

Some Reactions of Thiohydrazides and Related Compounds

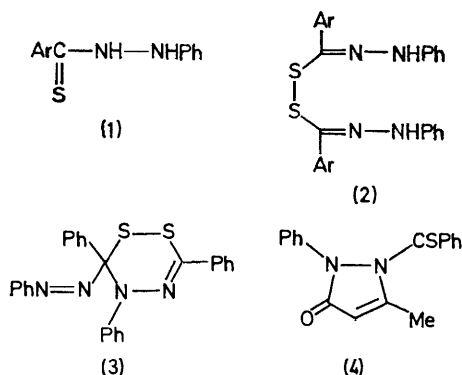
By Derek H. R. Barton, John W. Ducker, W. Anthony Lord, and Philip D. Magnus,* Chemistry Department, Imperial College, London SW7 2AY

Oxidation of the thiohydrazides (1; Ar = Ph, 1-naphthyl, or *p*-MeO·C₆H₄) gave the corresponding disulphides (2). Oxidation of the disulphide (2; R = Ph) produced the dithiadiazine (3) and the thiadiazole (7). Some other reactions of the disulphide (2; Ar = Ph) are described.

WHILE preparing thiohydrazides of the general formula (1) we observed that during chromatographic purification over alumina the thiohydrazide (1; Ar = Ph) was converted into a new compound. The spectral data and, in

(2; Ar = Ph) could be conveniently prepared from the thiohydrazide (1; Ar = Ph) merely by treatment with triethylamine in the presence of air. Analogous products (2; Ar = 1-naphthyl or *p*-MeO·C₆H₄) were prepared from the corresponding thiohydrazides (1).

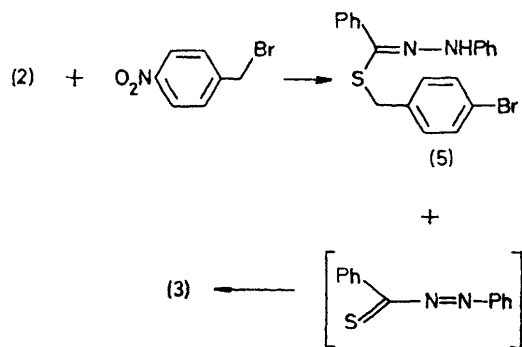
Subsequent to the one reference¹ to these disulphides no chemistry of these unusual molecules has been reported. Oxidation of the disulphide (2; Ar = Ph) with potassium ferricyanide gave the dithiadiazine (3) (see later for proof of structure). Treatment of (2; Ar = Ph) with acetic anhydride gave the pyrazolone (4) (18%), also formed from the thiohydrazide (1; Ar = Ph) and acetic anhydride. The disulphide (2; Ar = Ph) reacted with *p*-nitrobenzyl bromide to give the sulphide (5) (64%) and the dithiadiazine (3) (see Scheme 1). Reaction of the disulphide with *N'*-phenylbenzohydrazonoyl chloride gave the disulphide (6) (30%), and a new oxidation product, the thiadiazole (7) (see later for proof of structure). Many attempts were made to oxidise the disulphide (2; Ar = Ph), and the dithiadiazine (3) and the thiadiazole (7) were formed as the major products in many reactions. Attempted methylation of the disul-



particular, molecular weight determination showed that oxidation to the disulphide (2; Ar = Ph) had taken place. Oxidation of the thiohydrazide (1; Ar = Ph) with iodine gave the disulphide (2; Ar = Ph) in accord with a literature report.¹ Furthermore, the disulphide

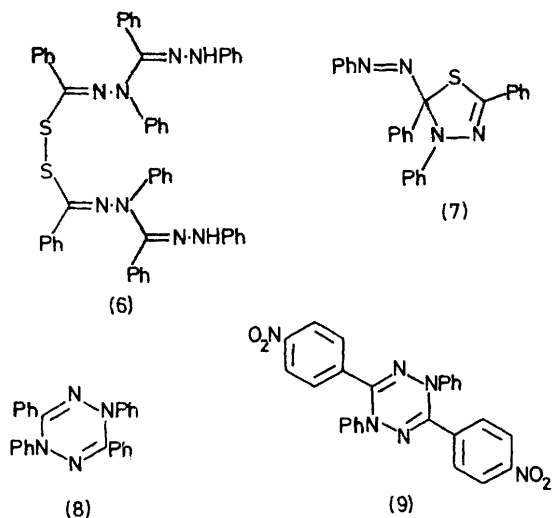
¹ H. Wuyts and A. Lacourt, *Bull. Soc. chim. belges*, 1939, **48**, 193.

phide (2; Ar = Ph) with silver oxide-methyl iodide gave the thiadiazole (7) (26%) and the dihydrotetrazine



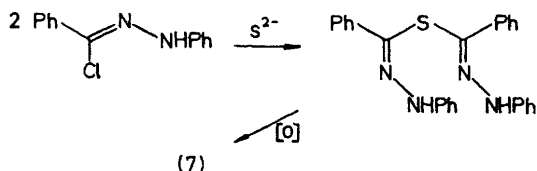
SCHEME 1

(8) (19%). Compound (8) was synthesised (25% yield) by fusion of *N*'-phenylbenzohydrazonoyl chloride at 190 °C for 30 min.² The thiadiazole (7) was synthesised by the reaction of *N*'-phenylbenzohydrazonoyl chloride



SCHEME 2

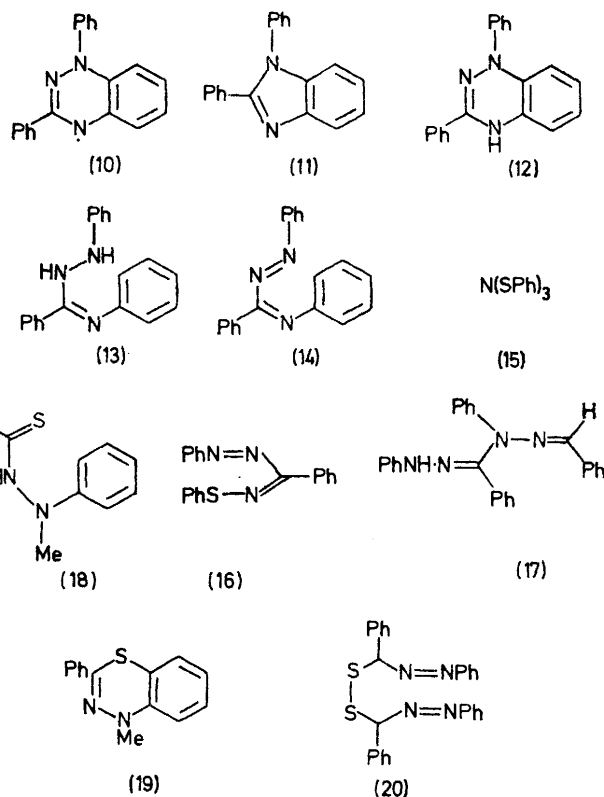
with sodium sulphide followed by oxidation with potassium ferricyanide (Scheme 2). The reaction of the



disulphide (2; Ar = Ph) with silver oxide alone gives little improvement in the yield of the thiadiazole (7)

(33%), although it was the only isolated product. Treatment of the disulphide (2; Ar = Ph) with tetranitromethane gave the dihydrotetrazine (9) (20%).

The dihydrodithiadiazine (3) is stable at room temperature; however, conversion into the dihydrothiadiazole (7) (70%) is achieved in acetone at reflux. The dihydrodithiadiazine (3) is a known oxidation product of the thiohydrazide (1; Ar = Ph), although its structure had not been determined.³ Dichlorodicyanobenzoquinone (DDQ) oxidised the disulphide (2; Ar = Ph) to



give the dihydrodithiadiazine (3) (91%) in good yield, providing a proof of structure of (3) and hence of (7). Attempted oxidation of the disulphide (2; Ar = Ph) with nitrobenzene gave the 1,4-dihydro-1,3-diphenyl-1,2,4-benzotriazinyl radical (10) (24%).⁴ Reductive acetylation of this radical gave 1,2-diphenylbenzimidazole⁵ (11). The radical (10) was synthesised from benzanilide phenylhydrazone⁶ (13) by treatment with an excess of silver oxide to give the imino-azo-compound⁷ (14), which cyclises to the precursor of the radical (12) on treatment with hydrogen bromide. Oxidation of this compound in air gave the radical (10). Treatment of benzanilide phenylhydrazone (13) with *N*-bromosuccinimide gave the radical (10) (74%) in one step.

² M. K. Saxena, M. N. Gudi, and M. V. George, *Tetrahedron*, 1973, **29**, 101.

³ H. Bock, E. Baltin, and J. Kroner, *Chem. Ber.*, 1966, **99**, 3337.

⁴ H. M. Blatter and H. Lukaszewski, *Tetrahedron Letters*, 1968 2701.

⁵ L. Wolff, *Annalen*, 1912, **394**, 67.

⁶ H. V. Pechmann, *Ber.*, 1895, **28**, 2362.

⁷ M. Busch and R. Ruppenthal, *Ber.*, 1910, **43**, 3001.

The reaction of the disulphide (2; Ar = Ph) with tris(phenylsulphenyl)amine⁸ (15) gave the same product (16) as formed from the trisulphenamide (15) and (1; Ar = Ph).

The dihydrodithiadiazine (3) and the dihydrothiadiazole (7) gave the tetrazine (8) on reduction with zinc and aqueous ammonium chloride. Desulphurisation of either (3) or (7) with triethyl phosphite gave a complex mixture, whereas the action of triphenylphosphine in methanol at room temperature on the dihydrothiadiazine (3) gave the dihydrothiadiazole (7) (70%). Desulphurisation of the dihydrothiadiazole (7) with Raney nickel gave the product (17) (40%). This was also obtained from the dihydrodithiadiazine (3), in 12% yield. The benzaldehyde derivative (17) was synthesised by fusion of benzaldehyde phenylhydrazone and *N*-phenylbenzohydrazonoyl chloride at 130 °C for 10 min.

N'-Methyl-*N'*-phenylbenzothiohydrazide (18) reacted with iodine to give, not the expected disulphide, but 1-methyl-3-phenyl-4,1,2-benzothiadiazine (19) (26%).⁹

The ¹³C n.m.r. spectrum of the disulphide (2; Ar = Ph) showed three different types of carbon atom to which H was *not* bound. This excludes an alternative formula (20), which otherwise explains much of the chemical evidence.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were measured for Nujol mulls unless otherwise stated. N.m.r. spectra were recorded with a Varian A60 instrument for solutions in CDCl₃ with tetramethylsilane as internal standard. U.v. spectra were measured for solutions in ethanol unless otherwise stated. All solvents were purified prior to use by standard techniques. Light petroleum refers to the fraction of b.p. 40–60°.

Wt. of Et ₃ N (g)	Wt. of alumina (g) (grade in parentheses)	Yield of disulphide (2; Ar = Ph) (%)
0	0	15
5.0	0	55
0	45.0 (1)	15
0	45.0 (2)	20
0	45.0 (3)	28
0	45.0 (4)	51
0	45.0 (5)	64
0	45.0	77
	(5 + 12% water)	
0	15.0 (5)	55
0	30.0 (5)	91
5.0	30.0 (5)	86

Bis-(α -phenylhydrazonobenzyl) Disulphide (2; Ar = Ph).—*N'*-Phenylbenzothiohydrazide (1; Ar = Ph) (1.0 g) in benzene (100 ml) was stirred for 12 h with the amounts of alumina indicated in the Table and triethylamine (no precautions were taken to exclude air). Product-containing solutions were concentrated and filtered through alumina to remove starting material (1; Ar = Ph) and polar by-products. The disulphide (2; Ar = Ph) was obtained as orange-red needles, m.p. 140–142° (from benzene-ethanol), ν_{\max} . 1 602, 1 518, 1 262, 762, 745, and 690 cm⁻¹, λ_{\max} .

⁸ D. H. R. Barton, I. A. Blair, P. D. Magnus, and R. K. Norris, *J.C.S. Perkin I*, 1973, 1031 and 1037.

(CHCl₃) 324, 304, and 400 nm (ϵ 21 800, 19 100, and 13 100), τ 1.9–3.2 (m) [Found: C, 68.3; H, 5.0; N, 12.2; S, 13.9%; *M* (osmometry), 436.0. Calc. for C₂₆H₂₂N₄S₂: C, 68.4; H, 5.3; N, 12.3; S, 14.0%; *M*, 484].

Use of the method of Wuyts and Lacourt¹ for the preparation of the disulphide (2; Ar = Ph) gave material of m.p. and mixed m.p. 140–142°.

Bis-[1-naphthyl(phenylhydrazono)methyl] Disulphide (2; Ar = 1-naphthyl).—*N'*-Phenyl-1-naphthothiohydrazide (1; Ar = 1-naphthyl)¹ (350 mg) in benzene (60 ml) was treated with alumina (15.0 g; G5). The mixture was stirred at room temperature for 12 h with *no* precautions to exclude air. The disulphide (2; Ar = 1-naphthyl) (57%) was isolated by p.l.c.; m.p. 165–166° (lit.,¹ 165°).

N'-Phenyl-4-methoxybenzothiohydrazide (1; Ar = *p*-MeO-C₆H₄).—4-Methoxythiobenzoylthioglycolic acid (1.0 g) in aqueous *N*-sodium hydroxide (4 ml) was treated with phenylhydrazine (0.5 g). The mixture was heated on a steam-bath until the deep red colouration had disappeared and a yellow oil separated. Water (20 ml) was added to the mixture, and the oil extracted with benzene. The washed [water (2 × 50 ml)] and dried (Na₂SO₄) extract was evaporated to give the *hydrazide* (1; Ar = *p*-MeO-C₆H₄) (0.84 g, 80%), m.p. 95.5–96.5° (from benzene-light petroleum), ν_{\max} . 3 200, 1 605, 1 500, 1 267, 1 190, 960, and 835 cm⁻¹, λ_{\max} . (EtOH) 282 nm (ϵ 12 000) (Found: C, 65.1; H, 5.4; N, 10.9; S, 12.7. C₁₄H₁₄N₂OS requires C, 65.1; H, 5.5; N, 10.9; S, 12.6%).

Bis-(4-methoxy- α -phenylhydrazonobenzyl) Disulphide (2; Ar = *p*-MeO-C₆H₄).—The *hydrazide* (1; Ar = *p*-MeO-C₆H₄) (1 g) in benzene (200 ml) was treated with alumina (45 g; G5) and the mixture stirred at room temperature for 16 h. The mixture was filtered and the filtrate evaporated to give the *disulphide* (2; Ar = *p*-MeO-C₆H₄) (0.56 g, 57%), m.p. 114–116° (from benzene-ethanol), ν_{\max} . 1 605, 1 505, 1 250, 1 175, 1 030, and 685 cm⁻¹, λ_{\max} . (EtOH) 302 and 407 nm (ϵ 30 400 and 15 200) [Found: C, 65.4; H, 5.2; N, 10.8; S, 12.6%; *M* (osmometry), 522. C₂₈H₂₆N₄O₂S₂ requires C, 65.3; H, 5.1; N, 10.9; S, 12.4%; *M*, 516].

5-Methyl-2-phenyl-1-thiobenzoylpyrazol-3(2H)-one (4).—The disulphide (2; Ar = Ph) (20 mg) in acetic anhydride (2 ml) and pyridine (1 ml) was heated at 100 °C for 2 h. The mixture was poured into water and extracted with chloroform (3 × 10 ml). P.l.c. gave the *pyrazolone* (4) (18%). Similar treatment of the thiohydrazide (1; Ar = Ph) gave the *pyrazolone* (4) (60%), m.p. 152–153° (from ethanol), ν_{\max} . 1 590 cm⁻¹, λ_{\max} . 386 nm (ϵ 17 000), τ 7.82 (3 H, s), 3.98 (1 H, s), and 2.0–2.9 (10 H, m) (Found: C, 69.4; H, 5.1; N, 9.4; S, 11.2. C₁₇H₁₄N₂OS requires C, 69.4; H, 4.8; N, 9.4; S, 10.9%).

Reaction of the Disulphide (2; Ar = Ph) with *p*-Nitrobenzyl Bromide.—The disulphide (2; Ar = Ph) (250 mg) in acetone (10 ml) containing *p*-nitrobenzyl bromide (250 mg) and sodium hydrogen carbonate (1 g) was stirred at room temperature for 2 days. Work-up and p.l.c. gave the *sulphide* (5) (64%), m.p. 90–91° (from benzene-light petroleum), ν_{\max} . 1 602, 1 520, 1 345, and 690 cm⁻¹, λ_{\max} . (CHCl₃) 348 nm (ϵ 19 400), τ 6.1 (2 H, s) and 4.5–1.6 (15 H, m) (Found: C, 66.4; H, 4.9; N, 11.5; S, 8.8. C₂₀H₁₇N₃O₂S requires C, 66.1; H, 4.7; N, 11.6; S, 8.8%). The dithiadiazine (3) was also isolated.

Reaction of the Disulphide (2; Ar = Ph) with *N'*-Phenyl-

⁹ I. T. Barnish and M. S. Gibson, *J. Chem. Soc. (C)*, 1970, 854; P. D. Callaghan, and M. S. Gibson, *ibid.*, 1970, 2106; I. T. Barnish, P. D. Callaghan and M. S. Gibson, *ibid.*, 1974, 215.

benzohydrazonoyl Chloride.—The disulphide (2; Ar = Ph) (120 mg) and the imino-chloride (120 mg) in dry dichloromethane (15 ml) and triethylamine (1 ml) were heated at reflux for 2 h. Work-up and p.l.c. gave the *disulphide* (6) (30%), m.p. 175–177° (from ethanol), ν_{\max} 1 580, 1 515, 1 490, 1 250, 760, 780, and 690 cm^{-1} , λ_{\max} (CHCl₃) 344 and 300 nm (ϵ 80 000 and 40 000) (Found: C, 73.9; H, 5.3; N, 13.3; S, 7.6. C₂₂H₁₄N₄S₂ requires C, 74.1; H, 5.0; N, 13.3; S, 7.6%). A by-product from this reaction is the thiadiazole (7) (30%) (see later for physical constants).

Attempted Methylation of the Disulphide (2; Ar = Ph).—The disulphide (2; Ar = Ph) (240 mg) and methyl iodide (500 mg) in benzene (10 ml) were stirred with an excess of silver oxide (400 mg) at room temperature for 3 days. Work-up and p.l.c. gave *2,3-dihydro-2,3,5-triphenyl-2-phenylazo-1,3,4-thiadiazole* (7) (26%) as a gum which crystallised after 3 months at 0 °C to give dark red nuggets, m.p. 106–108° (from benzene–ethanol), ν_{\max} 1 590, 1 490, 1 345, 1 130, 980, 770, 750, and 695 cm^{-1} , λ_{\max} (CHCl₃) 347 nm (ϵ 15 700) (Found: C, 74.3; H, 4.8; N, 13.3; S, 7.6. C₂₆H₂₀N₄S requires C, 74.4; H, 4.7; N, 13.3; S, 7.6%). A by-product was isolated and crystallised from benzene–light petroleum to give the tetrazine (8) (19%), identical with an authentic specimen.²

The thiadiazole (7) was synthesised as follows. *N'*-Phenylbenzohydrazonoyl chloride (60 mg) in acetone (5 ml) containing sodium sulphide (10 mg) was stirred at room temperature for 3 h. Filtration, evaporation of the filtrate, and p.l.c. gave *bis-(α -phenylhydrazonobenzyl) sulphide* (45 mg, 81%), m.p. 151–152° (from benzene–light petroleum), ν_{\max} 1 580, 1 480, 1 440, 1 330, 1 250, 760, and 600 cm^{-1} , λ_{\max} 242, 284, and 335 nm (ϵ 30 000, 17 600, and 15 200) (Found: C, 74.3; H, 5.4; N, 13.8; S, 7.7. C₂₆H₂₂N₄S requires C, 73.9; H, 5.3; N, 13.3; S, 7.6%). The sulphide (50 mg) in benzene (50 ml) was treated with aqueous alkaline potassium ferricyanide and the two-phase mixture was shaken vigorously until the benzene layer changed colour from yellow to red. The benzene layer was separated, washed with water (3 \times 50 ml), dried (Na₂SO₄), and evaporated to give the thiadiazole (7) (70%), m.p. 106–108° (from ethanol).

Reaction of the Disulphide (2; Ar = Ph) with *Silver Oxide*.—The disulphide (2; Ar = Ph) (200 mg) in benzene (15 ml) was stirred with silver oxide (1.0 g) for 2 days. Filtration and evaporation gave the thiadiazole (7) (33%), identical with an authentic sample.

Reaction of the Disulphide (2; Ar = Ph) with *Tetranitromethane*.—The disulphide (2; Ar = Ph) (100 mg) in dichloromethane (20 ml) was treated with tetranitromethane (600 mg). After 1 h, work-up and p.l.c. gave *1,4-dihydro-3,6-bis-(4-nitrophenyl)-1,2,4,5-tetrazine* (9) (20%), m.p. 308–315° (from dichloromethane–ether) (lit.,⁹ 305°), ν_{\max} 1 590, 1 500, 1 308, 1 110, 1 000, 852, and 700 cm^{-1} .

Reaction of the Disulphide (2; Ar = Ph) with *Potassium Ferricyanide*.—The disulphide (2; Ar = Ph) (1.0 g) in benzene (40 ml) and ethanol (40 ml) was treated with aqueous potassium ferricyanide (1.65 g) in water (10 ml) containing sodium hydroxide (400 mg). After vigorous shaking (1 h) of the two-phase mixture the benzene layer was separated, washed with water (3 \times 20 ml), and dried (Na₂SO₄). Evaporation gave *3,4-dihydro-3,4,6-triphenyl-3-phenylazo-1,2,4,5-dithiadiazine* (3), m.p. 119–121° (from dichloromethane–acetone), ν_{\max} 1 495, 1 300, 1 230, 990, 790, and 710 cm^{-1} , λ_{\max} (CHCl₃) 286 nm (ϵ 20 000), τ 2.0–3.1 (20 H, m) (Found: C, 68.8; H, 4.6; N, 12.2; S, 13.9.

C₂₆H₂₀N₄S₂ requires C, 69.0; H, 4.5; N, 12.4; S, 14.1%). If the recrystallisation is not conducted rapidly the dithiadiazine (3) is converted into the thiadiazole (7) and sulphur. The dithiadiazine (3) (100 mg) in acetone (25 ml) was heated at reflux for 2 h. Evaporation and crystallisation of the residue from ethanol gave the thiadiazole (7) (60 mg, 70%).

Reaction of the Disulphide (2; Ar = Ph) with *Dichlorodicyanobenzoquinone (DDQ)*.—The disulphide (2; Ar = Ph) (114 mg) in benzene (10 ml) containing DDQ (103 mg) was stirred at room temperature for 10 min. Filtration through alumina and evaporation gave the dithiadiazine (3) (91%), m.p. 119–121°.

Reaction of the Disulphide (2; Ar = Ph) with *Nitrosobenzene*.—The disulphide (2; Ar = Ph) (120 mg) in dichloromethane (25 ml) at 0 °C was treated with nitrosobenzene (500 mg) and the mixture was kept at 0 °C for 2 days. Work-up and p.l.c. gave *1,4-dihydro-1,3-diphenyl-1,2,4-benzotriazinyl* (10) (24%), identical with an authentic sample.⁴

Reductive Acetylation of 1,4-Dihydro-1,3-diphenyl-1,2,4-benzotriazinyl (10).—The radical (10) (100 mg) in acetic anhydride (5 ml) and glacial acetic acid (5 drops) was treated with zinc dust (200 mg) and the mixture stirred at room temperature for 8 h. Filtration and evaporation gave *1,2-diphenylbenzimidazole* (11)⁵ (39%), m.p. 110–111° (from benzene–light petroleum) (lit.,⁵ 112–113°).

α -Phenyl- α -phenyliminotoluene (14).—Benzanilide phenylhydrazone (13)⁶ (200 mg) in benzene (5 ml) containing silver oxide (500 mg) was stirred at room temperature for 2 h. The resulting red solution was filtered and the filtrate evaporated to give the imino-azo-compound (14) (91%), m.p. 101–102° (lit.,⁷ 101–102°). Treatment of this compound with hydrogen bromide in acetic acid gave the benzotriazine (12) which is rapidly oxidised (air) to the radical (10).

1,4-Dihydro-1,3-diphenyl-1,2,4-benzotriazinyl (10).—Benzanilide phenylhydrazone (13) (287 mg) in dichloromethane (30 ml) and pyridine (3 ml) was treated with *N*-bromosuccinimide (238 mg). After 0.5 h the mixture was washed with aqueous sodium thiosulphate and water, and dried (Na₂SO₄). Evaporation of the dried dichloromethane layer gave the radical (10) (210 mg, 74%).

Reaction of the Disulphide (2; Ar = Ph) with *Tris(phenylsulphenyl)amine*.—The disulphide (2; Ar = Ph) (114 mg) and the trisulphenamide (15) (340 mg) in dichloromethane (20 ml) were heated at reflux for 2 h. Evaporation and p.l.c. of the residue gave *α -phenylazobenzaldehyde S-phenylthio-oxime* (16) (67 mg, 42%), m.p. 119–120° (from light petroleum), identical with an authentic specimen.¹⁰

Reduction of the Dihydrothiadiazole (7) with *Zinc-Ammonium Chloride*.—The thiadiazole (7) (84 mg), zinc dust (100 mg), and ammonium chloride (100 mg) were stirred in ethanol (10 ml) for 6 h. Filtration and evaporation, followed by p.l.c. gave the tetrazine (8) (40%), m.p. 204–205° (from ethanol), identical with an authentic sample.

Similar treatment of the dihydrodithiadiazine (3) gave the dihydrothiadiazole (7) (10%) and the tetrazine (8) (40%).

Reaction of the Dihydrodithiadiazine (3) with *Triphenylphosphine*.—The dihydrodithiadiazine (3) (120 mg) and triphenylphosphine (200 mg) in methanol (10 ml) were stirred at room temperature for 2 days. Red crystals of the dihydrothiadiazole (7) (70%) separated.

¹⁰ J. Almog, D. H. R. Barton, P. D. Magnus, and R. K. Norris, *J.C.S. Perkin I*, 1974, 863.

Desulphurisation of the Dihydrothiadiazole (7) with Raney Nickel.—The dihydrothiadiazole (7) (120 mg) in benzene (5 ml) containing Raney nickel (1 g) was stirred at room temperature for 3 h. The mixture was filtered and the filtrate evaporated. P.l.c. of the residue gave α -[*N*-phenyl-*N*-(α -phenylhydrazonobenzyl)hydrazono]toluene (17) (40%), m.p. 207–209° (decomp.) (from benzene-ethanol), ν_{\max} 1 600, 1 485, 1 480, 1 380, 1 250, 1 130, and 755 cm^{-1} , λ_{\max} (CHCl₃) 336 and 300 nm (ϵ 42 000 and 15 000) (Found: C, 80.2; H, 5.5; N, 14.4. C₂₆H₂₂N₄ requires C, 80.0; H, 5.7; N, 14.4%).

Similar desulphurisation of the dihydrodithiadiazine (3) gave the hydrazone (17) (12%).

An authentic sample of the hydrazone (17) was prepared by fusion of *N*'-phenylbenzohydrazonoyl chloride (200 mg) and benzaldehyde phenylhydrazone (1 g) at 130 °C for 10 min. P.l.c. gave the hydrazone (17) (40%), m.p. 207–209°

(decomp.) (from benzene-ethanol), identical with the foregoing product.

Oxidation of N'-Methyl-N'-phenylbenzothiohydrazide (18) with Iodine.—The thiohydrazide (18) (116 mg) (prepared in the usual way from *N*-methyl-*N*-phenylhydrazine and thio-benzoylthioglycolic acid) in benzene (10 ml) was treated with iodine (100 mg) in benzene (5 ml). Work-up and p.l.c. gave 1-methyl-3-phenyl-4,1,2-benzothiadiazine (19) (26%), m.p. 53–54° (from ethanol), ν_{\max} 1 570, 1 580, 1 440, 1 180, 1 115, 990, 920, 755, and 700 cm^{-1} , λ_{\max} 229, 265, 316, and 380 nm (ϵ 15 800, 20 600, 3 600, and 3 400), τ 6.5 (3 H, s), 2.5–3.2 (7 H, m), and 2.0–2.2 (2 H, m) (Found: C, 70.1; H, 5.3; N, 11.8; S, 13.8. C₁₄H₁₂N₂S requires C, 70.0; H, 5.0; N, 11.7; S, 13.3%).

We thank Dr. L. Phillips and Dr. R. B. Jones for the ¹³C n.m.r. measurements.

[5/1261 Received, 26th June, 1975]