioxide (XVI; R = Cl) and into the dihydro-derivative (XVIII; R = Cl).

The dioxides (XV; R = H and Cl) and the trioxides (XVI; R = H and Cl) were treated with zinc and sodium hydroxide in aqueous dioxan at 20° and at reflux, and the products were chromatographed. The dioxides were recovered in high yield, but the trioxides were attacked extensively to give the azo-derivatives (XV), 2,2′-diaminodiaryl sulphones, and other products (Table 2). Dihydro-compounds (XVIII) were probably formed initially, and then converted into the azo-derivatives (XV) during work-up; this oxidation is apparently base-catalysed, since the dihydro-derivative (XVIII; R = H), although stable in organic solvents, gave dibenzo[*b*,*f*][1,4,5]thiadiazepine 11,11-dioxide quantitatively when chromatographed on alumina. Phenazines were not detected in any of these reactions, showing that thiadiazepines (XV) and (XVI) cannot be precursors of the phenazines formed in the reduction of 2,2′-dinitrodiaryl sulphones.

EXPERIMENTAL

Light petroleum had b. p. 30—40°. Dioxan was passed through an alumina column and then distilled. Spence type H activated alumina was used. Ultraviolet spectra were determined in ethanol solution with an Optica CF4 recording spectrometer.

2,2′-Dinitrodiaryl Sulphides.—A solution of the appropriate *o*-chloronitrobenzene (100 g.) and ethyl potassium xanthate (80 g.) in ethanol (400 ml.) was refluxed for 60 hr.; the precipitate of the diaryl sulphide separated from acetic acid (charcoal). This procedure gave 2,2′-dinitrodiphenyl sulphide (40%), m. p. 119—122° (lit.,[12] m. p. 122—123°), 4,4′-dichloro-2,2′-dinitrodiphenylsulphide (45%), m. p. 153—155° (lit.,[13] m. p. 149—150°), and 4,4′-dimethyl-2,2′-dinitrodiphenyl sulphide (33%), m. p. 125—126° (lit.,[14] m. p. 125—126°).

4,4′-Dichloro-2,2′-dinitrodiphenyl Sulphoxide.—A solution of the corresponding sulphide (30 g.) in acetic acid (300 ml.) containing 30% hydrogen peroxide (10 ml., 1 mol.) was refluxed for 15 hr. Crystallisation of the precipitate from acetic acid gave the sulphoxide (22·5 g., 72%), m. p. 243—244° (lit.,[15] m. p. 236°) (Found: C, 40·0; H, 1·7;

[9] H. H. Szmant and R. L. Lapinski, *J. Amer. Chem. Soc.*, 1956, **78**, 458.
[10] N. H. Szmant and Y.-L. Chow, *J. Amer. Chem. Soc.*, 1957, **79**, 3282, 5583.
[11] N. L. Allinger and G. A. Youngdale, *J. Org. Chem.*, 1959, **24**, 2059.
[12] F. Challenger and A. D. Collins, *J. Chem. Soc.*, 1924, 1377.
[13] F. Beilstein and A. Kurbatow, *Annalen*, 1879, **197**, 75.
[14] M. T. Bogert and M. R. Mandelbaum, *J. Amer. Chem. Soc.*, 1923, **45**, 3045.
[15] E. Riesz, A. Lorenz, C. Myschalow, and O. Strakosch, *Monatsh.*, 1928, **50**, 263.

N, 7·3. Calc. for $C_{12}H_6Cl_2N_2O_5S$: C, 39·8; H, 1·7; N, 7·7%).

2,2′-Dinitrodiaryl Sulphones.—A solution of the sulphide (20 g.) in acetic acid (250 ml.) and 30% hydrogen peroxide (100 ml.) was refluxed for 2 hr. Crystallisation of the precipitate from acetic acid gave the sulphones. 2,2′-Dinitrodiphenyl sulphone was obtained as needles (87%), m. p. 179—181° (lit.,[16] m. p. 189°) (Found: C, 46·8; H, 2·4; N, 9·0. Calc. for $C_{12}H_8N_2O_6S$: C, 46·7; H, 2·6; N, 9·1%), 4,4′-dichloro-2,2′-dinitrodiphenyl sulphone as plates (80%), m. p. 172—174° (lit.,[15] m. p. 176°) (Found: C, 38·2; H, 1·5; N, 7·2. Calc. for $C_{12}H_6Cl_2N_2O_6S$: C, 38·2; H, 1·6; N, 7·4%), and *4,4′-dimethyl-2,2′-dinitrodiphenyl sulphone* as plates (88%), m. p. 176—177° (Found: C, 49·9; H, 3·5; N, 8·4. $C_{14}H_{12}N_2O_6S$ requires C, 50·0; H, 3·6; N, 8·3%).

Reduction of 2,2′-Dinitrodiphenyl Sulphide.—(*a*) Zinc dust (20 g.) was added to a solution of the sulphide (10 g.) in dioxan (650 c.c.) containing 40% aqueous sodium hydroxide (100 c.c.), and the mixture was stirred at 20° for 2 hr. The mixture was filtered, and the filtrate was concentrated, diluted with water, and extracted with methylene chloride. The residue obtained by evaporation of the solvent was chromatographed on alumina (125 g.). Elution with benzene–light petroleum (1 : 1) gave three fractions. Crystallisation of the first fraction from benzene gave 2,2′-dinitrodiphenyl sulphide (0·7 g., 7%), m. p. and mixed m. p. 115—122°. The second fraction separated from ethanol in crimson needles (63 mg., 1%), m. p. 150—152°, $\nu_{max.}$ 3320 cm.$^{-1}$ (NH) (Found: C, 58·8; H, 3·4. Calc. for $C_{24}H_{18}N_4O_4S_2$: C, 58·8; H, 3·7%). This is probably the disulphide (XI) (lit.,[7] m. p. 150°). Trituration of the third fraction with ether yielded *dibenzo*[b,f][1,4,5]*thiadiazepine 5-oxide* (0·99 g., 12%), m. p. 162—165°, separating from ethanol in needles, m. p. 166—167°, $\lambda_{max.}$ 246 (ε 16,000), and 318 mμ (ε 5090) (Found: C, 63·2; H, 3·4; N, 12·3. $C_{12}H_8N_2OS$ requires C, 63·3; H, 3·6; N, 12·3%).

In some similar experiments, less of the 5-oxide was obtained, and was accompanied by dibenzo[1,4,5]thiadiazepine (6—13%) as yellow needles (from ethanol), m. p. 140—141° (lit.,[5] m. p. 139—140°), $\lambda_{max.}$ 246 (ε 12,800), 313 (ε 4160), and 426 mμ (ε 724).

(*b*) The sulphide (4 g.) was reduced as in (*a*) except that the mixture was stirred and refluxed for 3 hr. Chromatography of the product on alumina and elution with benzene–light petroleum (1 : 1) gave yellow needles (54 mg., 1%), m. p. 140—150°. The infrared spectrum indicated that this was phenazine containing a small proportion of dibenzo[*b,f*][1,4,5]thiadiazepine. Elution with benzene afforded 2-amino-2′-nitrodiphenyl sulphide as yellow prisms (171 mg., 5%) (from ethanol), m. p. 86°, undepressed by admixture with an authentic sample, m. p. 86°, prepared by a known method.[17]

Reduction of Dibenzo[b,f][1,4,5]*thiadiazepine 5-Oxide.*—(*a*) The 5-oxide (193 mg.) was reduced with zinc and sodium hydroxide in aqueous dioxan at 20° for 1 hr. in the usual way. Chromatography yielded first dibenzo[*b,f*][1,4,5]-thiadiazepine (33 mg., 18%), m. p. and mixed m. p. 139—140° and then the 5-oxide (139 mg., 72%), m. p. and mixed m. p. 165—167°.

(*b*) A mixture of the 5-oxide (140 mg.), arsenious oxide (800 mg.), sodium hydroxide (1·5 g.), dioxan (25 c.c.), and water (25 c.c.) was refluxed for 22 hr., diluted with water, and extracted with chloroform. The chloroform was evaporated, and the residue was chromatographed on alumina (14 g.). Elution with benzene–light petroleum (1 : 1) afforded first dibenzo[*b,f*][1,4,5]thiadiazepine (30 mg., 23%), m. p. and mixed m. p. 137—140°, and then the 5-oxide (95 mg., 67%), m. p. and mixed m. p. 164—167°.

Reduction of 4,4′-Dichloro-2,2′-dinitrodiphenyl Sulphide.—(*a*) The sulphide (2 g.) was reduced with zinc and alkali at 20° for 7 hr. as described for 2,2′-dinitrodiphenyl sulphide. Chromatography of the product on alumina, and elution with benzene furnished 2,7-dichlorophenazine in yellow needles (from methanol) (85 mg., 6%), m. p. 255—265° (decomp.), identical (infrared spectrum) with an authentic sample, m. p. 260—265° (decomp.) prepared by Vivian's method.[18]

(*b*) The reactants given in (*a*) were refluxed for 2 hr., and the product was chromatographed on alumina. Elution with benzene–light petroleum (1 : 1), and trituration of the fraction with chloroform yielded 2,7-dichlorophenothiazine (99 mg., 6%), separating from ethanol in yellow needles, m. p. 200—209° (decomp.), $\nu_{max.}$ 3350 cm.$^{-1}$ (NH) (Found: C, 53·3; H, 2·7; N, 4·9. Calc. for $C_{12}H_7Cl_2NS$: C, 53·7; H, 2·7; N, 5·2%). The compound was identical with an authentic sample,[8] m. p. 208—212° (decomp.).

Reduction of 2,2′-Dinitrodiphenyl Sulphone.—(*a*) Reduction of the sulphone (2 g.) with zinc and alkali at 20° for 2 hr., and chromatography of the neutral products gave first phenazine (210 mg., 18%), m. p. and mixed m. p. 168—172°, and then dibenzo[*b,f*][1,4,5]thiadiazepine 11,11,-dioxide (100 mg., 6%), m. p. and mixed m. p. 169—172°.

(*b*) The reactants were refluxed for 30 min. and the neutral product was chromatographed on alumina (70 g.). Elution with benzene–light petroleum (1 : 1) gave three fractions. The first fraction was steam-distilled and the distillate was extracted with ether. Evaporation of the ether furnished phenazine (150 mg., 14%), m. p. and mixed m. p. 169—172°. Crystallisation of the second fraction from ethanol gave unchanged sulphone (108 mg., 5%), m. p. and mixed m. p. 182—184°. The third fraction was dibenzo[*b,f*][1,4,5]thiadiazepine 5,11,11-trioxide (from ethanol), m. p. and mixed m. p. 242—248°. The original aqueous alkaline solution was treated with acetone (100 c.c.) and methyl iodide (5 c.c.), and then refluxed for 30 min. Acetone was removed, water was added, and the mixture was extracted with chloroform. The chloroform was evaporated and the residue was chromatographed on alumina. Elution with benzene–light petroleum (1 : 1) gave yellow prisms (from ethanol), m. p. 132—134°, $\nu_{max.}$ 3350 (NH) and 1540 cm.$^{-1}$ (NO_2). This is probably methyl 2-(*o*-nitroanilino)phenyl sulphone (lit.,[7] m. p. 132°). Elution with benzene afforded *methyl 2-(o-aminoanilino)-phenyl sulphone* in plates (from ethanol) (52 mg., 5%), m. p. 156—158°, $\nu_{max.}$ 3400, 3350 cm.$^{-1}$ (NH_2) (Found: C, 59·4; H, 5·3; N, 10·5. $C_{13}H_{14}N_2O_2S$ requires C, 59·5; H, 5·4; N, 10·7%).

When this reaction was conducted for 13 hr., phenazine (16%) and dibenzo[*b,f*][1,4,5]thiadiazepine 11,11-dioxide (2%) were isolated, and elution of the alumina column with ether gave 2,2′-diaminodiphenyl sulphone, m. p. and mixed m. p. 139—146°.

Reduction of 4,4′-Dichloro-2,2′-dinitrodiphenyl Sulphone and Sulphoxide.—The sulphone (2 g.) was reduced with zinc and alkali at 20° for 2 hr. Crystallisation of the crude

[16] E. Grandmougin, *Compt. rend.*, 1922, **174**, 39.
[17] A. Levi, L. A. Warren, and S. Smiles, *J. Chem. Soc.*, 1933, 1490.
[18] D. L. Vivian, *J. Amer. Chem. Soc.*, 1951, **73**, 457.

product from ethanol gave 2,7-dichlorophenazine (340 mg., 25%), m. p. and mixed m. p. 264—266° (decomp).

When the reactants were refluxed for 30 min., 2,7-dichlorophenazine was obtained in the same way, and a further quantity was obtained by chromatographing the ethanol-soluble fraction on alumina and eluting with benzene (total yield, 165 mg., 12%).

Reduction of the sulphoxide (2 g.) at 20° for 2 hr. gave 2,7-dichlorophenazine (180 mg., 13%).

Reduction of 4,4′-*Dimethyl*-2,2′-*dinitrodiphenyl Sulphone*.—The sulphone (1·5 g.) was refluxed with zinc and alkali for 1·5 hr., and the product was chromatographed. Elution with benzene–light petroleum (1 : 1) afforded 2,7-dimethylphenazine (112 mg., 11%), m. p. 159—162° (from ethanol), identical (mixed m. p. and infrared spectrum) with an authentic sample.[2] Elution with benzene gave first 3,8-dimethyldibenzo[*b*,*f*][1,4,5]thiadiazepine 11,11-dioxide, separating from acetic acid in orange needles (100 mg., 9%), m. p. and mixed m. p. 262—265°, and then 2,2′-diamino-4,4′-dimethyldiphenyl sulphone (52 mg., 4%), m. p. and mixed m. p. 136—140°.

When the reduction was carried out at 20° for 2 hr., 2,7-dimethylphenazine was isolated in 10% yield, but the thiadiazepine dioxide was not obtained. Elution of the alumina column with benzene furnished 3,8-dimethyldibenzo[*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxide, separating from acetic acid in plates, m. p. and mixed m. p. 263—265°.

Reaction of 2-*Amino*-2′-*nitrodiphenyl Sulphone*.—(*a*) A mixture of the sulphone [7] (1 g.), dioxan (80 ml.), 40% aqueous sodium hydroxide (10 ml.), and zinc dust (2 g.) was stirred at room temperature for 40 min., and then filtered. The product was obtained in the usual way, and chromatographed on alumina (30 g.). Elution with benzene gave the starting compound (80 mg., 8%), m. p. and mixed m. p. 131—133° and 2,2′-diaminodiphenyl sulphone (90 mg., 10%) (from ethanol), m. p. 139—147°, identical (mixed m. p. and infrared spectrum) with an authentic sample.

When the experiment was conducted in the absence of zinc, the starting compound was recovered in 97% yield.

(*b*) The sulphone (0·56 g.) was treated as in (*a*) except that the mixture was refluxed for 30 min. Crystallisation of the product from ethanol gave phenothiazine 5,5′-dioxide in prisms (0·25 g., 61%), $\nu_{max.}$ 3340 cm.$^{-1}$ (NH), m. p. 255—260°, raised by recrystallisation to 262—263° (lit.,[19] m. p. 257—259°).

In the absence of zinc, phenothiazine 5,5′-dioxide was obtained in 95% yield.

2,2′-*Diamino*-4,4′-*dimethyldiphenyl Sulphone*.—Concentrated hydrochloric acid (150 c.c.) was added slowly to a stirred mixture of 2,2′-dinitro-4,4′-dimethyldiphenyl sulphone (5 g.), tin powder (15 g.), and ethanol (100 c.c.), and the mixture was refluxed for 30 min., and then filtered. The filtrate was made alkaline with aqueous sodium hydroxide, ethanol was evaporated, and the mixture was extracted with methylene chloride. Evaporation of the solvent, and trituration of the residue with ethanol afforded the *diamine* as prisms (3·3 g., 75%), m. p. 136—140°, raised to 140—141° by crystallisation from ethanol (Found: C, 60·8; H, 5·7. $C_{14}H_{16}N_2O_2S$ requires C, 60·8; H, 5·8%).

2,2′-Diaminodiphenyl sulphone (55%), m. p. 146—147° (lit.,[11] m. p. 147—148°), and 2,2′-diamino-4,4′dichlorodiphenyl sulphone (55%), m. p. 161—163° (lit.,[4] m. p. 165°), were prepared by a similar method.

Dibenzo[b,f][1,4,5]*thiadiazepine* 11,11-*Dioxides*.—2,2′-Diaminodiphenyl sulphones were oxidised with phenyl iodosodiacetate as described by Szmant *et al.*[4,9] The products were chromatographed on alumina and eluted with benzene–light petroleum (1 : 1) or with benzene. Dibenzo[*b*,*f*]1,4,5]thiadiazepine 11,11-dioxide (32%), separated from ethanol in yellow needles, m.p. 172—173° (lit.,[9,10] m. p. 174°), $\lambda_{max.}$ 230 (ε 20,500), 320 (ε 4980), and 436 mμ (ε 576) (Found: C, 59·4; H, 3·6; N, 11·3. Calc. for $C_{12}H_8N_2O_2S$: C, 59·0; H, 3·3; N, 11·5%). Starting material (30%) was recovered by elution of the alumina column with benzene–ether (1 : 1). 3,8-Dichlorodibenzo[*b*,*f*][1,4,5]thiadiazepine 11,11-dioxide (55%) was obtained as yellow needles (from ethanol), m. p. 172—174° (lit.,[4] m. p. 175°) $\lambda_{max.}$ 246 (ε 36,500), 316 (ε 5200), and 430 mμ (ε 599) (Found: C, 46·0; H, 1·9; N, 8·8. Calc. for $C_{12}H_6Cl_2N_2O_2S$: C, 46·0; H, 2·0; N, 8·9%). In some preparations an orange product, m. p. 181—182°, was isolated, but reverted to the lower-melting form on further crystallisation. On standing, the product, m. p. 172—174°, became more coloured and the m. p. increased. The infrared spectra of the two forms were almost identical. 3,8-*Dimethyldibenzo*[b,f][1,4,5]*thiadiazepine* 11,11-*dioxide* (25%) separated from acetic acid in orange prisms, m. p. 268—269°, $\lambda_{max.}$ 243 (ε 31,000), 320 (ε 6760), and 430 mμ (ε 614) (Found: C, 61·2; H, 4·5; N, 10·7. $C_{14}H_{14}N_2O_2S$ requires C, 61·8; H, 4·4; N, 10·3%).

Dibenzo[b,f][1,4,5]*thiadiazepine* 5,11,11-*Trioxides*.—A solution of the thiadiazepine 11,11-dioxide (0·5 g.) in acetic acid (40 c.c.) containing 30% hydrogen peroxide (10 c.c.) was heated on a steam-bath for 2 hr., and then filtered. On cooling alone, or after dilution with water, the filtrate deposited the trioxide. Dibenzo[*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxide (80%) crystallised from acetic acid in needles, m. p. 255—257° (lit.,[9,10] m. p. 251—252°), $\lambda_{max.}$ 234 (ε 25,700) and 334 mμ (ε 5750). 3,8-Dichloro[*b*,*f*][1,4,5]-thiadiazepine 5,11,11-trioxide (78%) separated from acetic acid in needles, m. p. 247—249° (lit.,[4] m. p. 245°), $\lambda_{max.}$ 244 (ε 30,000) and 330 mμ (ε 5550) (Found: C, 43·2; H, 1·8; N, 8·6. Calc. for $C_{12}H_6Cl_2N_2O_2S$: C, 43·7; H, 1·9; N, 8·5%). 3,8-*Dimethyldibenzo*[b,f][1,4,5]*thiadiazepine* 5,11,11-*trioxide* (78%) crystallised from acetic acid in needles, m. p. 269—270° (decomp.), $\lambda_{max.}$ 240 (ε 35,000) and 334 mμ (ε 6900) (Found: C, 58·2; H, 4·3; N, 10·1. $C_{14}H_{14}N_2O_2S$ requires C, 58·4; H, 4·2; N, 9·6%).

A similar oxidation of dibenzo[*b*,*f*][1,4,5]thiadiazepine 5-oxide furnished the corresponding trioxide (78%), m. p. and mixed m. p. 253—255°.

5,6-*Dihydrodibenzo*[b,f][1,4,5]*thiadiazepine* 11,11-*Dioxides*.—A mixture of the thiadiazepine 5,11,11-trioxide (0·2 g.), tin powder (0·2 g.), concentrated hydrochloric acid (3 c.c.), and ethanol (15 c.c.) was refluxed for 1 hr., and then filtered. Most of the ethanol was evaporated, water was added, and the mixture was extracted with methylene chloride. Evaporation of the solvent, and crystallisation of the residue from ethanol furnished the following dihydro-derivatives in almost quantitative yield: 5,6-dihydrodibenzo[*b*,*f*][1,4,5]thiadiazepine 11,11-dioxide, prisms, m. p. 195—197° (lit.,[10] m. p. 194—196°), $\nu_{max.}$ 3370 cm.$^{-1}$ (NH); 3,8-*dichloro*-5,6-*dihydrodibenzo*[b,f][1,4,5]*thiadiazepine* 11,11-*dioxide*, needles, m. p. 156—158°, $\nu_{max.}$ 3340, 3270 (NH), and 1300, 1160 cm.$^{-1}$ (SO_2) (Found: C, 45·5; H, 2·6; N, 9·4. $C_{12}H_8Cl_2N_2O_2S$ requires C, 45·8; H, 2·6; N, 8·9%). This structure was assigned by Szmant and

[19] A. Bernthsen, *Ber.*, 1906, **39**, 1804.

Infante [4] to a compound, m. p. 130° (see below); *5,6-dihydro-3,8-dimethyldibenzo*[b,f][1,4,5]*thiadiazepine* 11,11-*dioxide*, needles, m. p. 201—202°, $\nu_{max.}$ 3330 cm.$^{-1}$ (NH) (Found: C, 61·3; H, 5·2; N, 10·3. $C_{14}H_{14}N_2O_2S$ requires C, 61·4; H, 5·2; N, 10·2%).

The same three dihydro-compounds (92—97% yield) were obtained by reduction of the requisite dibenzo[1,4,5]thiadiazepine 11,11-dioxides with tin and hydrochloric acid.

Oxidation of 5,6-Dihydrodibenzo[b,f][1,4,5]*thiadiazepine 11,11-Dioxides.*— 5,6-Dihydro-3,8-dimethyldibenzo[*b,f*]-[1,4,5]thiadiazepine 11,11-dioxide (122 mg.) in methylene chloride (25 c.c.) was treated with aqueous sodium hypobromite (2 c.c.) [prepared from bromine (1 c.c.), sodium hydroxide (2 g.), and water (20 c.c.)]. The organic layer was separated and evaporated to yield 3,8-dimethyldibenzo-[*b,f*][1,4,5]thiadiazepine 11,11-dioxide (117 mg., 96%) as yellow needles (from acetic acid), m. p. and mixed m. p. 263—266°.

A similar oxidation of 5,6-dihydrodibenzo[*b,f*][1,4,5]-thiadiazepine 11,11-dioxide afforded the corresponding azo-derivative (81%), m. p. and mixed m. p. 170—173°.

Oxidation of 3,8-dichloro-5,6-dihydrodibenzo[*b,f*][1,4,5]-thiadiazepine 11,11-dioxide gave the azo-compound (80%), m. p. and mixed m. p. 171—174°. The compound, m. p. 130°, obtained by Szmant and Infante [4] by reduction of 4,4′-dichloro-2,2′-dinitrodiphenyl sulphone with hydrogen and Raney nickel was reported to be oxidised by air to a mixture of products including the azoxy-derivative; it is therefore unlikely to be the hydrazo-derivative.

A solution of the dihydro-derivative (XVIII; R = H) in benzene was chromatographed on alumina. A yellow band was formed, and elution with benzene gave the azo-derivative (XV; R = H) (95%), m. p. and mixed m. p. 174°.

Reaction of Dibenzo[b,f][1,4,5]*thiadiazepine 11,11-Dioxides and 5,11,11-Trioxides with Zinc and Alkali.*—A mixture of the dioxide or trioxide (0·5 g.), zinc dust (1 g.), 40% aqueous sodium hydroxide (10 c.c.), and dioxan (100 c.c.) was stirred, and then filtered. The filtrate was concentrated under reduced pressure, diluted with water, and extracted with methylene chloride. The residue obtained by evaporation of the solvent was usually chromatographed on alumina.

Dibenzo[*b,f*][1,4,5]thiadiazepine 11,11-dioxide was recovered almost quantitatively when reacted with zinc and alkali for 5 hr. at 20° and at reflux. 3,8-Dichlorodibenzo-[*b,f*][1,4,5]thiadiazepine 11,11-dioxide was recovered in 70% yield when reacted at 20° for 1·5 hr.

The reactions of the trioxides are summarised in Table 2.

TABLE 2

Reaction of dibenzo[*b,f*][1,4,5]thiadiazepine 5,11,11-trioxides (XVI) with zinc and sodium hydroxide in aqueous dioxan

R	Temp.	Time (hr.)	Recovery (%)	Yield (%) of dioxide (XV)
H	20°	1	9	7 *
H	100	0·5	0	33 †
Cl	20	0·5	45	0
Cl	100	0·5	0	59 ‡

* A compound, m. p. 171—173° was also isolated. † 2,2′-Diamino-diphenyl sulphone (16%) was obtained. ‡ 2,2′-Diamino-2,2′-dichlorodiphenyl sulphone was also isolated.

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