Proximity Effects in Diaryl Derivatives. Part IV.[1] Base-catalysed Reactions of 2,2′-Di(hydroxyamino)diaryl Sulphones and of 2-(Hydroxyamino)aryl Phenyl Sulphones

By M. F. Grundon, B. T. Johnston, and W. L. Matier

Reaction of 2,2′-di(hydroxyamino)diaryl sulphones with sodium hydroxide in aqueous dioxan at 20° yields dibenzo [*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxides (X), phenazine 5-oxides (XIV), and phenazine 5,10-dioxides (XV). The formation of the phenazine derivatives probably involves disproportionation of the aryl hydroxylamines, followed by Smiles rearrangement, and then loss of the sulphino-group. In the presence of zinc, the arylhydroxylamines are converted into phenazines (IV) and thiadiazepine 11,11-dioxides (VII). The mechanism of the alkaline reduction of 2,2′-dinitrodiaryl sulphones [1] is discussed in the light of these results. Some of this work has been reported.[2]

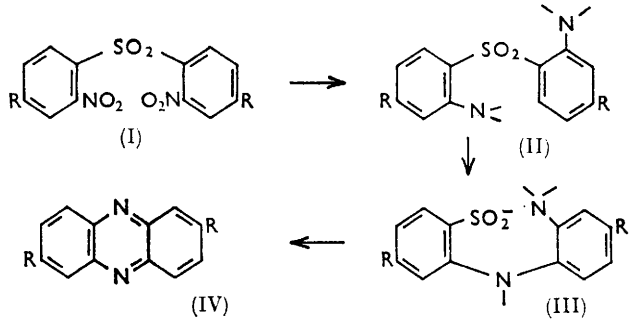
Treatment of 2-(hydroxyamino)aryl phenyl sulphones with sodium hydroxide at 20° results in loss of the phenylsulphonyl group. For example, 6-chloro-2-(hydroxyamino)diphenyl sulphone affords sodium benzenesulphinate and 3,3′-dichloroazoxybenzene. Cleavage of a C–S bond does not occur in 4-(hydroxyamino)diphenyl sulphone. Possible mechanisms for the reaction are discussed.

In Part III,[1] we described the formation of phenazines (IV) by reduction of 2,2′-dinitrodiaryl sulphones (I) with zinc and sodium hydroxide at 20°, and the general mechanism given below was suggested. It was shown that 2-amino-2′-nitrodiaryl sulphones were not intermediates, and did not undergo rearrangement (II) ⟶ (III) under our conditions. In a further search for intermediates, (II), we have studied the base-catalysed reactions of 2,2′-di(hydroxyamino)diaryl sulphones (V). The simplest member of this series (V; R = H) was

[1] Part III, M. F. Grundon and B. T. Johnston, preceding Paper.

[2] M. F. Grundon, B. T. Johnston, and W. L. Matier, *Chem. Comm.*, 1965, 67.

prepared by reduction of 2,2′-dinitrodiphenyl sulphone (I; R = H) with Raney nickel and hydrogen,[3] and Michel and Matter [4] improved this preparation by using platinum and hydrogen in tetrahydrofuran. Employing the latter procedure, we find that the dinitro-derivatives



(I; R = H, Cl, and Me) absorb only 4 mols. of hydrogen at room temperature and give the di(hydroxyamino)-diaryl sulphones (V; R = H, Cl, and Me) quantitatively. The structure of compound (V; R = H) was confirmed by reaction with peroxyacetic acid (1 mol.) to give dibenzo-[*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxide (X; R = H) in high yield; the product is formed, presumably, *via* the nitrosophenylhydroxylamine (IX; R = H).

When the 2,2′-di(hydroxyamino)diaryl sulphones (V; R = H, Cl, and Me) were stirred vigorously with sodium hydroxide in aqueous dioxan at 20° under nitrogen, the solutions became coloured immediately, and after 15 min. the non-acidic products were isolated, and were separated by chromatography on alumina.

Thiadiazepine derivatives were obtained in all reactions (Table 1). The three di(hydroxyamino)-compounds gave the trioxides (X; R = H, Cl, and Me, respectively) and in one case, the corresponding dioxide (VII; R = H) was also isolated. The formation of these azo- and azoxy-derivatives suggests that disproportionation of the di(hydroxyamino)-compounds is a key step in the reaction. Bamberger and Brady [5] showed that, in the absence of oxygen, phenylhydroxylamine with aqueous alkali at 20° afforded aniline and azoxybenzene in accord with the equation:

$$3\ \mathrm{Ph{\cdot}NHOH} \longrightarrow \mathrm{PhNH_2} + \mathrm{PhN{=}\overset{+}{N}{-}Ph}\ (\mathrm{O^-})$$

Nitrosobenzene is presumably produced initially and then reacts with phenylhydroxylamine to give azoxybenzene. Analogous base-catalysed reactions of the di(hydroxyamino)-derivatives (V) can account for the formation of the observed products. We suggest that rapid disproportionation occurs, in which intermolecular reaction giving the nitrosohydroxylamines (IX) and the amino-hydroxylamines (VIII) competes with an intramolecular process yielding the aminonitroso-derivative (VI). The azo- and azoxy-products could then arise by addition of amino- or hydroxyamino-groups to nitroso-substituents (by a heterolytic or radical [6] mechanism). In this way, the aminonitroso-compounds (VI) and the nitrosohydroxylamines (IX) can yield, respectively, the thiadiazepine derivatives (VII) and (X). The nitrosohydroxylamine intermediates (IX) could also arise by oxidation of the di(hydroxyamino)-derivatives with oxygen, but this seems unlikely to be a major route, since the reactions described above were conducted under nitrogen, and the yield of trioxide (X; R = Cl) from (V; R = Cl) was not increased by exposing the reaction mixture to air.

TABLE 1

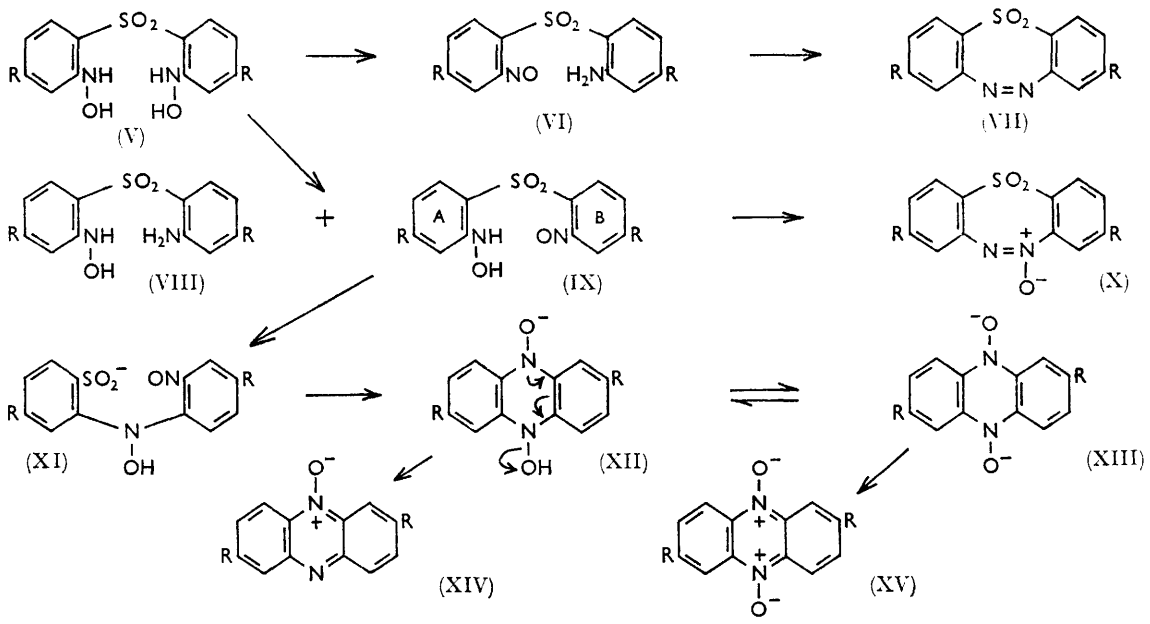
Reactions of 2,2′-di(hydroxyamino)diaryl sulphones (V) in aqueous dioxan at 20°

Starting compound	Reagent	Yield (%) of thiadiazepine trioxide (X)	thiadiazepine dioxide (VII)	phenazines (IV)	phenazine 5-oxides (XIV)	phenazine 5,10-dioxides (XV)
(V; R = H)	OH^-	10	14	—	19	9
(V; R = Cl)	OH^-	32	—	—	15	15 *
(V; R = Me)	OH^-	22	—	—	—	9
(V; R = H)	Zn/OH^-	—	5	35	—	—
(V; R = Cl)	Zn/OH^-	—	1	21	—	— †
(V; R = Me)	Zn/OH^-	—	5	7	—	— ‡

* When the reaction mixture was exposed to air, the thiadiazepine trioxide was obtained in 29% yield. † 2,2′-Diamino-4,4′-dichlorodiphenyl sulphone (18%) was also isolated. ‡ 2,2′-Diamino-4,4′-dimethyldiphenyl sulphone (37%) was also isolated.

Phenazine 5-oxides (XIV) and 5,10-dioxides (XV) are other major products of the reaction of di(hydroxyamino)-derivatives with alkali (Table 1). We believe that the phenazine oxides are also derived from the disproportionation products (IX), and one possible route is suggested in the Scheme. In alkaline solutions of hydroxylamines, the species $-NHOH$ and $-\overline{N}OH$ are presumably in equilibrium with the predominant form, $-NHO^-$, but, for simplicity of presentation, some of the participating species, for example of compound (IX), have been omitted from the diagram. The stage (IX) ⟶ (XI) is in intramolecular nucleophilic rearrangement of the type investigated extensively by

[3] H. H. Szmant and R. L. Lapinski, *J. Amer. Chem. Soc.*, 1956, **78**, 458; H. H. Szmant and T.-L. Chow, *ibid.*, 1957, **79**, 5584.
[4] K. Michel and M. Matter, *Helv. Chim. Acta*, 1961, **44**, 2204.
[5] E. Bamberger and F. Brady, *Ber.*, 1900, **33**, 271.
[6] C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, 1965, 751; E. J. Geels, R. Konaka, and C. A. Russell, *Chem. Comm.*, 1965, 13.



Scheme

Smiles and his collaborators.[7] The Smiles rearrangement of *o*-aminodiaryl sulphones is catalysed by strong bases and probably involves attack of $\geq N^-$ at the carbon atom of a C–S bond. Rearrangement at room temperature normally requires the presence of two extra activating groups (usually NO_2) in ring B [cf. (IX)], and the extraordinary facility of the present reaction can be attributed to special factors, for example, the presence of a nitroso-group *ortho* to the position of nucleophilic attack. Few nucleophilic substitutions activated by nitroso-groups have been reported, but the group is possibly more electron-attracting than a nitro-substituent.[8] Secondly, the hydroxyamino-group may be particularly effective in the rearrangement, since the transition state involving the nucleophilic nitrogen can be stabilised by electron-donation from the adjacent oxygen atom (the alpha effect[9]). The fate of the sulphino-group has not yet been established, but the reaction, (XI) ⟶ (XII), of the intermediate sulphinates may be analogous to the formation of chloromercuribenzenes from sodium phenylsulphinates :[10]

$$ArSO_2^-Na^+ + HgCl_2 \longrightarrow ArHgCl + SO_2 + NaCl$$

Subsequently, phenazine 5-oxides (XIV) could arise by elimination from the dihydroxydihydrophenazines (XII) as shown, and there are many analogies for this process.[11] Successive one-electron oxidations of the dianion (XII) could give phenazine dioxides (XV). This apparently occurs in the course of the reaction rather than during work-up, because treatment of the dichloro-derivative (V; R = Cl) with alkali soon yields a precipitate of 2,7-dichlorophenazine 5,10-dioxide (XV; R = Cl); recent results show that radicals are indeed formed from arylhydroxylamines and nitrosobenzenes in alkaline solution.[6]

The results described above have an important bearing on the conversion of 2,2′-dinitrodiaryl sulphones (I) into phenazines (IV) by reaction with zinc and alkali, and it was of interest therefore to study the reduction of 2,2′-di(hydroxyamino)diaryl sulphones (V). The latter compounds (V; R = H, Cl, and Me) were treated with sodium hydroxide in aqueous dioxan at 20° under nitrogen in the presence of an excess of zinc. Chromatography of the non-acidic fraction yielded a variety of products (Table 1). Thus, 2,2′-diaminodiaryl sulphones were identified, and were major products after longer periods of reduction. In contrast to the reactions of di(hydroxyamino)-derivatives with alkali alone, the thiadiazepine trioxides (X) were not isolated, but the corresponding dioxides (VII) were obtained in each case. These azo-derivatives (VII) could arise either from the disproportionation intermediates (VI) or by reduction of the azoxy-derivatives (X). The latter pathway is probably more important, since the azoxy-compounds are formed rapidly in the absence of zinc (see above), and were shown previously[1] to afford the corresponding azo-derivatives (VII) when reduced with zinc and alkali. Phenazine 5-oxides or 5,10-dioxides were not formed in the reactions of the di(hydroxyamines) (V; R = H, Cl, and Me) with zinc and alkali, but phenazines (IV) were isolated in 7—35% yields. Phenazines probably arise by reduction of intermediates (XII) or products (XIV) and (XV) of the alkali-catalysed reaction. We

[7] S. Smiles *et al.*, *J. Chem. Soc.*, 1931, 914, and succeeding Papers; J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273.

[8] R. J. W. Le Fèvre, *J. Chem. Soc.*, 1931, 810, but cf. C. W. L. Bevan, J. Hirst, and A. J. Foley, *J. Chem. Soc.*, 1960, 4543.

[9] J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16; W. P. Jencks and J. Carriuolo, *ibid.*, 1960, **82**, 1778.

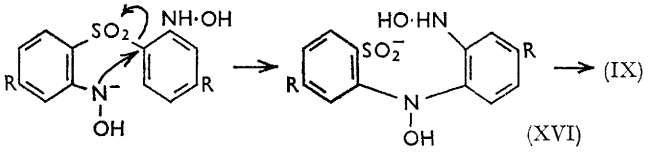
[10] W. J. Evans and S. Smiles, *J. Chem. Soc.*, 1935, 181.

[11] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389.

have confirmed that these products, phenazine 5-oxides (XIV) and 5,10-dioxides (XV), are readily reduced to phenazines by zinc and alkali; in the course of the reactions the solutions became colourless, suggesting that dihydrophenazines are formed first, and then are oxidised to phenazines during isolation.

The results imply that similar mechanisms, involving arylhydroxylamines, operate in the reductive rearrangement of 2,2′-dinitrodiaryl sulphones to phenazines,[1] but in this case several routes are available and may be followed simultaneously. For example, nitroso-hydroxylamines (IX) are again likely to be key intermediates, but they may be produced either by direct reduction of the dinitro-compounds or by alkali-catalysed disproportionation of di(hydroxyamino)-derivatives. An alternative pathway to the nitrososulphinates (XI) and hence to phenazines may involve intramolecular rearrangement of a 2-hydroxyamino-2′-nitrodiaryl sulphone (IX; NO_2 instead of NO) to a sulphinate (XI; NO_2 instead of NO), followed by partial reduction of the nitro-group.

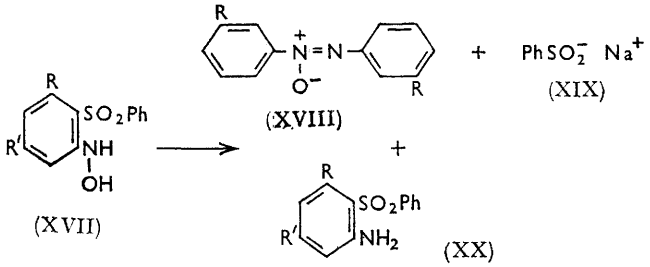
An alternative route to phenazine oxides from 2,2′-di(hydroxyamino)diaryl sulphones (V) might involve direct Smiles rearrangement to the (hydroxyamino)sulphinate (XVI), followed by disproportionation to the nitrososulphinate (IX):



We decided to explore the possibility of such an unactivated rearrangement by studying the base-catalysed reactions of 2-(hydroxyamino)diaryl sulphones (XVII), in which one aryl ring is inow unsubstituted.

Arylhydroxylamines (XVII) were prepared quantitatively by catalytic reduction of the corresponding 2-nitrodiaryl sulphones. They were treated with sodium hydroxide in aqueous dioxan at 20° under nitrogen, but none of the identified products arose by Smiles rearrangement. We conclude that the analogous unactivated rearrangement (V) ⟶ (XVI) is unlikely to occur readily, and we favour, therefore, the pathway (V) ⟶ (IX) ⟶ (XI) ⟶ (XV) for the formation of phenazine oxides from 2,2′-di(hydroxyamino)diaryl sulphones.

Base-catalysed reactions of 2-(hydroxyamino)diaryl sulphones proved to be of intrinsic interest, and we now report a study of the products derived from the compounds (XVII; R = R′ = H; R = Cl; R′ = H; and R = H, R′ = Cl) (Table 2). In each case, the



corresponding aminodiaryl sulphones (XX) were formed, and originate probably by disproportionation of the arylhydroxylamines:[5]

$$2\text{Ar·NHOH} \longrightarrow \text{ArNH}_2 + \text{ArNO}$$

2-(Hydroxyamino)diphenyl sulphone also furnished 2-nitrodiphenyl sulphone, perhaps by oxidation of the second disproportionation product, 2-nitrosodiphenyl sulphone.

The disproportionation was accompanied by a remarkable reaction involving loss of the phenylsulphonyl group. For example, reaction of the chloroarylhydroxylamine (XVII; R = Cl, R′ = H) with sodium hydroxide gave sodium benzenesulphinate (XIX) in 44% yield; the product rapidly precipitated from the aqueous dioxan solution, and a further quantity was detected in the alkaline layer by methylation with methyl iodide to methyl phenyl sulphone. A major product (30%) lacking the phenylsulphonyl group was 3,3′-dichloroazoxybenzene (XVIII; R = Cl). The 2-hydroxyamino-derivatives (XVII; R = R′ = H) and (XVII; R = H, R′ = Cl) behaved similarly, and yielded sodium benzenesulphinate; the corresponding sulphur-free products were azoxybenzene and 3,3′-dichloroazoxy benzene, respectively (Table 2). More of the latter compound was obtained when the reaction was conducted in aqueous 2-methoxyethanol instead of in aqueous dioxan.

We tentatively suggest the following mechanism in which rearrangement of the anion (XXI) to the *o*-phenylsulphonylarylhydroxylamine derivative (XXII) is followed by formation of the nitrosobenzene (XXIII), which subsequently affords the azoxybenzene (XVIII). The arrangement involves attack of $^-O^-$ on the sulphur

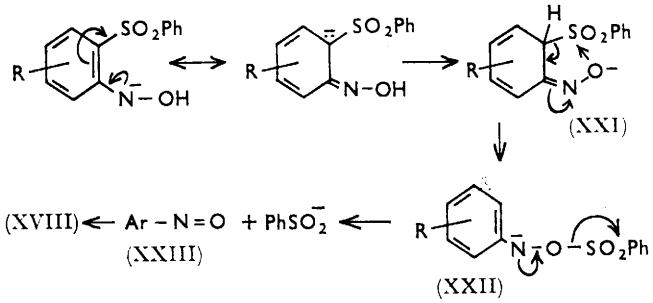
TABLE 2

Reactions of 2-(hydroxyamino)aryl phenyl sulphones (XVII) with sodium hydroxide at 20°

Starting compound	Solvent	Yield (%) of aminodiaryl sulphone (XX)	Yield (%) of sodium phenylsulphinate *	Yield (%) of azoxybenzene (XVIII)
(XVII; R = R′ = H)	Aq. dioxan	10	40	4 †
(XVII; R = Cl, R′ = H)	Aq. dioxan	16	44	30
(XVII; R = H, R′ = Cl)	Aq. dioxan	10	24	2
(XVII; R = H, R′ = Cl)	Aq. 2-methoxy-ethanol	14	29	9

* Usually estimated as methyl phenyl sulphone. † 2-Nitrodiphenyl sulphone (7%) was also isolated.

atom of a sulphone group. This is a well-known reaction of N–SO_2, O–SO_2, and Cl–SO_2 groups [12] but is rarely encountered when the sulphonyl group is attached to

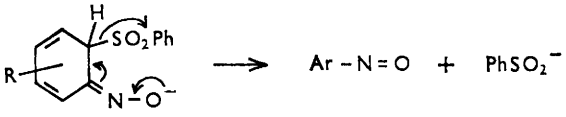


carbon; it has been invoked [13] to rationalise the rearrangement of αα′-dichlorosulphones by means of an episulphone intermediate. The elimination (XXII) ⟶ (XXIII) has some analogy with the reaction of *N*-phenylsulphonylphenylhydroxylamine with alkali: [14]

$$Ph{-}\underset{\displaystyle OH}{\underset{|}{N}}{-}SO_2Ph \longrightarrow PhNO + PhSO_2^-$$

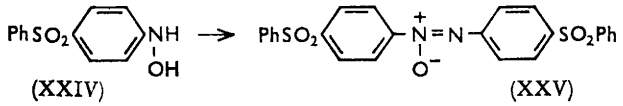
In the latter case, nitrosobenzene was a stable product of the reaction. This seems at first to exclude a nitrosobenzene (XXIII) as an intermediate in the reaction of 2-(hydroxyamino)diaryl sulphones with alkali. However, when an alkaline solution of an arylhydroxylamine, ArNHOH, reacts with a nitrosobenzene, Ar′NO, mutual oxidation–reduction takes place, and a mixture of azoxybenzenes usually results.[15] In the presence of a reducing agent, for example the arylhydroxylamine (XVII), the intermediate nitroso-derivative (XXIII) would be expected to behave similarly, and yield the azoxybenzene (XVIII) as one product. We find, indeed, that although an alkaline solution of *m*-chloronitrosobenzene is stable at 20°, addition of the reducing agent, hydroxylamine (NH_2OH), gives 3,3′-dichloroazoxybenzene.

An alternative mechanism for the loss of the phenylsulphonyl group from arylhydroxylamines (XVII) involves ejection of the substituent by electron-donation from the anion (XXI):



In contrast to the previous mechanism, this process does not require a cyclic transition state, and should be applicable to a *para*-substituted derivative. We decided to test this possibility. 4-(Hydroxyamino)-diphenyl sulphone (XXIV), prepared by reduction of the corresponding nitro-derivative with zinc and ammonium chloride, was treated with alkali. The azoxy-derivative (XXV) was obtained in high yield, and cleavage of a C–S bond was not observed. This result does not exclude the ejection mechanism, since the reaction leading to the azoxy-derivative (XXV) may in this case compete particularly successfully with other processes, but it does favour the cyclic mechanism.

We are at present exploring further the scope and mechanism of the reaction.



EXPERIMENTAL

Spence type H alumina was used. Dioxan was passed through an alumina column and distilled.

2,2′-Di(hydroxyamino)diaryl Sulphones.—The products were obtained quantitatively by the method of Michel and Matter.[3] 2,2′-Di(hydroxyamino)diphenyl sulphone separated from acetone in prisms, m. p. 126—127° (decomp.) (lit.,[3] m. p. 126—127°). *4,4′-Dichloro-2,2′-di(hydroxyamino)diphenyl sulphone* crystallised from isopropyl ether in prisms, m. p. 129—130° (decomp.) (Found: C, 41·7; H, 3·0; N, 7·8. $C_{12}H_{10}Cl_2N_2O_4S$ requires C, 41·3; H, 2·9; N, 8·0%), and *2,2′-di(hydroxyamino)-4,4′-dimethyldiphenyl sulphone* in prisms, m. p. 129—130° (decomp.) (Found: C, 54·3; H, 5·2. $C_{14}H_{16}N_2O_4S$ requires C, 54·5; H, 5·2%).

A solution of 2,2′-di(hydroxyamino)diphenyl sulphone (1 g.) in acetic acid (20 ml.) containing 3% aqueous hydrogen peroxide (3·6 ml., 1 mol.) was kept at 20° for 3 days. The precipitate of dibenzo[*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxide (667 mg., 72%), m. p. 254—257°, was identical (mixed m. p. and infrared spectrum) with an authentic sample.[1]

Reactions of 2,2′-Di(hydroxyamino)diaryl Sulphones with Sodium Hydroxide.—The 2,2′-di(hydroxyamino)diaryl sulphone (1 g.), dioxan (50 ml.), and 40% aqueous sodium hydroxide (20 ml.) under nitrogen was stirred vigorously at 20° for 15 min. Any precipitate was filtered off, and the lower alkaline aqueous layer was separated. The dioxan layer was evaporated under reduced pressure, the residue in methylene chloride was washed with water, and the solvent was evaporated.

In the case of 4,4′-dichloro-2,2′-di(hydroxyamino)diphenyl sulphone, a precipitate of 2,7-dichlorophenazine 5,10-dioxide formed during the reaction, and separated from acetic acid in red needles (70 mg.), m. p. 228—230° (decomp.). Chromatography of the remaining product on alumina and elution with benzene furnished 2,7-dichlorophenazine 5-oxide, obtained from benzene in yellow needles (112 mg.), m. p. 237—238° (decomp.). Elution with methylene chloride–benzene (1 : 1) gave a further quantity (49 mg.) of 2,7-dichlorophenazine 5,10-dioxide. Elution with chloroform gave 3,8-dichlorodibenzo[*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxide, separating from chloroform in yellow prisms (305 mg.), m. p. 246—248°.

Products from other di(hydroxyamino)-derivatives (Table 1) were separated similarly. All products were compared (mixed m. p. and infrared spectra) with authentic samples, except *2,7-dimethylphenazine 5,10-dioxide*, which is new; it separated from ethanol in red needles, m. p. 201—203° (decomp.) (Found: C, 69·9; H, 5·0. $C_{14}H_{12}N_2O_2$ requires C, 70·0; H, 5·0%).

Reduction of 2,2′-Di(hydroxyamino)diaryl Sulphones.—

[12] D. Klamann and H. Bertsch, *Chem. Ber.*, 1958, **91**, 212, 1427; R. V. Vizzert, *Russ. Chem. Rev.*, 1963, **32**, 1.
[13] F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 5187; L. A. Paquette, *ibid.*, 1964, **86**, 4089.
[14] O. Piloty, *Ber.*, 1896, **29**, 1559.
[15] T. W. J. Taylor and W. Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford, 1942, p. 427; W. Anderson, *J. Chem. Soc.*, 1952, 1722.

A mixture of the sulphone (1 g.), dioxan (50 ml.), 40% aqueous sodium hydroxide (20 ml.), and zinc dust (2 g.) under nitrogen was stirred at 20° for 15 min. to 3 hr. After filtration, the mixture was treated as described for the reaction in the absence of zinc, and the products were separated by chromatography on alumina. The products (Table 1) were identical (mixed m. p. and infrared spectra) with authentic samples.

Reduction of Phenazine Oxides.—A mixture of phenazine 5,10-dioxide [16] (150 mg.), zinc dust (1 g.), dioxan (25 ml.), and 40% aqueous sodium hydroxide (10 ml.) under nitrogen was stirred at 20° for 3 hr. After filtration, the colourless solution was added to water to give a colourless precipitate which became coloured rapidly. When a solution of the solid in methylene chloride was passed through an alumina column, phenazine (130 mg.), m. p. and mixed m. p. 171—173°, was obtained.

Reduction of phenazine 5-oxide (61 mg.) for 30 min. afforded phenazine (40 mg., 70%), m. p. and mixed m. p. 168—172°.

Nitroaryl Phenyl Sulphides and Sulphones.—The nitroaryl phenyl sulphides were prepared by refluxing a solution of thiophenol (0·3 mole), the appropriate chloronitrobenzene (0·3 mole) and sodium carbonate (0·375 mole) in 50% aqueous ethanol (300 ml.) for 12 hr. 2-Nitrodiphenyl sulphide was obtained from ethanol in yellow prisms (85%), m. p. 78—80° (lit.,[17] m. p. 79°), 4-nitrodiphenyl sulphide from light petroleum (b. p. 60—80°) in yellow needles (78%), m. p. 55—56° (lit.,[18] m. p. 55°), 4-chloro-2-nitrodiphenyl sulphide from ethanol in yellow prisms (82%), m. p. 81—83° (lit.,[19] m. p. 84°), and 6-*chloro*-2-*nitrodiphenyl sulphide* from ethanol in yellow prisms (75%), m. p. 73—74° (Found: C, 54·3; H, 3·0; N, 5·4. $C_{12}H_8ClNO_2S$ requires C, 54·3; H, 3·0; N, 5·3%).

Refluxing a solution of the nitroaryl phenyl sulphides (0·1 mole) in acetic acid (250 ml.) containing 30% hydrogen peroxide (50 ml.) furnished the corresponding sulphones. 2-Nitrodiphenyl sulphone was obtained from ethanol in needles (95%), m. p. 147° (lit.,[20] m. p. 147·5°), 4-nitrodiphenyl sulphone from methylene chloride–isopropyl ether in needles (85%), m. p. 142—143° (lit.,[20] m. p. 143°), 4-chloro-2-nitrodiphenyl sulphone from ethanol in needles (82%), m. p. 121° (lit.,[21] m. p. 121°), and 6-*chloro*-2-*nitrodiphenyl sulphone* from ethanol in needles (90%), m. p 116—117° (Found: C, 48·5; H, 2·7; N, 4·9. $C_{12}H_8ClNO_4S$ requires C, 48·4; H, 2·7; N, 4·7%).

2-(*Hydroxyamino*)*aryl Phenyl Sulphones.*—Catalytic reduction of the appropriate 2-nitroaryl phenyl sulphones by the method described for the preparation of 2,2′-di(hydroxyamino)diaryl sulphones gave the 2-hydroxyamino-derivatives quantitatively. 2-(*Hydroxyamino*)*diphenyl sulphone* separated from isopropyl ether in prisms, m. p. 152—154° (decomp.) (Found: C, 57·5; H, 4·5; N, 5·7. $C_{12}H_{11}NO_3S$ requires C, 57·8; H, 4·5; N, 5·6%), 4-*chloro*-2-(*hydroxyamino*)*diphenyl sulphone* from isopropyl ether–methanol in prisms, m. p. 170—171° (decomp.) (Found: C, 51·1; H, 3·6; N, 5·2. $C_{12}H_{10}ClNO_3S$ requires C, 50·8; H, 3·6; N, 4·9%), and 6-*chloro*-2-(*hydroxyamino*)*diphenyl sulphone* from benzene in prisms, m. p. 120—121° (decomp.) (Found: C, 50·8; H, 3·6; N, 5·0. $C_{12}H_{10}ClNO_3S$ requires C, 50·8; H, 3·6; N, 4·9%).

4-(*Hydroxyamino*)*diphenyl Sulphone.*—A mixture of 4-nitrodiphenyl sulphone (2·63 g.), ammonium chloride (2·7 g.,) zinc dust (3·27 g.), water (10 ml.), and ethanol (100 ml.) was stirred and refluxed for 30 min. The hot mixture was filtered, and the residue was extracted with boiling ethanol. Evaporation of the combined solution gave 4-(*hydroxyamino*)*diphenyl sulphone* (2·37 g.), separating from chloroform–light petroleum (b. p. 40—60°) in prisms, m. p. 166—168° (decomp.) (Found: C, 58·0; H, 4·6; N, 5·6. $C_{12}H_{11}NO_3S$ requires C, 57·8; H, 4·5; N, 5·6%).

2-*Aminoaryl Phenyl Sulphones.*—Reduction of the corresponding 2-nitroaryl phenyl sulphones with tin and hydrochloric acid afforded the amines. 2-Aminodiphenyl sulphone crystallised from isopropyl ether in plates (87%), m. p. 121—122° (lit.,[20] m. p. 122°), 2-*amino*-6-*chlorodiphenyl sulphone* from isopropyl ether–methylene chloride in plates (85%), m. p. 158—159° (Found: C, 53·7; H, 4·0; N, 5·4. $C_{12}H_{10}ClNO_2S$ requires C, 53·8; H, 3·8; N, 5·2%), and 2-amino-4-chlorodiphenyl sulphone from isopropyl ether in prisms (90%), m. p. 119—121° (lit.,[22] m. p. 120—121°).

Reactions of (*Hydroxyamino*)*aryl Phenyl Sulphones with Sodium Hydroxide.*—40% Aqueous sodium hydroxide (20 ml.) was added to a solution of the (hydroxyamino)aryl phenyl sulphone (1 g.) in dioxan (50 ml.), and the mixture was stirred vigorously for 2 hr. under nitrogen. Any precipitate was filtered off, and the lower alkaline layer was separated. The dioxan layer was evaporated at 20°, and the residue in methylene chloride was washed with water. The organic layer was evaporated, and the aqueous washings were added to the alkaline solution. Acetone and methyl iodide was added to the alkaline solution which was then refluxed for 1 hr. The product was obtained with methylene chloride.

In the case of 6-chloro-2-(hydroxyamino)diphenyl sulphone, a precipitate soon appeared in the reaction mixture; filtration gave a colourless solid (80 mg.) which was insoluble in ether but soluble in water and which was identical (infrared spectrum) with sodium benzenesulphinate. Chromatography of the non-acidic fraction on alumina, elution with benzene, and crystallisation of the product from ethanol gave 3,3′-dichloroazoxybenzene in yellow needles (140 mg.), m. p. 96—97°. Elution with benzene–methylene chloride (1 : 1) and crystallisation of the product from methylene chloride–isopropyl ether, gave 2-amino-6-chlorodiphenyl sulphone in plates (150 mg.), m. p. 158—159°. Crystallisation of the methylated acidic fraction from isopropyl ether gave methyl phenyl sulphone in needles (160 mg.), m. p. 86—87°.

The products from other 2-(hydroxyamino)aryl phenyl sulphones (Table 2) were separated similarly. All products were identical (mixed m. p. and infrared spectra) with authentic samples.

After the reaction of 4-(hydroxyamino)diphenyl sulphone with alkali, filtration of the mixture gave a red solid. A solution of this precipitate in methylene chloride was washed with water, and the organic layer was evaporated. The residue combined with the remainder of the non-acidic product separated from chloroform to give 4,4′-di(phenylsulphonyl)azoxybenzene in orange plates (0·85 g., 90%), m. p. 272—273° (lit.,[23] m. p. 262—263°) (Found: C, 60·7;

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H, 4·4; N, 5·8. Calc. for $C_{24}H_{18}N_2O_5S_2$: C, 60·3; H, 3·8; N, 5·9%).

Reactions of m-*Chloronitrosobenzene*.—(*a*) When hydroxylamine hydrochloride (0·23 g.) was added to *m*-chloronitrosobenzene [24] (0·47 g.) in dioxan (25 ml.) and 40% aqueous sodium hydroxide (10 ml.), the colour of the solution changed from green to orange. After 3 hr., water was added, and the mixture was extracted with methylene chloride. The solvent was evaporated, and the residue was chromatographed on neutral alumina. Elution with benzene gave 3,3′-dichloroazoxybenzene (0·24 g., 55%), m. p. and mixed m. p. 92—96°.

(*b*) Experiment (*a*) was repeated in the absence of hydroxylamine. After 2 hr., the colour of the solution remained green, and work-up gave *m*-chloronitrosobenzene (85%), m. p. and mixed m. p. 68—70°.

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