

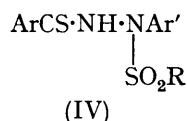
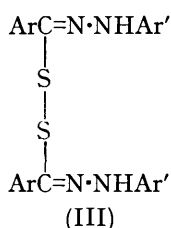
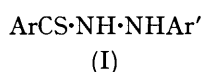
Formation of Bis- $[\alpha$ -(arylhydrazono)aralkyl] Disulphides from *N*-Aryl-*N'*-thioaroylhydrazines and Sulphonyl Chlorides, and Related Topics

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The reaction of *N*-aryl-*N'*-thioaroylhydrazines (I) with various alkane-, arylalkane-, and arene-sulphonyl chlorides in the presence of triethylamine gave the bis- $[\alpha$ -(arylhydrazono)aralkyl] disulphides (III) and *N*-aryl-*N*-alkyl(or aryl)sulphonyl-*N'*-thioaroylhydrazines (IV), together with the sulphinate ion derived from the sulphonyl chloride. Similar reactions [of (ID)] with benzenesulphonyl and 2-nitrobenzenesulphonyl chlorides gave the disulphide (IIID). The disulphides (III) were also formed by reaction between compounds of types (I) and (IV) in the presence of triethylamine. Compounds (IV) alone gave the disulphides in refluxing ethanol, but in refluxing acetonitrile-triethylamine (1:1) they afforded the corresponding bis- $[\alpha$ -(arylhydrazono)aralkyl] sulphides (VII).

THE present work was undertaken following an observation ‡ that the reaction of the thiohydrazide (ID) with methanesulphonyl chloride (IIa) in the presence of base gave the hydrazone disulphide (IIID), identical with a sample prepared by oxidation¹ of (ID). We report here a more detailed study of this and similar reactions and an examination of corresponding reactions of (ID) with benzenesulphonyl and 2-nitrobenzenesulphonyl chlorides. A discussion of reactions of the corresponding sulphonyl derivatives (IV) is also included.

The reaction of (ID) with methanesulphonyl chloride (IIa) and triethylamine (molar ratio 2:1:2) was conducted in chloroform to maximize yields of the hydrazone disulphide (IIID). Under these circumstances, the yield of (IIID) was almost quantitative and similar results were obtained with other sulphonyl chlorides (IIc–e) under comparable conditions. The reactions of other *N*-aryl-*N'*-thioaroylhydrazines (IA–C and E) with (IIa) and triethylamine in the same molar ratio (2:1:2) gave the corresponding hydrazone disulphides (IIIA–C and E) in 82–100% yield.



A; Ar = Ar' = Ph
B; Ar = 4-MeO·C₆H₄, Ar' = Ph
C; Ar = 4-Pr^tC₆H₄, Ar' = Ph
D; Ar = Ph, Ar' = 2,4-Br₂C₆H₃
E; Ar = Ph, Ar' = 2-Br-4-EtO·C₆H₃
F; Ar = Ph, Ar' = 4-Br-2-EtO·C₆H₃

a; R = Me
b; R = PhCH₂
c; R = Ph
d; R = 4-MeC₆H₄
e; R = 4-MeO·C₆H₄
f; R = 2-NO₂·C₆H₄
g; R = 4-NO₂·C₆H₄

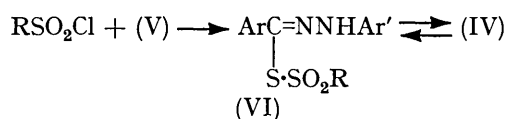
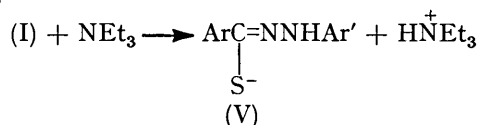
When methanesulphonyl chloride was added to a solution of (ID) and triethylamine (molar ratio 1:1:1) in chloroform, the yield of (IIID) was lower (82%). A

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further compound, considered to be *N*-(2,4-dibromophenyl)-*N*-methylsulphonyl-*N'*-thiobenzoylhydrazine (IVDa), was isolated in 18% yield. An independent experiment revealed that (IVDa) was not formed from (IIID). Under similar conditions, (ID) and benzenesulphonyl chloride (IIc) gave (IIID) (61%) and (IVDc) (37%); (ID) and 4-nitrobenzenesulphonyl chloride (IIg) gave (IIID) in almost quantitative yield. The mass spectra of compounds (IV) showed the presence of PhCS⁺ and RSO₂⁺ or [RSO₂H]⁺, consistent with attachment of the sulphonyl group to nitrogen rather than to sulphur.

The formation of compounds (III) and (IV) can be explained in terms of nucleophilic displacement of chlorine from the sulphonyl chloride (II) by thiohydrazide anion (V) formed from (I) and triethylamine to give the *S*-hydrazone thiosulphonate (VI). This intermediate can then either undergo *S* → *N*-sulphonyl transfer to give (IV), or nucleophilic attack at the *S*-SO₂ bond by (V) to produce (III) and the corresponding sulphinate ion; the formation of the latter was confirmed by isolation of the *S*-benzylisothiuronium salt in some experiments.² The differences between the reactions of (ID) with benzenesulphonyl chloride and with 4-nitrobenzenesulphonyl chloride under comparable conditions are explicable on this basis; in the latter case, the electron-attracting nitro-group facilitates departure of the sulphinate ion and so favours formation of (IIID) at the expense of (IVDg). Direct *N*-sulphonylation of (I) by (II) as an alternative pathway to (IV) is also possible and is perhaps supported in some cases by a decrease in the yield of (III) caused by inverse addition of reagents.



¹ Cf. M. H. Wuyts and A. Lacourt, *Bull. Soc. chim. belges*, 1939, 48, 193.

² F. Kurzer and J. R. Powell, *J. Chem. Soc.*, 1952, 3728.

Of interest in this connection is the recent report that the reaction of magnesium dithiobenzoate with (II) gives bithiobenzoyl disulphide.³ The mixed anhydride of dithiobenzoic and toluene-4-sulphonic acids is presumably formed first and then suffers displacement of toluene-4-sulphinat ion by dithiobenzoate ion. Again formation of *NN'*-diphenyl-*N*-thiobenzoylbenzamidine from thiobenzanilide (sodium salt) and (IIc) probably involves an intermediate similar to (VI), though in this case benzenethiosulphonate ion is displaced.⁴

Reaction of (ID) with benzenesulphonyl chloride (PhSOCl) and triethylamine (molar ratio 2 : 1 : 2) gave (IIID) in 78% yield. When the molar ratio was adjusted to 1 : 1 : 1, (IIID) was obtained in 57% yield. This formation of (IIID) may be rationalized in terms of an intermediate hydrazone thiosulphinat analogous to (VI). Imidoyl thiosulphinat has been proposed as intermediate in the formation of bis- α -phenylimino-benzyl sulphide from thiobenzanilide, benzenesulphonyl chloride, and pyridine.⁵

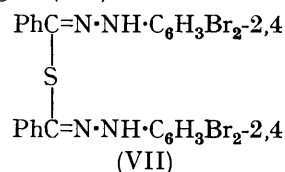
When (ID) was treated with 2-nitrobenzenesulphenyl chloride (2-NO₂·C₆H₄SOCl) and triethylamine (molar ratio 2 : 1 : 2), (IIID) was isolated in 44% yield; at molar ratio 1 : 1 : 1, the yield of (IIID) was 70%. The formation of disulphides from reactions involving displacement of chlorine from sulphenyl chlorides has been documented,⁶ and in the present case an intermediate hydrazone 2-nitrophenyl disulphide is implicated. Displacement of 2-nitrothiophenoxide ion from this intermediate by (V) would give the hydrazone disulphide (III). The former ion may now compete with (V) for unchanged sulphenyl chloride and at a reactant molar ratio of 2 : 1 : 2 the relatively low yield (44%) of (IIID) and the recovery of (ID) (39%) can be understood. At molar ratio 1 : 1 : 1 virtually all (ID) reacts and the isolable yield of (IIID) rises to 70%.

A number of reactions of the sulphonyl derivatives (IV) were examined. When (IVDa) was refluxed in ethanol, the disulphide (IIID) was slowly produced; under slightly different conditions, (IVDc) gave (IIID). These results may be accommodated if the process (VI) \rightarrow (IV) is reversible, for then formation of (VI) followed by ethanolysis would give (V), and (V) by reaction with (VI) would give (III).

Other reactions seem to indicate that such interconversion [(IV) \rightleftharpoons (VI)] is probably rapid under basic conditions. Thus addition of triethylamine to a mixture of (ID) and (IVDc) or (IVDd) in chloroform at room temperature rapidly gave (IIID) in almost quantitative yield. In an analogous experiment using (IA) and (IVDc), t.l.c. of the reaction mixture showed the

presence of (IIIA), (IIID) and, by inference, the *asym*-disulphide (IIIAD). This experiment provided the basis for a preparation of the *asym*-disulphide (IIIDE); *sym*-disulphides (IIID and E) were also detected (t.l.c.) in this reaction. The equilibration of (IA) and (IIID) in the presence of triethylamine, producing (IIIA) and (IIIAD), was demonstrated (t.l.c.) in a separate experiment, but this matter was not pursued further.

Finally, (IVDc) and (IVDd) were each refluxed in acetonitrile-triethylamine (1 : 1). In both cases, the hydrazone sulphide (VII)⁷ was obtained in virtually the same yield; it was likely that (IIID) was also formed, but largely decomposed under the reaction conditions (t.l.c.). A possible route to (VII) involves formation of the nitrilimine (PhC \equiv N \bar{N} Ar)⁸ from (VI) under the strongly basic conditions of the reaction; capture of the nitrilimine by (V), produced by desulphonylation of (VI), can then give (VII).



EXPERIMENTAL

Microanalyses were performed by Mr. P. Hansen and his staff, The H.C. Ørsted Institute, Copenhagen. M.p.s were determined with a Reichert microscope. N.m.r. spectra (solvent CDCl₃) were recorded on a Varian A60 instrument. Mass spectra were obtained with an A.E.I. MS 30 double-beam instrument operating at 70 eV. The samples were introduced directly into the ion source at 200°. All reactions were carried out under nitrogen at room temperature unless otherwise stated. Methanesulphonyl chloride and benzenesulphonyl chloride were distilled *in vacuo* before use.

Reaction of N-Phenyl-N'-thiobenzoylhydrazine (IA) with Methanesulphonyl Chloride (IIa).—Methanesulphonyl chloride (0.19 ml, 2.5 mmol) was added to a stirred solution of (IA)⁹ (1.14 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform (25 ml). After 25 min the solution was washed with water, dried (Na₂SO₄), and evaporated *in vacuo*. Crystallization of the crude product (1.14 g) from ethanol-ethyl acetate (1 : 1) gave the disulphide (IIIA) (0.82 g, 72%) as orange needles, m.p. 134–137°, raised to 138–140° by recrystallization (lit.,¹ 145°); *m/e* 454 (*M*⁺).

Reaction of Compound (IB) with Methanesulphonyl Chloride.—Methanesulphonyl chloride (0.19 ml, 2.5 mmol) was added to a stirred solution of (IB)⁹ (1.29 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform (25 ml). After 25 min the solution was evaporated *in vacuo* and ethanol (25 ml) was added; crystallization was induced by stirring. The crude product (2.30 g, 89%), m.p. 98–103°, was crystallized from ethanol to give *bis*-[4-

³ D. H. R. Barton, C. Chavis, M. K. Kaloustian, P. D. Magnus, G. A. Poulton, and P. J. West, *J.C.S. Perkin I*, 1973, 1571.

⁴ I. Ishikawa, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 1927, 7, 277; R. N. Hurd and G. De La Mater, *Chem. Rev.*, 1961, 61, 45.

⁵ W. Walter and P.-M. Hell, *Annalen*, 1969, 727, 50.

⁶ W. Walter and P.-M. Hell, *Annalen*, 1969, 727, 22; D. E. L. Carrington, K. Clarke, and R. M. Scowston, *J. Chem. Soc. (C)*, 1971, 3262; W. A. Pryor, 'Mechanisms of Sulfur Reactions,' McGraw-Hill, New York, 1962.

⁷ I. T. Barnish and M. S. Gibson, *J. Chem. Soc. (C)*, 1970, 854.

⁸ R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, 2, 566.

⁹ (a) K. A. Jensen, H. R. Baccaro, O. Buchardt, G. E. Olsen, C. Pedersen, and J. Toft, *Acta Chem. Scand.*, 1961, 15, 1109; G. Sherowsky, *Tetrahedron Letters*, 1971, 4985; (b) W. Walter and K. J. Reubke, *Tetrahedron Letters*, 1968, 5973; P. Wolkoff, S. Hammerum, P. D. Callaghan, and M. S. Gibson, *Canad. J. Chem.*, in the press.

methoxy- α -(phenylhydrazono)benzyl] disulphide (IIIB) (1.25 g, 49%) as violet prisms, m.p. 109–111° (Found: C, 65.45; H, 5.1; N, 10.95; S, 12.3. $C_{28}H_{26}N_4O_2S_2$ requires C, 65.35; H, 5.1; N, 10.9; S, 12.45%).

Reaction of Compound (IC) with Methanesulphonyl Chloride.—Methanesulphonyl chloride (0.19 ml, 2.5 mmol) was added to a stirred solution of (IC) (1.35 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform (25 ml). After 25 min, the solution was poured into ethanol (50 ml), cooled, and filtered. The crude product (1.10 g, 82%), m.p. 121–124° was crystallized from ethanol to give *bis*-[4-isopropyl- α -(phenylhydrazono)benzyl] disulphide (IIIC) (0.90 g, 67%) as red prisms, m.p. 124–126° (Found: C, 71.25; H, 6.35; N, 10.35; S, 11.8. $C_{32}H_{34}N_4S_2$ requires C, 71.35; H, 6.35; N, 10.4; S, 11.9%).

Reaction of Compound (IE) with Methanesulphonyl Chloride.—Methanesulphonyl chloride (50 μ l, 0.63 mmol) was added to a stirred solution of (IE) (0.44 g, 1.3 mmol) and triethylamine (0.18 ml, 1.3 mmol) in chloroform (13 ml). After 12 min, the solution was poured into ethanol (40 ml), stirred for 5 min, and filtered. The crude product (0.37 g, 85%), m.p. 123–125°, was crystallized from ethyl acetate to give *bis*-[α -(2-bromo-4-ethoxyphenyl)hydrazono]benzyl] disulphide (IIIE) as red-orange needles, m.p. 124–126° (Found: C, 51.45; H, 4.05; Br, 23.2; N, 7.95. $C_{30}H_{28}Br_2N_4O_2S_2$ requires C, 51.45; H, 4.05; Br, 22.8; N, 8.0%).

The isomeric 4-bromo-2-ethoxy-analogue (IIIF), similarly prepared from (IF) and (IIa), crystallized as red-violet prisms, m.p. 122–124° (from ethanol-ethyl acetate) (Found: C, 51.0; H, 4.1; Br, 22.5; N, 8.05%).

Reaction of Compound (ID) with Methanesulphonyl Chloride.—(i) Methanesulphonyl chloride (0.19 ml, 2.5 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform (25 ml). After 25 min, the solution was poured into ethanol (75 ml), stirred for 5 min, and filtered. The crude product (1.80 g, 98%), m.p. 164–167°, on crystallization from ethyl acetate, gave the disulphide (IIID) (1.44 g, 75%), m.p. 166–169° (mixed m.p. 168–169°), identical with an authentic specimen (t.l.c., i.r. spectrum).

(ii) Methanesulphonyl chloride (0.39 ml, 5.0 mmol), added to a solution identical with that described in (i), gave the disulphide (IIID) in 78% yield. The ethanolic filtrate was concentrated *in vacuo* to ca. one-third volume, cooled and filtered. The crude product (0.33 g, 14%) was crystallized from benzene-hexane (2:9) to give *N*-(2,4-dibromophenyl)-*N*-methylsulphonyl-*N'*-thiobenzoylhydrazine (IVDa) as yellow needles, m.p. 130–134° (Found: C, 36.45; H, 2.6; N, 5.95; S, 13.5. $C_{14}H_{12}Br_2N_2O_2S_2$ requires C, 36.2; H, 2.6; N, 6.05; S, 13.8%); δ 3.2 (CH₃); *m/e* 466/464/462 (*M*⁺), 121 (C₇H₅S), and 80 (CH₄O₂S) (peaks at *m/e* 354/352/350 were detected at low intensity).

(iii) A mixture of the disulphide (IIID), methanesulphonyl chloride, and triethylamine (molar ratio 1:2:2) in chloroform was set aside for 11 days; 91% of the disulphide (IIID) was recovered.

(iv) When similar experiments were carried out at different molar ratios of (ID), (IIa), and NEt₃, the following yields of (IIID) (in parentheses) were obtained: molar ratio 1:2:2 (76%); 1:2:2, with inverse addition of (IIa) and NEt₃ (62%); 1:4:1 (87%); 1:2, conducted in pyridine both as base and solvent (71%).

Reaction of Compound (ID) with Phenylmethanesulphonyl Chloride (IIb).—Phenylmethanesulphonyl chloride (0.59 g,

3.1 mmol) was added to a solution of (ID) (1.20 g, 3.1 mmol) and triethylamine (0.44 ml, 3.1 mmol) in chloroform (16 ml) as described for (ID) and (IIa) (molar ratio 1:1:1). This resulted in 53% yield of the disulphide (IIID). From the ethanolic filtrate was isolated a yellow solid (0.45 g) which, after two crystallizations, still contained a considerable amount of the disulphide (IIID) (t.l.c.); however the mass spectrum showed peaks at *m/e* 542/540/538 consistent with the formation of *N*-(2,4-dibromophenyl)-*N'*-phenylmethylsulphonyl-*N'*-thiobenzoylhydrazine (IVDb).

Reaction of Compound (ID) with Benzenesulphonyl Chloride (IIc).—(i) Benzenesulphonyl chloride (0.32 ml, 2.5 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform (25 ml). After 25 min, the solution was poured into ethanol (75 ml) and stirred for 5 min to give the disulphide (IIID) (1.90 g, 100%). The ethanolic filtrate was evaporated *in vacuo* and washed carefully with water (20 ml). The aqueous extract was acidified with aqueous hydrochloric acid to pH 4 and a saturated solution of *S*-benzylisothiuronium chloride (1.50 g) was added. After cooling for 2 h, *S*-benzylisothiuronium benzenesulphinate (0.50 g, 65%) was collected, m.p. (after one recrystallization) 154–155° (lit.,² 154–155°); mixed m.p. 153–155°.

(ii) Benzenesulphonyl chloride (0.66 ml, 5.0 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) as described for (ID) and (IIa) (molar ratio 1:1:1), and gave the disulphide (IIID) in 61% yield. From the ethanolic filtrate was isolated *N*-(2,4-dibromophenyl)-*N*-phenylsulphonyl-*N'*-thiobenzoylhydrazine (IVDc) (0.96 g, 37%), m.p. 148–154° (slow heating); crystallization from benzene-hexane gave yellow prisms, m.p. 155–159° (Found: C, 43.45; H, 2.7; N, 5.25; S, 12.15. $C_{19}H_{14}Br_2N_2O_2S_2$ requires C, 43.35; H, 2.7; N, 5.3; S, 12.2%); *m/e* 141 (C₆H₅O₂S) and 121 (C₇H₅S).

Reaction of Compound (ID) with Toluene-4-sulphonyl Chloride (IID).—(i) Toluene-4-sulphonyl chloride (0.86 g, 5.0 mmol) was added to a stirred solution of (ID) (3.86 g, 10.0 mmol) and triethylamine (1.40 ml, 10.0 mmol) in chloroform (50 ml) as described for (ID) and (IIa) in molar ratio 2:1:2. The disulphide (IIID) was obtained in 95% yield and *S*-benzylisothiuronium toluene-4-sulphinate (87%), m.p. 163–165° (lit.,² 167–168°), was isolated from the ethanolic filtrate.

(ii) Toluene-4-sulphonyl chloride (0.86 g, 5.0 mmol) was added to a solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform (25 ml) as described for (ID) and (IIa) in molar ratio 1:1:1. This gave the disulphide (IIID) (58%). *N*-(2,4-dibromophenyl)-*N'*-thiobenzoyl-*N*-4-tolylsulphonylhydrazine (IVDd) (1.11 g, 41%), m.p. 141–144°, was isolated from the ethanolic filtrate; crystallization from benzene gave yellow prisms, m.p. 147–151° (Found: C, 44.3; H, 3.05; N, 5.1; S, 11.95. $C_{20}H_{16}Br_2N_2O_2S_2$ requires C, 44.45; H, 3.0; N, 5.2; S, 11.85%); *m/e* 542/540/538 (*M*⁺), 387/385/383 (*M* – C₇H₇O₂S), 155 (C₇H₇SO₂), and 121 (C₇H₇S) [peaks were noted at 354/352/350 (low intensity)].

(iii) Repetition of (ii) with inverse addition of (IID) and base resulted in 84% yield of the disulphide (IIID) and 18% yield of (IVDd).

Reaction of Compound (ID) with 4-Methoxybenzenesulphonyl Chloride (IIe).—(i) 4-Methoxybenzenesulphonyl chloride (0.52 g, 2.5 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml,

5.0 mmol) as described for (ID) and (IIa) in the ratio 2 : 1 : 2. This gave the disulphide (IIID) (92%). From the ethanolic filtrate was isolated *S*-benzylisothiouronium 4-methoxybenzenesulphinatate (0.55 g, 65%), which crystallized from ethanol–light petroleum (b.p. 30–60°) (3 : 1) as white needles, m.p. 155–157° (Found: C, 53.25; H, 5.35; N, 8.35. $C_{15}H_{18}N_2O_3S_2$ requires C, 53.25; H, 5.35; N, 8.3%).

(ii) 4-Methoxybenzenesulphonyl chloride (1.03 g, 5.0 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) as described for (ID) and (IIa) (molar ratio 1 : 1 : 1). This gave the disulphide (IIID) [1.40 g; contaminated with (IVDe)] and *N*-(2,4-dibromophenyl)-*N*-4-methoxyphenylsulphonyl-*N'*-thiobenzoylhydrazine (IVDe); the latter crystallized from benzene–hexane (1 : 1) as yellow prisms (22%), m.p. 140–142° (Found: C, 43.1; H, 2.9; N, 5.0; S, 11.6. $C_{20}H_{16}Br_2N_2O_3S_2$ requires C, 43.2; H, 2.9; N, 5.05; S, 11.55%); *m/e* 558/556/554 (M^+), 387/385/383 ($M - C_7H_7O_3S$), 171 ($C_7H_7O_3S$), and 121 (C_7H_7S) (peaks at *m/e* 354/352/350 were present at low intensity).

Reaction of Compound (ID) with 2- or 4-Nitrobenzenesulphonyl Chloride (II f or g).—2- or 4-Nitrobenzenesulphonyl chloride (1.11 g, 5.0 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) as described for (ID) and (IIa) in molar ratio 1 : 1 : 1. This resulted in 92 and 99% yields of the disulphide (IIID) from use of (II f) and (II g), respectively.

Reaction of Compound (ID) with Benzenesulphinyl Chloride.—(i) Benzenesulphinyl chloride (0.30 ml, 2.5 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform as described for (ID) and (IIa) in molar ratio 2 : 1 : 2. This resulted in 78% yield of the disulphide (IIID); the yield was unaltered after 4 h reaction time and t.l.c. of the reaction mixture indicated the presence of unchanged (ID).

(ii) Benzenesulphinyl chloride (0.60 ml, 5.0 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform as described for (ID) and (IIa) in molar ratio 1 : 1 : 1. This resulted in 57% yield of the disulphide (IIID); a further small quantity was recovered from the ethanolic reaction liquors.

Reaction of Compound (ID) with 2-Nitrobenzenesulphenyl Chloride.—(i) 2-Nitrobenzenesulphenyl chloride (0.95 g, 5.0 mmol) was added to a stirred solution of (ID) (1.94 g, 5.0 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform as described for (ID) and (IIa) in molar ratio 1 : 1 : 1. This gave the disulphide (IIID) (1.34 g, 70%, after crystallization from ethyl acetate). Evaporation of the combined mother and reaction liquors followed by crystallization from benzene–hexane (3 : 2) gave bis-2-nitrophenyl disulphide (0.44 g, 58%), m.p. 195–198° (lit.,¹⁰ 195°).

(ii) 2-Nitrobenzenesulphenyl chloride (0.38 g, 2.0 mmol) was added to a stirred solution of (ID) (1.55 g, 4.0 mmol) and triethylamine (0.57 ml, 4.0 mmol) in chloroform (20 ml) as described for (ID) and (IIa) in molar ratio 2 : 1 : 2. This yielded the disulphide (IIID) (0.67 g, 44%, after crystallization from ethyl acetate); bis-2-nitrophenyl disulphide (0.19 g, 62%) precipitated upon addition of ethanol to the mother liquor. The reaction filtrate was evaporated to dryness and extracted with boiling ethanol (15 ml); upon cooling, this gave material (0.10 g) which on further purification yielded (IIID). Compound (ID) (0.60 g, 39%) was recovered from the ethanolic mother liquor.

Formation of (IIID) from (IVDa) and from (IVDc).—

(i) Compound (IVDa) (0.23 g, 0.5 mmol) was refluxed in ethanol (10 ml) for 11 h; ethanol (10 ml) was added and the hot solution was filtered to give the disulphide (IIID) (0.08 g, 42%). Unchanged (IVDa) (0.1 g) was recovered from the filtrate.

(ii) Refluxing (IVDc) in ethanol–chloroform (1 : 1) for 24 h gave the disulphide (IIID) in 42% yield. Refluxing (IVDc) in chloroform produced no significant change even after 2 days (t.l.c.).

(iii) A mixture of (IVDc) (0.52 g, 1.0 mmol) and triethylamine (0.14 ml, 1.0 mmol) was refluxed in chloroform (5 ml) for 9 h. T.l.c. of the dark red mixture indicated the presence of the disulphide (IIID) together with the thiohydrazide (ID) and starting material (IVDc). Ethanol (20 ml) was added and the disulphide (IIID) (7%) was recovered by filtration.

Preparation of (IIID) by Reactions of (ID) with (IVDc) and (IVDd).—(i) Triethylamine (70 μ l, 0.5 mmol) was added to a mixture of (ID) (0.19 g, 0.5 mmol) and (IVDc) (0.26 g, 0.5 mmol) in chloroform (10 ml). After 15 min, the solution was poured into ethanol (15 ml) and the disulphide (IIID) (0.38 g, 100%) was filtered off.

(ii) Triethylamine (70 μ l, 0.5 mmol) was added to a mixture of (ID) (0.19 g, 0.5 mmol) and (IVDd) (0.27 g, 0.5 mmol) in chloroform (5 ml). After 15 min, the solution was poured into ethanol (15 ml) and the disulphide (IIID) (0.39 g, 100%) was filtered off.

Preparation of the asym-Hydrazonyl Disulphide (IIIDE) and Related Experiments.—(i) Triethylamine (70 μ l, 0.5 mmol) was added to a mixture of (IA) (0.11 g, 0.5 mmol) and (IVDc) (0.26 g, 0.5 mmol) in chloroform (10 ml). T.l.c. of the red solution showed the presence of the disulphides (IIIA) and (IIID), and an intermediate spot probably corresponding to the *asym*-disulphide (IIIAD).

(ii) Compounds (ID) (0.97 g, 2.5 mmol) and (IIa) (0.19 ml, 2.5 mmol) were mixed together in chloroform (15 ml). After 2 h, the mixture was added to a stirred solution of compound (IE) (0.88 g, 2.5 mmol) and triethylamine (0.70 ml, 5.0 mmol) in chloroform (15 ml). After 2 h, the solution was poured into ethanol (75 ml) and, after 10 min, the solid was filtered off. The red product (1.70 g) was crystallized from carbon tetrachloride–ethanol (1 : 1) to give red-brown prisms of the essentially pure α -(2-bromo-4-ethoxyphenylhydrazono)benzyl α -(2,4-dibromophenylhydrazono)benzyl disulphide (IIIDE) (1.00 g, 54%), m.p. 126–127° (Found: C, 45.55; H, 3.1; N, 7.5; S, 8.4. $C_{28}H_{23}Br_3N_4OS_2$ requires C, 45.75; H, 3.15; N, 7.6; S, 8.7%). T.l.c. of the analytical sample showed the presence of traces of disulphides (IIID and E); the last two compounds were also present in the mother liquors (t.l.c.).

(iii) Similar experiments with (ID) and 4-nitrobenzenethiol resulted in almost quantitative isolation of both the disulphide (IIID) and bis-4-dinitrophenyl disulphide, m.p. 181–183° (lit.,¹⁰ 182°).

(iv) Triethylamine (70 μ l, 0.5 mmol) was added to a mixture of (IA) (0.11 g, 0.5 mmol) and (IIID) (0.39 g, 0.5 mmol) in chloroform (10 ml). After 5 h, t.l.c. of the solution showed three main spots, two corresponding to the disulphides (IIIA) and (IIID). The third spot lay between (IIIA) and (IIID) and probably corresponds to the *asym*-disulphide (IIIAD).

Formation of (VII) from (IVDc) and from (IVDd); Stability of (IIID) under Reaction Conditions.—(i) A

¹⁰ 'Handbook of Physics and Chemistry,' Chemical Rubber Co., Cleveland, 52nd edn., 1971–1972.

mixture of (IVDc) (1.08 g, 2.1 mmol), triethylamine (7 ml), and acetonitrile (7 ml) was boiled under reflux for 30 min, and then cooled. Filtration gave bis- $[\alpha$ -(2,4-dibromophenylhydrazono)benzyl] sulphide (VII) (24%), m.p. (after one crystallization) 199—201°; mixed ⁷ m.p. 198—201°. Evaporation of the filtrate gave a dark intractable oil.

(ii) Compound (IVDd) (2.70 g, 5.0 mmol) was boiled under reflux for 1.5 h in a mixture of triethylamine (15 ml) and acetonitrile (15 ml). From the cooled brown solution was isolated the sulphide (VII) in 22% yield. T.l.c. of the mother liquor showed several spots, including one corresponding to (IIID).

(iii) The disulphide (IIID) (1.54 g, 2.0 mmol) was refluxed for 45 min in a mixture of acetonitrile (5 ml) and triethylamine (5 ml). The brown solution was evaporated to dryness *in vacuo* and ethanol (20 ml) was added. Filtration of the cooled solution resulted in 29% recovery of starting material. T.l.c. of the solution indicated the presence of the thiohydrazide (ID).

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