Oxidation, Thermolysis, and Photolysis of Diarylsulphamides

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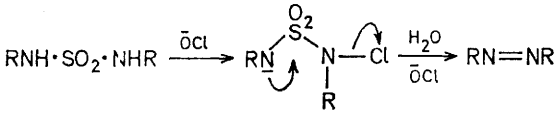
In contrast with *NN'*-dialkylsulphamides the oxidation of diarylsulphamides by hypochlorite is not a general route to aromatic azo-compounds; instead the major products are usually quinone anils, formed in a new aromatic rearrangement. The photolysis of the arylsulphamides and the thermolysis of their *NN'*-dichloro-derivatives do give azo compounds, however. The photochemical reaction appears to be intramolecular, possibly involving extrusion of sulphur dioxide as the first step.

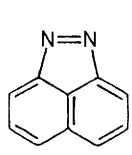
BENZ[*cd*]INDAZOLE (I), a potential source of 1,8-dehydronaphthalene, has so far eluded synthesis.[1] In 1965, Ohme and Schmitz reported[2] that *NN'*-dialkylsulphamides could be oxidised by hypochlorite to give the corresponding azoalkanes, intramolecularly and in good yield (Scheme 1). We considered extensions of this



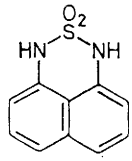
SCHEME 1

reaction, in particular the oxidation of the naphthothiadiazine 2,2-dioxide (II) as a possible route to benz[*cd*]indazole. This led to a more general study of the reactions with hypochlorite of the substituted sulphanilides (III) and (IV) and of the cyclic sulphamides (II), (V), and (VI).

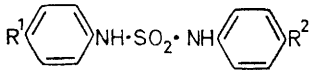
Preparation of Sulphamides.—The symmetrical diarylsulphamides (IIIa, b, and d) and (IVb) were prepared from the corresponding arylamines and sulphuryl chloride in the presence of pyridine, according to the procedure of Parnell.[3] Attempts to prepare the cyclic sulphamides (II), (V), and (VI) from the appropriate diamines and sulphuryl chloride were unsuccessful,[4] but



(I)

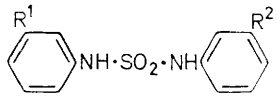


(II)



(III)

a; $R^1 = H$, $R^2 = H$
b; $R^1 = Cl$, $R^2 = Cl$
c; $R^1 = Br$, $R^2 = Cl$
d; $R^1 = NO_2$, $R^2 = NO_2$



(IV)

a; $R^1 = H$, $R^2 = Me$
b; $R^1 = Me$, $R^2 = Me$

the use of sulphamide, $NH_2 \cdot SO_2 \cdot NH_2$, instead of sulphuryl chloride gave all three compounds in good yields.[5]

The unsymmetrical sulphanilides (IIIc) and (IVa) were prepared by the reaction of an aromatic *N*-(chlorosulphonyl)amide with an arylamine, followed by alkaline

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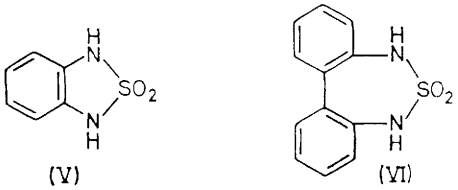
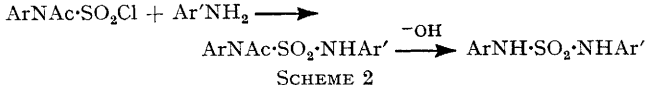
[1] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 760.
[2] R. Ohme and E. Schmitz, *Angew. Chem. Internat. Edn.*, 1965, **4**, 433.
[3] E. W. Parnell, *J. Chem. Soc.*, 1960, 4366.
[4] A. Wohl and F. Koch, *Ber.*, 1910, **43**, 3295.
[5] J. Carson, U.S.P. 3,177,221/1965.

hydrolysis (Scheme 2).[6] Attempts to form these sulphanilides by the reaction of an arylsulphamide with an arylamine (Scheme 3) at 75° were unsuccessful; amide

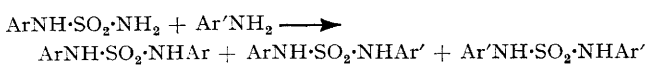


(V) (VI)

exchange competed effectively with condensation and an approximately statistical mixture of products was obtained.



SCHEME 2

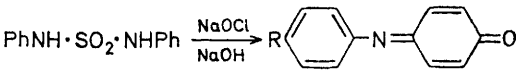


SCHEME 3

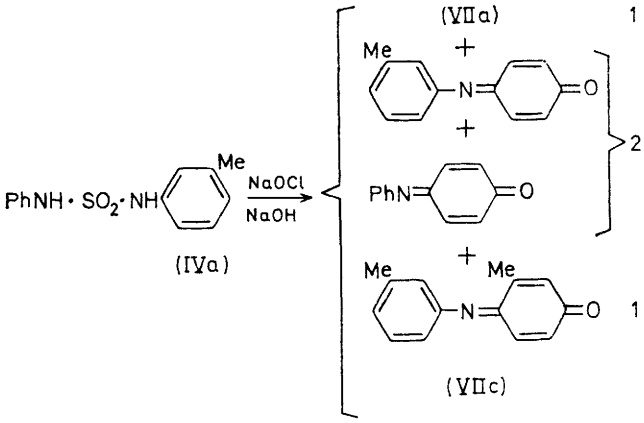
Oxidations.—The oxidation of naphthothiadiazine dioxide (II) with sodium hypochlorite in sodium hydroxide, under conditions similar to those used [2] for the oxidation of dialkylsulphamides, resulted in the quantitative formation of an acid polymer. When the reaction was repeated in the presence of tetraphenylcyclopentadienone (tetracyclone), to intercept any benz[*cd*]indazole formed, the same acidic polymer was again isolated and the tetracyclone was recovered. It therefore seemed that the reaction took a different course from the dialkylsulphamide oxidations. The oxidation of the sulphanilide (IIIa) under the same conditions was then investigated, on the basis that any azobenzene formed would be stable under the conditions used and could be isolated. No azobenzene was detected in the oxidation product, however; the major product was *p*-benzoquinone anil (VIIa). The possibility that this product was being formed by hydrolysis of the sulphamide to give aniline, and subsequent oxidation of the aniline, was ruled out since the sulphamide was resistant to alkaline hydrolysis. Also, oxidation of aniline under these conditions gave no quinone anil. Similarly, 3,3′-dimethylsulphanilide gave the quinone anil (VIIc). The intermolecularity of the reaction was established by oxidation of the unsymmetrical 3-methylsulphanilide (IVa) which gave a mixture of quinone anils in the correct statistical ratio (Scheme 4).

The effect of *para* blocking substituents was investigated. When 4,4′-dichlorosulphanilide was oxidised under the same conditions, a small amount (2%) of 4,4′-dichloroazobenzene was obtained, together with the 4-chloro-*p*-quinone anil (VIIb).[7] The dichloroazobenzene was probably formed by an intermolecular pathway; this was demonstrated by two experiments in which a mixture of t-butyl hypochlorite and potassium t-butoxide

[6] J. Meybeck, *Ann. Chim.* (*France*), 1932, **17**, 129.
[7] A. E. Bradfield, L. H. N. Cooper, and K. J. P. Orton, *J. Chem. Soc.*, 1927, 2854.



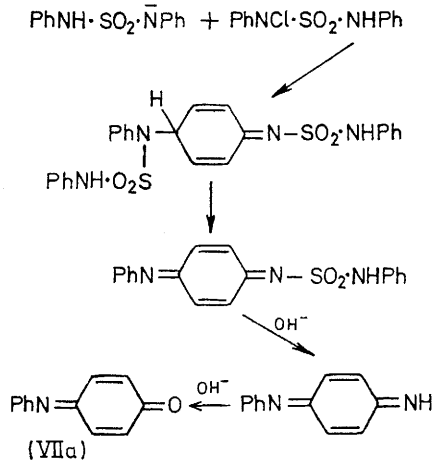
(IIIa) (VII) a; R = H b; R = Cl



SCHEME 4

was used as the oxidising system. With 4,4′-dichlorosulphanilide, the yield of azobenzene was increased to 19%. 4-Bromo-4′-chlorosulphanilide gave a mixture of the three 4,4′-dihalogenated azobenzenes (15%) in the ratio expected for an intermolecular reaction.

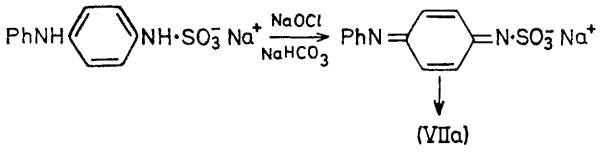
A possible mechanism for the formation of the quinone anils involves *N*-chlorination followed by nucleophilic attack at the *para* carbon atom by a second sulphanilide anion. Subsequent elimination and hydrolysis would give *N*-phenyl-*p*-benzoquinone di-imine and hence



SCHEME 5

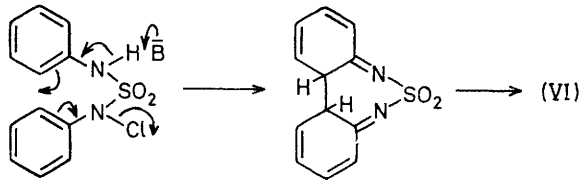
p-benzoquinone anil (VIIa). There is an analogy for the last part of this mechanism in the formation of *p*-benzoquinone anil (VIIa) in the oxidation of sodium *N*-(*p*-anilinophenyl)sulphamate, which was shown to go *via* the quinone di-imine *N*-sulphonate [8] (Scheme 6):

[8] R. Lantz, J. Gascon, and H. Delarue, *Compt. rend.*, 1957, **244** (*C*), 3159.



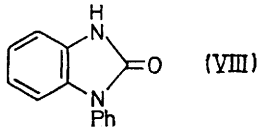
SCHEME 6

In an attempt to obtain intermediates in the oxidation, the sulphanilide (IIIa) was oxidised with sodium hypochlorite in the presence of sodium carbonate instead of sodium hydroxide as the base. A small amount of quinone anil (VIIa) was again obtained; the major product (32%) was, however, the cyclic sulphamide (VI). The unexpected formation of this biphenyl derivative can most simply be rationalised by a type of oxidative coupling mechanism (Scheme 7).

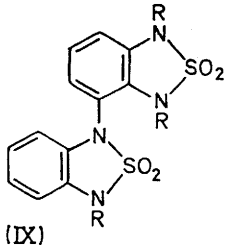


SCHEME 7

The reaction contrasts with that of *NN*-diphenylurea with hypochlorite and base, which gives a different oxidation product, *N*-phenylbenzimidazolone (VIII).[9]

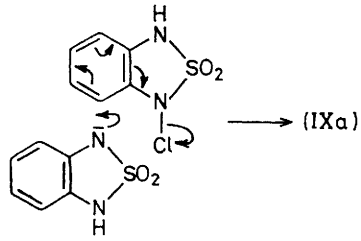


The oxidation products of the cyclic sulphamides (V) and (VI) were next investigated. Benzothiadiazoline 2,2-dioxide (V) reacted with sodium hypochlorite and sodium hydroxide to give, quantitatively, an acidic polymer. Oxidation with 0·5 equiv. of sodium hypochlorite gave a dimer, assigned structure (IXa), and characterised as the trimethyl derivative (IXb), obtained by treatment with diazomethane. The position of coupling, that is, *ortho* or *meta* to the heterocyclic ring, could not be unambiguously assigned from the available data.



a; R = H. b; R = Me

As polymerisation required both base and hypohalite, a possible mechanism for the reaction would involve nucleophilic attack on, and displacement of chlorine from, an *N*-chlorinated sulphamide (Scheme 8). In the presence of an excess of hypochlorite, repeated coupling reactions of this type probably take place, leading to the formation of the polymer.

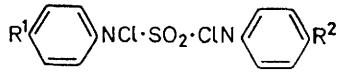


SCHEME 8

The thiadiazepine dioxide (VI), under similar conditions, also gave mainly a polymer, but in addition a mixture of benzo[*c*]cinnoline and 2-chlorobenzo[*c*]cinnoline. The combined yield of these very stable azo-compounds was only 6%, however. The picture that emerges, therefore, from these arylsulphamide oxidations is that azo-compounds are formed in low yield or not at all, since there are usually easier reaction paths available, and that the intramolecular azoalkane synthesis discovered by Ohme and Schmitz cannot be extended to aromatic azo-compounds. 4,4′-Dinitrosulphanilide has been reported to give a good yield of 4,4′-dinitroazobenzene under these conditions,[10] but this reaction almost certainly involves a prior hydrolysis to *p*-nitroaniline. We showed that 4,4′-dinitrosulphanilide, unlike sulphanilide itself, was very readily hydrolysed by base, and that oxidation of *p*-nitroaniline with alkaline hypochlorite gave 4,4′-dinitroazobenzene as the only detectable product.

Schemes 5, 7, and 8 all depict variants of the same basic reaction—nucleophilic attack by a sulphamide anion on an aromatic ring leading to displacement of chloride from a conjugated *N*-chlorosulphamide group.

Preparation and Thermolysis of NN′*-Dichlorosulphanilides.*—The dechlorination of the *NN*′-dichlorosulphanilides (X) was then considered as a possible alternative route to the thiadiaziridine intermediates, and hence to the azo-compounds. *NN*′-Dichlorosulphanilides have



(X)

a; $R^1 = R^2 = H$ b; $R^1 = R^2 = Cl$ c; $R^1 = Br$, $R^2 = Cl$

not previously been reported, but it was found that they could be prepared by the action of an excess of chlorine in aqueous sodium hydroxide[11] on the corresponding sulphanilides. With sulphanilide itself, some ring chlorination also occurred, so that the *NN*′-dichlorosulphanilide (Xa) was obtained slightly contaminated with a trichlorosulphanilide. The other dichlorosulphanilides (Xb and c) were obtained pure; they were unstable

[9] M. L. Oftedahl, R. W. Radue, and M. W. Dietrich, *J. Org. Chem.*, 1963, **28**, 578; L. Rosnati, *Gazzetta*, 1956, **86**, 275.

[10] R. Ohme and H. Preuschhof, *Annalen*, 1968, **713**, 74.

[11] R. Sowada, *J. prakt. Chem.* 1964, **23**, 128.

solids which decomposed within a few days at room temperature. They were therefore used immediately after preparation. Surprisingly, attempts to *N*-chlorinate the cyclic sulphamides (II), (V), and (VI) in the same way failed.

When *NN'*-dichlorosulphanilide (Xa) was heated under reflux in dry carbon tetrachloride, chlorine was slowly evolved. After 12 hr. chlorine evolution had ceased, and azobenzene (31%) was isolated from the reaction mixture. Similarly, 4,4',*NN'*-tetrachlorosulphanilide (Xb) gave 4,4'-dichloroazobenzene (36%). These compounds were formed by an intermolecular mechanism, however. The bromochlorosulphanilide (Xc) gave a mixture of substituted azobenzenes (26%) which could not be separated by chromatography. The products were shown by mass spectral analysis to be in the ratio expected for an intermolecular reaction.

Photolysis of Sulphanilides.—It was noticed that the cyclic sulphamides were sensitive to light. A brief investigation of the photochemistry of the diarylsulphamides was therefore undertaken.

Sulphanilide (IIIa) was irradiated in dry methanol with light of wavelength 250—300 nm. The products isolated were azobenzene, aniline, and unchanged sulphanilide, which together accounted for 75% of the initial sulphanilide, although hydrazobenzene could also be detected (t.l.c.) in the reaction mixture before work-up. The aniline and azobenzene were in a 2 : 1 molar ratio.

Under similar conditions, 3-methylsulphanilide (IVa) gave 3-methylazobenzene, but no azobenzene or 3,3'-dimethylazobenzene; and a mixture of aniline and *m*-toluidine. Again, the arylamine–azobenzene molar ratio was *ca.* 2 : 1. Thus, it seemed that the azobenzenes were being formed by an intramolecular process. The 2 : 1 molar ratio of aniline to azobenzene, and the detection of hydrazobenzene in the reaction mixture, suggested that hydrazobenzene might be the primary product of the photolysis, but that it then photochemically disproportionated to aniline and azobenzene, this last step being a known reaction.[12] Thus, sulphanilide appears to dissociate photochemically into sulphur dioxide and hydrazobenzene, the latter being formed intramolecularly.

Although the cyclic sulphamides (II), (V), and (VI) were rapidly destroyed by photolysis under similar conditions, they all gave complex mixtures of products, the components of which were not identified. The thiadiazepine dioxide (VI) gave no benz[*c*]cinnoline, as shown by t.l.c.

EXPERIMENTAL

M.p.s are corrected. I.r. spectra were recorded for Nujol mulls, except where indicated otherwise. Mass spectra were obtained with an A.E.I. MS9 spectrometer. Diglyme (diethylene glycol dimethyl ether) was dried by distillation from calcium hydride and was stored over molecular sieves (type 5A). Petroleum refers to light petroleum, b.p. 60—80°.

Preparation of Sulphamides.—NN'-*Sulphonyldianiline* (IIIa). Prepared (59 g., 47%) from sulphuryl chloride (0·49 mole), aniline (1 mole), and pyridine (0·8 mole) in ethanol-free chloroform (500 ml.), according to the method of Parnell,[3] this yielded prisms, m.p. 111—112° (from chloroform) (lit.,[4] 111—112°), $\nu_{max.}$ 3260, 1600, 1490, 1340, 1155 1145, 745, and 695 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 207 (ε 10,800), 232 (15,200), and 273 nm. (1420).

Similarly prepared were pp'-*dichloro*-NN'-*sulphonyldianiline* (IIIb) (25%), m.p. 119—120° (lit.,[3] 120—121°) and pp'-*dinitro*-NN'-*sulphonyldianiline* (IIId) (45%), m.p. 185—190° (decomp.; variable with rate of heating) (lit.,[3] 195—197°; lit.,[13] 204—205°), *m/e* 338.

p-*Bromo*-p'-*chloro*-NN'-*sulphonyldianiline* (IIIc).—(a) p-*Chloro*-N-*chlorosulphonylacetanilide.* Sodium hydride (50% dispersion in oil; 2·4 g., 0·05 mole) was added to a suspension of *p*-chloroacetanilide (8·5 g., 0·05 mole) in dry benzene (175 ml.). The mixture was heated under reflux for 12 hr., then cooled to 7°, and sulphuryl chloride (4·05 ml., 0·05 mole) in dry petroleum was added dropwise, with stirring. The mixture was stirred for 2 hr. at 7°, then filtered, and the filtrate was evaporated to give an oil (13·7 g.). The oil was triturated with petroleum to give p-*chloro*-N-*chlorosulphonylacetanilide* (10·0 g., 75%), m.p. 92·5—93·5° (from CCl_4) (Found: C, 35·5; H, 2·7; N, 5·4%; *m/e* 271, 269, and 267. $C_8H_7Cl_2NO_3S$ requires C, 35·8; H, 2·6; N, 5·2%; *M*, 267) $\nu_{max.}$ 1730, 1400, 1230, 1190, 1090, 1010, 910, 740, and 710 cm.$^{-1}$.

(b) *Reaction with* p-*bromoaniline.* *p*-Bromoaniline (2·6 g., 0·015 mole) in dry ether (30 ml.) was added dropwise to a stirred solution of *p*-chloro-*N*-chlorosulphonylacetanilide (1·3 g., 0·005 mole) in dry ether (50 ml.) at 3°. The mixture was then heated under reflux for 12 hr. and filtered, and the filtrate was evaporated to leave an oil (2·7 g.), $\nu_{max.}$ 3250 and 1700 cm.$^{-1}$, which contained two components (t.l.c.). The oil was heated with aqueous sodium hydroxide (N; 100 ml.) at 80° for 5 min., and the mixture was filtered. The filtrate was acidified with 2N-hydrochloric acid, to precipitate p-*bromo*-p'-*chloro*-NN'-*sulphonyldianiline* (1·5 g., 83%), m.p. 119—121° (from chloroform–petroleum) (Found: C, 39·8; H, 2·7; N, 7·7; S, 8·6%; *m/e* 364, 362, and 360. $C_{12}H_{10}BrClN_2O_2S$ requires C, 39·8; H, 2·8; N, 7·7; S, 9·0%; *M*, 360), $\nu_{max.}$ 3270, 1490, 1330, 1150, 1010, 805, and 720 cm.$^{-1}$.

mm'-*Dimethyl*-NN'-*sulphonyldianiline* (IVb).—*m*-Toluidine (1 mole) and sulphamide (0·2 mole) were treated according to the general method described by Kirsanov and Zolotov,[14] to give mm'-*dimethyl*-NN'-*sulphonyldianiline* (8%), m.p. 132—133° (from chloroform) (Found: C, 60·6; H, 5·7; N, 9·2; S, 11·6. $C_{14}H_{16}N_2O_2S$ requires C, 60·9; H, 5·8; N, 10·1; S, 11·6%), $\nu_{max.}$ 3250, 1610, 1590, 1490, 1320, 1150, 780, and 690 cm.$^{-1}$, τ ($CDCl_3$) 2·9—3·5 (10H, m) and 7·78 (6H, s).

m-*Methyl*-NN'-*sulphonyldianiline* (IVa).—Acetanilide (25·3 g., 0·185 mole) was converted into *N*-chlorosulphonylacetanilide, without isolation from the final benzene solution, by the method of Battegay.[15] *m*-Toluidine (64 g., 0·6

[12] J. Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856; S. Hashimoto, J. Sunamoto, and S. Nishitani, *Bull. Chem. Soc. Japan*, 1968, **41**, 623.

[13] E. Haack, D.R.P. 55,279/1939; ' Methoden der organischen Chemie ' (Houben-Weyl), **11/2**, 714.

[14] A. V. Kirsanov and I. M. Zolotov, *J. Gen. Chem. U.S.S.R.*, 1958, **28**, 340.

[15] M. Battegay and J. Meybeck, *Compt. rend.*, 1932, **194** (*C*), 186.

mole) in dry benzene (150 ml.) was added dropwise to a solution of the sulphonyl chloride in benzene at 3—5°. The mixture was filtered and the filtrate was washed successively with hydrochloric acid (2N; 3 × 150 ml.) and aqueous sodium hydroxide (2N; 3 × 100 ml.). When the alkaline solution was acidified, a colourless solid (6·1 g.), m.p. 98—100°, was precipitated. This was purified by chromatography on silica; petroleum–ether (1 : 1) eluted m-*methyl*-NN′-*sulphonyldianiline* (4·9 g., 10%), m.p. 105—106° (from chloroform) (Found: C, 58·9; H, 5·3; N, 10·5; S, 12·2%; *m/e* 262. $C_{13}H_{14}N_2O_2S$ requires C, 59·5; H, 5·4; N, 10·7; S, 12·0%; *M*, 262), $\nu_{max.}$ 3260, 1620, 1600, 1500, 1330, 1160, 790, 760, and 690 cm.$^{-1}$, τ ($CDCl_3$) 2·65—3·24 (11H, m) and 7·83 (3H, s).

1H,3H-2,1,3-*Benzothiadiazoline* 2,2-*Dioxide* (V).—A solution of *o*-phenylenediamine (10·8 g., 0·1 mole) and sulphamide (9·6 g., 0·1 mole) in dry diglyme (100 ml.) was added during 30 min. to dry diglyme (200 ml.) heated under reflux. After a further 15 min., the mixture was cooled in ice and filtered, and the solvent was distilled from the filtrate at 55°/15 mm. The residue was dissolved in ether (200 ml.) and washed successively with hydrochloric acid (2N; 3 × 50 ml.) and saturated brine (50 ml.). The ether solution was dried, and benzylamine was (10 ml.) added. The sulphamide salt was precipitated; it was filtered off, washed with ether, and shaken with hydrochloric acid (2N; 200 ml.). The acidic solution was extracted with ether (4 × 100 ml.) and the combined extracts were dried and evaporated to leave 1*H*, 3*H*-2,1,3-benzothiadiazoline 2,2-dioxide (14·2 g., 83%), m.p. 175—177° (lit.,[5] 181—183°), $\nu_{max.}$ 3280, 1600, 1485, 1330, 1160, 740, and 730 cm.$^{-1}$. If the diglyme was not rigorously dried before use, the yield was drastically reduced.

1H,3H-*Naphtho*[1,8cd][1,2,6]*thiadiazine* 2,2-*Dioxide* (II).—By the procedure of the previous experiment, 1,8-diaminonaphthalene (0·049 mole) and sulphamide (0·049 mole), gave the *naphthothiadiazine dioxide* (II) as prisms (68%), m.p. 219—222° (Found: C, 54·5; H, 3·6; N, 12·7; S, 14·2%; *m/e* 220. $C_{10}H_8N_2O_2S$ requires C, 54·5; H, 3·7; N, 12·7; S, 15·5%; *M*, 220), $\nu_{max.}$ 3210, 3180, 1600, 1310, 1150, 810, and 750 cm.$^{-1}$.

3,4-*Dihydro*-NN′-*dimethyl*-2,1,3-*benzothiadiazine* 2,2-*Dioxide*.—3,4-Dihydro-2,1,3-benzothiadiazine 2,2-dioxide (0·750 g., 5·0 mmoles) in ether (20 ml.) was treated at 0° with an excess of ethereal diazomethane. Evaporation of the solvent left the *dimethyl derivative* (0·983 g., 99%), m.p. 81—82° (from benzene) (Found: C, 49·0; H, 5·2; N, 14·0%; *m/e* 198. $C_8H_{10}O_2S$ requires C, 48·5; H, 5·1; N, 14·1%; *M* 198), $\nu_{max.}$ 1610, 1490, 1290, 1210, 1155, 870, and 730 cm.$^{-1}$, τ ($CDCl_3$) 2·9—3·4 (4H, m) and 6·73 (6H, s).

5H,7H-*Dibenzo*[d,f][2,1,3]*thiadiazepine* 2,2-*Dioxide* (VI).—A solution of 2,2′-diaminobiphenyl (9·1 g., 0·049 mole) and sulphamide (4·7 g., 0·049 mole) in dry diglyme (50 ml.) was added dropwise during 25 min. to dry diglyme (100 ml.) heated under reflux. After a further 20 min., the flask and its contents were cooled, and the solvent was distilled off at 55°/15 mm. A solution of the residue in ether (150 ml.) was shaken with aqueous sodium hydroxide (2N; 2 × 50 ml.). The aqueous solution was acidified with acetic acid and the precipitate was washed with water, dried, and crystallised from chloroform to give the *dibenzothiadiazepine dioxide* (63%), m.p. 209—212° (decomp.) (Found: C, 58·2; H, 4·1; N, 11·0; S, 12·7%; *m/e* 246. $C_{12}H_{10}N_2O_2S$ requires C, 58·5; H, 4·1; N, 11·4; S, 13·0%; *M*, 246), $\nu_{max.}$ 3250, 1490, 1290, 1150, 970, 760, and 720 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 220 (ε 15,600) and 250 nm. (7800).

Preparation of N-*Chlorinated Sulphamides*.—pp′,NN′-*Tetrachloro*-NN′-*sulphonyldianiline* (Xb). Chlorine (5·5 g.) was dissolved in aqueous sodium hydroxide (2N; 50 ml.) at 2°. Carbon tetrachloride (40 ml.), precooled to 2°, and *pp*′-dichloro-*NN*′-sulphonyldianiline (3·1 g., 0·01 mole) were added and the mixture was stirred vigorously at 2° for 4 hr. The aqueous layer was separated and shaken with carbon tetrachloride (3 × 40 ml.). The combined carbon tetrachloride layer and washings were dried and evaporated to give the *tetrachlorosulphanilide* (3·7 g., 95%), m.p. 84—85° (Found: *m/e* 383·9062. $C_{12}H_8{}^{35}Cl_4N_2O_2S$ requires *M*, 383·9061. Iodimetric analysis for chlorine, 90% of theoretical), $\nu_{max.}$ 1490, 1360, 1180, 1100, 1020, 900, 800, and 730 cm.$^{-1}$. The compound decomposed within 12 hr. at room temperature, but could be stored at −40°.

p-*Bromo*-p′,NN′-*trichloro*-NN′-*sulphonyldianiline* (Xc). By a similar procedure, *p*-bromo-*p*′-chloro-NN′-sulphonyldianiline (0·7 g.) gave the *bromotrichlorosulphanilide* (0·8 g., 97%), m.p. 90—92° (decomp.) (Found: *m/e* 432, 430, and 428. $C_{12}H_8{}^{79}Br^{35}Cl_3N_2O_2S$ requires *M*, 428), $\nu_{max.}$ 1170, 1090, 1020, 900, 800, and 730 cm.$^{-1}$.

NN′-*Dichloro*-NN′-*sulphonyldianiline* (Xa). By a similar procedure, *NN*′-sulphonyldianiline (2·4 g., 0·01 mole) gave a yellow solid (3·1 g.), m.p. 60—68° (from petroleum), which the mass spectrum showed to be a mixture of di- and tri-chlorinated sulphanilides (Found: *m/e* 354, 352, 350 (Cl_3); 320, 318, 316 (Cl_2); 283, 281 (Cl_1).

Oxidations.—*Oxidation of* NN′-*sulphonyldianiline* (IIIa). (a) *With sodium hypochlorite and sodium hydroxide*. To a stirred solution of sulphonyldianiline (5·0 g., 0·02 mole) in aqueous sodium hydroxide (N; 50 ml.) cooled to −5°, was added, dropwise, an aqueous solution of sodium hypochlorite (2·2N; 45 ml.) in aqueous sodium hydroxide (2N; 50 ml.). There was an immediate reaction. After about one-fifth of the hypochlorite had been added, the solution was shaken with ether (3 × 100 ml.); a red material was extracted. The addition of alkaline hypochlorite and extractions were repeated four times, after which no more of the red compound was being formed. The combined ether solutions were evaporated to give a red solid (1·01 g.; m.p. 85—90°), which was purified by column chromatography [basic alumina; elution with petroleum–ether (3 : 1)] to give *p*-benzoquinone anil (VIIa) (0·823 g., 23%), m.p. 102—103° (lit.,[16] 103—103·5°) (Found: C, 78·2; H, 4·9; N, 7·95%; *m/e* 183. Calc. for $C_{12}H_9NO$: C, 78·7; H, 4·9; N, 7·65%; *M*, 183), $\nu_{max.}$ 1640, 1610, 870, 790, and 690 cm.$^{-1}$, λ_{max} (EtOH) 264 (ε 17,300), 290 (13,600), and 460 nm. (3280). No azobenzene was present in the crude product mixture (t.l.c.). *NN*′-Sulphonyldianiline (0·33 g.) in aqueous sodium hydroxide (N; 50 ml.) was unchanged after 12 hr. at 30°; no aniline could be detected (t.l.c.) and sulphonyldianiline (0·32 g.) was recovered.

(b) *With sodium hypochlorite and sodium carbonate*. Aqueous sodium hypochlorite (N; 10 ml.) was added dropwise during 5 min. to a stirred solution of sulphonyldianiline (1·4 g., 0·006 mole) in aqueous sodium carbonate (2N; 100 ml.). The mixture was shaken with ether (3 × 100 ml.). From the ethereal layer was obtained an oil (0·108 g.) which, when chromatographed on silica (eluant benzene), gave *p*-benzoquinone anil (30 mg., 2·7%), m.p. 99—100°. The aqueous layer was saturated with sodium chloride, but

[16] H. J. Teuber and G. Staiger, *Chem. Ber.*, 1954, **87**, 1251.

there was no precipitate. The solution was acidified with 2M-hydrochloric acid and shaken with ether to give a gum (658 mg.). Recrystallisation from benzene gave *5H,7H*-dibenzo[*df*][2,1,3]thiadiazepine 2,2-dioxide (VI) (453 mg., 32%), m.p. and mixed m.p. 211—213°.

Oxidation of pp′-*dichloro*-NN′-*sulphonyldianiline* (IIIb). (*a*) A solution of dichlorosulphonyldianiline (0·160 g., 0·50 mmole) in aqueous sodium hydroxide (2N; 50 ml.) was oxidised with aqueous sodium hypochlorite (N; 5 ml.) as already described. Chromatography of the ether-soluble product on neutral alumina gave (elution with petroleum) *pp′*-dichloroazobenzene (3·0 mg., 1·2%), m.p. and mixed m.p. 185—187° (lit.,[17] 188°) and (elution with benzene) *N*-(*p*-chlorophenyl)-*p*-benzoquinone imine (22 mg., 20%), m.p. 82—83° (lit.,[7] 83·5°).

(*b*) *With t-butyl hypochlorite.* To a solution of t-butyl hypochlorite (0·182 g., 2 mmoles) and *pp′*-dichloro-*NN′*-sulphonyldianiline (0·534 g., 2 mmoles) in dry benzene at 5°, potassium t-butoxide (2 mmole) in t-butyl alcohol (20 ml.) was added. Chromatography of the product on silica gave (elution with petroleum) *pp′*-dichloroazobenzene (0·079 g., 19%), m.p. and mixed m.p. 183—185°.

Oxidation of p-*bromo*-p′-*chloro*-NN′-*sulphonyldianiline* (IIIc) *with t-butyl hypochlorite.* Under similar conditions to those (*b*) just described, bromochlorosulphonyldianiline (0·093 g., 0·26 mmole) gave a mixture of *pp′*-dihalogenated azobenzenes (0·012 g., 15%), *m/e* 342, 340, 338 ($C_{12}H_8Br_2N_2$); 298, 296, 294 ($C_{12}H_8BrClN_2$); 254, 252, 250 ($C_{12}H_8Cl_2N_2$); ion currents in the ratio 1·3 : 2·4 : 1·0 for the three groups of peaks.

Oxidation of mm′-*dimethyl*-NN′-*sulphonyldianiline* (IVb) *with sodium hypochlorite.* Aqueous sodium hypochlorite (2N; 5 ml.) was added dropwise to a solution of dimethylsulphonyldianiline (0·94 g., 3·4 mmoles) in aqueous sodium hydroxide (N; 50 ml.) under ether (100 ml.), stirred at 5°. After 10 min., the aqueous layer was separated and shaken with more ether (3 × 50 ml.), and the combined ethereal extracts were dried and evaporated to leave an oil (85 mg.). Chromatography on silica gave (elution with benzene) m-*methyl*-N-(m-*tolyl*)-p-*benzoquinone imine* (VIIc) (0·065 g., 9%), m.p. 37—39° (decomp.) (Found: C, 79·1; H, 5·9; N, 6·0. $C_{14}H_{13}NO$ requires C, 79·6; H, 6·2; N, 6·6%), $\nu_{max.}$ 1640, 1620, 1580, 1290, 1090, 800, and 690 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 265 (15,000), 285 (10,200), and 463 nm. (2100), τ ($CDCl_3$) 2·7—3·7 (7H, m), 7·63 (3H, s), and 7·73 (3H, s).

Oxidation of m-*methyl*-NN′-*sulphonyldianiline* (IVa) *with sodium hypochlorite.* By a similar procedure, *m*-methyl-*NN′*-sulphonyldianiline (0·48 g., 1·85 mmole) gave a mixture of quinone anils (0·076 g.) which were not separated by chromatography on silica. The mixture was analysed by mass spectrometry: *m/e* 212, 211, 198, 197, 196, 185, 183, 182; ratio of ion currents for *m/e* 211 : 197 : 183 = 19 : 33 : 18. The mass spectrum of *m*-methyl-*N*-(*m*-tolyl)-*p*-benzoquinone imine (VIIc) showed *m/e* 211 but no ions at *m/e* 197 and 183.

Oxidation of Cyclic Sulphamides with Sodium Hypochlorite.—(a) 1H,3H-2,1,3-*Benzothiadiazoline* 2,2-*dioxide* (V). Aqueous sodium hypochlorite (0·42 M; 3·6 ml., 1·51 mmole) was added during 5 min. to a stirred, cooled (0°) solution of benzothiadiazoline dioxide (0·506 g., 2·98 mmoles) in aqueous sodium hydroxide (2N; 10 ml.). The mixture was then stirred for a further 3 min., acidified with 2N-hydrochloric acid, and extracted with ether. The extract was immediately treated with an excess of ethereal diazomethane, evaporated to dryness, and chromatographed on silica to give (i) *NN′*-dimethyl-2,1,3-benzothiadiazoline 2,2-dioxide (0·118 g., 20%), needles, m.p. and mixed m.p. 81—82°, identical (i.r. spectrum and t.l.c.) with an authentic specimen; and (ii) 1,3-*dimethyl*-4 *or* 5-(3-*methyl*-2,1,3-*benzothiadiazolin*-1-*yl*)-2,1,3-*benzothiadiazoline* SSS′S′-*tetroxide* (IXb) (0·385 g., 67%), m.p. 180—190° (decomp.) (from benzene–cyclohexane) (Found: C, 47·7; H, 4·3; N, 14·6%; *m/e* 380. $C_{15}H_{16}N_4O_4S_2$ requires C, 47·4; H, 4·2; N, 14·7%; *M*, 380), $\nu_{max.}$ 1600, 1480, 1320—1260, 1150, 850, and 745 cm.$^{-1}$, τ ($CDCl_3$) 6·77, 6·73, and 6·72 (9H, 3 × s, unresolved), and 2·7—3·6 (7H, m). Oxidation of benzothiadiazoline dioxide (0·6 g., 3·5 mmoles) under similar conditions, with an excess (5-fold) of sodium hypochlorite, gave a polymeric solid on ethereal extraction (0·6 g., 100%), m.p. 140—160° (charred) (Found: C, 42·6; H, 3·7; N, 14·1; S, 17·9%; *m/e* 64), $\nu_{max.}$ 3520, 3180, 2660, 1720, 1600, 1260, 1150, and 740 cm.$^{-1}$, τ [$(CD_3)_2CO$] 5·1 (1H, exchangeable), 2·6—3·4 (4·5H, m), and 0·0 (1H, exchangeable), $\lambda_{max.}$ (EtOH) 210 ($E^{1\%}_{1\,cm.}$ 1·39 × 10^7) and 288 nm. (2·1 × 10^6). Methylation of the polymer with diazomethane gave (quantitatively) a further polymer m.p. 185—195° (decomp.) [Found: C, 46·4; H, 3·8; S, 17·3%; *m/e* 64. $(C_7H_6N_2O_2S)_n$ requires C, 46·2; H, 3·3; S, 17·6%], $\nu_{max.}$ 1730, 1600, 1480, 1320, 1270, 1150, and 740 cm.$^{-1}$, τ ($CDCl_3$) 4·65 and 4·75 (3H, 2 × s, unresolved), and 2·8—3·4 (3·8H, m).

(b) 1H,3H-*Naphtho*[1,8-cd][1,2,6]*thiadiazine* 2,2-*dioxide* (II). Under similar conditions, the sulphamide (1·1 g., 5 mmoles) gave a solid (1·1 g.), decomp. <290°. The reaction was repeated in the presence of an excess of 2,3,4,5-tetraphenylcyclopentadienone, which was recovered; the same solid was formed.

(c) 5H,7H-*Dibenzo*[d,f][2,1,3]*thiadiazepine* 2,2-*dioxide* (VI). Under similar conditions, the sulphamide (0·700 g., 2·8 mmoles) in aqueous sodium hydroxide (2M; 20 ml.) gave with aqueous sodium hypochlorite (2M; 7 ml.) a yellow solid (80 mg.). Chromatography of the solid on silica gave [elution with benzene–ether (20 : 1)] 2-chlorobenzo[*c*]cinnoline (0·024 g., 4%), m.p. 213—214° (lit.,[18] 211°; lit.,[19] 215·5—216°) (Found: C, 66·6; H, 3·4; N, 12·8%; *m/e* 216, 214. Calc. for $C_{12}H_7ClN_2$: C, 67·2; H, 3·3; N, 13·1%; *M*, 214), $\nu_{max.}$ 1615, 1600, 1575, 1550, 820, 780, and 750 cm.$^{-1}$, τ ($CDCl_3$) 1·11—1·67 (m, 4H), and 1·92—2·35 (m, 3H); and benzo[*c*]cinnoline (0·010 g., 2%), m.p. 150—155° (t.l.c., i.r. spectrum). Acidification of the aqueous layer and extraction with ether gave starting material (0·242 g., 35%).

Thermolysis of N-*Chlorinated Sulphamides.*—NN′-*Dichloro*-NN′-*sulphonyldianiline* (Xa). The crude *NN′*-dichlorosulphanilide, m.p. 60—68° (0·145 g.) was heated under reflux in dry carbon tetrachloride (25 ml.) for 12 hr. Chromatography of the product on silica gave [with petroleum–ether (10 : 1)] azobenzene (0·019 g., 23%) and (with ether) sulphanilide (0·040 g.).

pp′,NN′-*Tetrachloro*-NN′-*sulphonyldianiline* (Xb). The sulphanilide (1·05 g., 2·75 mmoles) was heated under reflux in carbon tetrachloride (50 ml.) for 24 hr. Chlorine was evolved. Chromatography of the product on neutral alumina gave [elution with petroleum–ether (20 : 1)]

[17] J. Burns, H. McCombie, and H. A. Scarborough, *J. Chem. Soc.*, 1928, 2928.

[18] D. Jerchel and H. Fischer, *Annalen*, 1954, **590**, 216.

[19] G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1964, **17**, 1036.

pp'-dichloroazobenzene (0·246 g., 36%), m.p. and mixed m.p. 184—185°.

p-*Bromo*-p',NN'-*trichloro*-NN'-*sulphonyldianiline* (Xc). Under the same conditions, the sulphanilide (0·430 g., 1 mmole) gave a mixture of azobenzenes (0·055 g., 26%), *m/e* 343, 341, 339 (Br_2); 298, 296, 294 (Br_1Cl_1); 254, 252, 250 (Cl_2) with total ion currents in the ratio 5 : 16 : 8.

Photolysis of Sulphamides.—(a) NN'-*Sulphonyldianiline* (IIIa). The sulphanilide (0·873 g., 3·5 mmoles) in dry, deoxygenated methanol (100 ml.) was irradiated with a Hanovia medium-pressure lamp (100 w) in quartz for 8 hr. T.l.c. indicated the presence of azobenzene, hydrazobenzene, and aniline. The volume of the solution was reduced to 5 ml. and aniline (0·88 g., 27%) was estimated by g.l.c. (Carbowax–KOH–Chromosorb W, 8 : 2 : 90). The solution was evaporated to dryness and partitioned between aqueous sodium hydroxide and ether. The ether layer was washed with dilute hydrochloric acid and water, and evaporated to give azobenzene (0·090 g., 14%), m.p. and mixed m.p. 65—68°. Acidification of the aqueous layer gave sulphanilide (0·177 g., 20% recovery).

(b) m-*Methyl*-NN'-*sulphonyldianiline* (IVa). *m*-Methylsulphonyldianiline (0·635 g., 2·4 mmoles) irradiated under identical conditions gave starting material (15% recovery), *m*-methylazobenzene (0·080 g., 17%), m.p. 15—17°, *m/e* 196, 182, 181, 91, and 77, and a basic oil (0·085 mg., 35%), whose i.r. spectrum was consistent with the presence of a mixture of aniline and *m*-toluidine (*ca.* 1 : 1).

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