99. *Reactions of Some Diaryl Sulphides.*

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4-Dimethylamino-2′-nitro- and 2,4-dihydroxy-2′-nitro-diphenyl sulphide have been brominated to their dibromo-compounds and reduced to the corresponding amines. Bromination of 2-amino-4′-dimethylaminodiphenyl sulphide gave *p*-bromodimethylaniline and 2,4,6-tribromoaniline. 2,4-Diacetoxy-2′-nitrodiphenyl sulphide and its sulphone were also reduced to the corresponding amines. 2-Chloro-2′-nitrodiphenylsulphenimide on reduction with hydrazine hydrate and palladised charcoal gave *o*-chloroaniline and 2,2′-diaminodiphenyl disulphide, and on reductive acetylation gave *o*-chloroacetanilide and 2-methylbenzothiazole. From the reaction between *o*-nitrobenzenesulphenyl chloride with acetanilide and *o*- and *m*-chloroacetanilide was isolated 2,2′-dinitrodiphenyl disulphone, which on reduction with hydrazine hydrate and palladised charcoal gave 2,2′-diaminodiphenyl disulphide.

o-NITROBENZENESULPHENYL CHLORIDE [1] reacts with dimethylaniline to form 4-dimethylamino-2′-nitrodiphenyl sulphide [2] (I) and this, on reduction with hydrazine hydrate and

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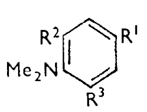
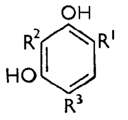
[1] Hubacher, *Org. Synth.*, Coll. Vol. II, 1943, p. 455.

[2] Zincke and Farr, *Annalen*, 1912, **391**, 55.

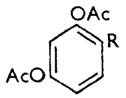
palladised charcoal,[3] yielded the corresponding diamino-compound (II). Bromination of the amine (II) in acetic acid produced *p*-bromo-*NN*-dimethylaniline or 2,4,6-tribromoaniline, or both according to the amount of bromine used. On the other hand, bromination of the 2-benzamido-derivative under similar conditions gave either *p*-bromo-*NN*-dimethylaniline or a mixture of this with 2,2′-dibenzamidodiphenyl disulphide. A point of interest in this connection is that, whereas it was shown that this disulphide was relatively stable to bromine, the parent amine, 2,2′-diaminodiphenyl disulphide, with excess of bromine gives 2,4,6-tribromoaniline. It has also been found that the bromination of the nitro-compound (I) gives 2,6-dibromo-4-dimethylamino-2′-nitrodiphenyl sulphide (III), no splitting of the C–S bond occurring in this case. Reduction [3] of the product (III) gave the corresponding dibromo-amine (IV).



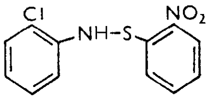
	R¹	R²	R³
(I)	o-$NO_2\cdot C_6H_4\cdot S$	H	H
(II)	o-$NH_2\cdot C_6H_4\cdot S$	H	H
(III)	o-$NO_2\cdot C_6H_4\cdot S$	Br	Br
(IV)	o-$NH_2\cdot C_6H_4\cdot S$	Br	Br



	R¹	R²	R³
(V)	o-$NO_2\cdot C_6H_4\cdot S$	H	H
(VI)	o-$NH_2\cdot C_6H_4\cdot S$	H	H
(VII)	o-$NO_2\cdot C_6H_4\cdot S$	Br	Br
(VIII)	o-$NO_2\cdot C_6H_4\cdot SO_2$	Br	Br



	R
(IX)	o-$NO_2\cdot C_6H_4\cdot S$
(X)	o-$NH_2\cdot C_6H_4\cdot S$
(XI)	o-$NO_2\cdot C_6H_4\cdot SO_2$
(XII)	o-$NH_2\cdot C_6H_4\cdot SO_2$



(XIII)

o-Nitrobenzenesulphenyl chloride adds to resorcinol to form the dihydroxy-sulphide [4] (V), and this on reduction [3] gave the corresponding amino-compound (VI) which quickly decomposed on storage. Acetylation [5] of this amine produced the *N*-monoacetyl derivative. Bromination of the dihydroxy-sulphide (V) produced its dibromo-derivative (VII) which with hydrogen peroxide in acetic acid gave the corresponding sulphone (VIII). Acetylation of the dihydroxy-nitro-sulphide (V) with acetic anhydride and sulphuric acid gave the diacetoxy-derivative [4] (IX), and this on reduction [3] gave the corresponding amino-compound (X). The diacetoxy-sulphide (IX) with hydrogen peroxide in acetic acid gave the sulphone [4] (XI), which on reduction [3] gives the amino-sulphone (XII).

o-Nitrobenzenesulphenyl chloride reacted with *o*-chloroaniline in ether to give 2-chloro-2′-nitrodiphenyl sulphenimide [6] (XIII), which on reduction [3] gave *o*-chloroaniline and 2,2′-diaminodiphenyl disulphide.[7] Reductive acetylation [8] of the sulphenimide gave 2-methylbenzothiazole and *o*-chloroacetanilide. Reductive acetylation of 2,2′-diaminodiphenyl disulphide [9] also gives 2-methylbenzothiazole. From these experiments it seems that 2,2′-diaminodiphenyl disulphide is an intermediate in the reduction of 2-chloro-2′-nitrodiphenyl sulphenimide.

Addition of *o*-nitrobenzenesulphenyl chloride to acetanilide, *o*-chloroacetanilide, or *m*-chloroacetanilide in acetic acid gave only 2,2′-dinitrodiphenyl disulphone. It was thought that *N*-chloroacetanilide [10] may have been an intermediate in this reaction, but addition of *o*-nitrobenzenesulphenyl chloride to *N*-chloroacetanilide gave 2,2′-dinitrodiphenyl disulphide and *p*-chloroacetanilide. Addition of *o*-nitrobenzenesulphenyl chloride to *p*-chloroacetanilide gave only 2,2′-dinitrodiphenyl sulphide and a 70% recovery of *p*-chloroacetanilide.

2,2′-Dinitrodiphenyl disulphone is reduced by palladised charcoal and hydrazine hydrate [3] to 2,2′-diaminodiphenyl disulphide.

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[3] Dewar and Mole, *J.*, 1956, 2556.
[4] Kent and Smiles, *J.*, 1934, 427.
[5] Friedlander, *Ber.*, 1893, **26**, 178.
[6] Moore and Johnson, *J. Amer. Chem. Soc.*, 1936, **58**, 1091.
[7] Mohlau, Beyschlag, and Kohser, *Ber.*, 1912, **45**, 131.
[8] Gebauer-Fülnegg and Beatty, *J. Amer. Chem. Soc.*, 1927, **49**, 1361.
[9] (*a*) Fraser and Homer, *J.*, 1936, 507; (*b*) Clark, *J.*, 1928, 2319.
[10] Barnes and Porter, *J. Amer. Chem. Soc.*, 1930, **52**, 1721.

EXPERIMENTAL

Reduction of Nitro-compounds. Palladised charcoal (0·2 g.) and 60% hydrazine hydrate [3] (4 c.c.) were refluxed for 1·5 hr. with the nitro-compound (2 g.) in 95% ethanol. The mixture was filtered hot, and the ethanol distilled from the filtrate. Addition of cold water to the residue gave the solid amines (Table 1). Since compound (IV) could not be obtained analytically pure and since compound (VI) was unstable, these compounds were analysed as the acetyl derivatives. (IV) had m. p. 59—61° (yield 75%) and gave an *acetyl derivative,* m. p. 116·5—117° (Found: C, 43·2; H, 3·6; N, 6·6; S, 7·55; Br, 36·3. $C_{16}H_{16}ON_2Br_2S$ requires C, 43·2; H, 3·6; N, 6·3; S, 7·2; Br, 36·0%). (VI) had m. p. 130—133° (yield 60%) and gave an *acetyl derivative,* m. p. 193° (Found: C, 61·0; H, 4·8; N, 4·9; S, 11·5. $C_{14}H_{13}O_3NS$ requires C, 61·1; H, 4·8; N, 5·1; S, 11·6%).

TABLE 1.

Amine	M. p.	Yield (%)	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
II	91·5—92° [a]	80	68·6	6·5	11·2	12·7	$C_{14}H_{16}N_2S$	68·8	6·55	11·4	13·1
X	138—139 [b]	70	60·0	4·6	4·5	10·3	$C_{16}H_{15}O_4NS$	60·1	4·7	4·4	10·1
XII	201—202 [c]	60	54·8	4·0	4·1	9·3	$C_{16}H_{15}O_6NS$	55·0	4·3	4·0	9·2

[a, b, c] Recrystallised from (*a*) aqueous ethanol, (*b*) benzene, and (*c*) acetone.

Bromination of Sulphides.—Bromine (3·2 g., 0·02 mole) in acetic acid (10 c.c.) was added slowly with shaking to a suspension of 4-dimethylamino-2′-nitrodiphenyl sulphide (I) (2·74 g., 0·01 mole) in acetic acid (25 c.c.), the mixture kept at room temperature for 15 min., and the resulting clear solution made alkaline with 10% aqueous sodium hydroxide and set aside. The precipitate recrystallised from aqueous ethanol, to give yellow needles of 2,6-*dibromo*-4-*dimethylamino*-2′-*nitrodiphenyl sulphide* (III) (3 g., 68%), m. p. 123—124° (Found: C, 38·5; H, 2·6; N, 6·6; S, 7·6; Br, 37·3. $C_{14}H_{12}O_2N_2Br_2S$ requries C, 38·8; H, 2·8; N, 6·5; S, 7·4; Br, 37·0%).

2,4-Dihydroxy-2′-nitrodiphenyl sulphide (V) in the same way gave 3,5-*dibromo*-2,4-*dihydroxy*-2′-*nitrodiphenyl sulphide* (VII) (92%), m. p. 214° (decomp.) (Found: C, 33·6; H, 1·7; N, 3·7; S, 7·6; Br, 38·2. $C_{12}H_7O_4NBr_2S$ requires C, 34·0; H, 1·9; N, 3·8; S, 7·7; Br, 38·0%), but in this case no addition of sodium hydroxide and water was necessary.

After brominations of 2-amino-4′-dimethylaminodiphenyl sulphide (II) (see Table 2) the mixture was made alkaline with sodium hydroxide and steam-distilled. *p*-Bromo-*NN*-dimethylaniline and 2,4,6-tribromoaniline were isolated from the distillate and identified by comparison with authentic specimens.

TABLE 2.

Amine (mole)	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01
Bromine (mole)	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·1
p-Bromodimethylaniline (%)	10	20	20—25	20—25	20—25	20—25	10	—
2,4,6-Tribromoaniline (%)	—	—	—	—	5	5—10	10—15	10—15

TABLE 3.

2-Benzamido-4′-dimethylaminodiphenyl sulphide (mole)	0·01	0·01	0·01	0·01
Bromine (mole)	0·01	0·02	0·04	0·06
p-Bromodimethylaniline (%)	70	55	20	—
2,2′-Dibenzamidodiphenyl disulphide (%)	40	20	—	—

2-Amino-4′-dimethylaminodiphenyl sulphide (II) was benzoylated and the *benzamido-compound,* m. p. 110—111° (Found: S, 8·95. $C_{21}H_{20}ON_2S$ requires S, 9·2%), was brominated as above (see Table 3), but in this case the mixture was made alkaline with sodium carbonate and then steam-distilled. 2,2′-Dibenzamidodiphenyl disulphide, m. p. 146°, was isolated from the residue. It was identified by comparison with a specimen prepared by direct benzoylation of 2,2′-diaminodiphenyl disulphide.[7] Addition of bromine (0·01 mole) to 2,2′-dibenzamidodiphenyl disulphide (0·01 mole) gave only recovered dibenzamido-compound (50%).

3,5-*Dibromo*-2,4-*dihydroxy*-2′-*nitrodiphenyl Sulphone* (VIII).—30% Hydrogen peroxide (8 c.c.) was added to a suspension of compound (VII) (4 g.) in acetic acid (50 c.c.), and the mixture heated on the steam-bath for 1—1·5 hr., allowed to cool, and poured on crushed ice. The precipitate, on recrystallisation from aqueous acetic acid, gave white needles of the *sulphone* (3·4 g., 80%), m. p. 205·5° (decomp.) (Found: C, 32·0; H, 1·5; N, 2·7; S, 6·8; Br, 35·4. $C_{12}H_7O_6NBr_2S$ requires C, 31·8; H, 1·5; N, 3·1; S, 7·0; Br, 35·3%).

Reduction of 2-*Chloro*-2′-*nitrodiphenylsulphenimide* (XIII).—(*a*) A mixture [3] of palladised charcoal (3 g.), 60% hydrazine hydrate (6 c.c.), and 2-chloro-2′-nitrodiphenyl sulphenimide (3 g.) in ethanol (100 c.c.) was refluxed for 1 hr., then filtered hot, the ethanol distilled from the filtrate, and the residue steam-distilled. The distillate contained a colourless oil which after extraction with ether was found to have b. p. 210° and was identified as *o*-chloroaniline (0·95 g., 70%). The residue after steam-distillation was recrystallised from aqueous ethanol, to give yellow plates of 2,2′-diaminodiphenyl disulphide,[7] m. p. 92—93° (0·55 g., 45%).

(*b*) A mixture of acetic anhydride (30 g.), anhydrous sodium acetate (18 g.), zinc dust (1·4 g.),[8] and the sulphenimide (6 g.) in acetic acid (100 c.c.) was refluxed for 3—3·5 hr., allowed to cool, made alkaline with sodium carbonate, and extracted with ether. The ether extract was dried (Na_2SO_4), the ether distilled off, and the residue was steam-distilled. The distillate contained 2-methylbenzothiazole (3·2 g., 50%), b. p. 238—241°, which was identified by comparison with an authentic specimen (b. p. 238—240°) prepared by the method of Fraser and Homer [9a] and by preparation of its picrate, m. p. 156° (Clark [9b] gives m. p. 155—156°). The residue on recrystallisation from aqueous ethanol gave *o*-chloroacetanilide (2 g., 55%).

Reaction between o-*Nitrobenzenesulphenyl Chloride and Acetanilide.*—A mixture of *o*-nitrobenzenesulphenyl chloride (3·8 g., 0·02 mole) and acetanilide (4·05 g., 0·03 mole) in acetic acid (150 c.c.) was heated on the steam-bath for 1·5 hr. The resulting dark solution was poured on crushed ice, and the precipitate (2·7 g.) was washed with hot water (200 c.c.) and recrystallised from acetic acid–water (9 : 1) to give yellow needles of 2,2′-dinitrodiphenyl disulphide,[7] m. p. 195—197° (0·8 g., 20%). The mother-liquor on dilution with water gave a solid (1·4 g.), m. p. 138—144°, which on repeated recrystallisation from aqueous acetic acid gave pale yellow plates of 2,2′-*dinitrodiphenyl disulphone* (1 g., 25—30%), m. p. 147—148° (Found: C, 38·3; H, 2·2; N, 7·45; S, 17·45. $C_{12}H_8O_8N_2S_2$ requires C, 38·7; H, 2·15; N, 7·5; S, 17·2%). Infrared analysis showed a sulphone peak [11] at 1150 cm.$^{-1}$ and peaks at 1534, 1357, 1333, and 1309 cm.$^{-1}$ which indicate the presence of both sulphone and nitro-groups.[12] Experiments carried out in the same way with *o*- and *m*-chloroacetanilide also gave the disulphone, m. p. 147—148° (25—30%), and the disulphide, m. p. 195—197° (20%). When, however, either *p*-chloroacetanilide or *N*-chloroacetanilide was used the product was 2,2′-dinitrodiphenyl disulphide, m. p. 195—197° (20%), with recovery of 70% of *p*-chloroacetanilide with the former, and the formation of a trace of *p*-chloroacetanilide with the latter. The disulphone on reduction with palladised charcoal and 60% hydrazine hydrate [3] gave 2,2′-diaminodiphenyl disulphide, m. p. 92—93° (90%).

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[11] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 360.

[12] *Op. cit.*, p. 300.