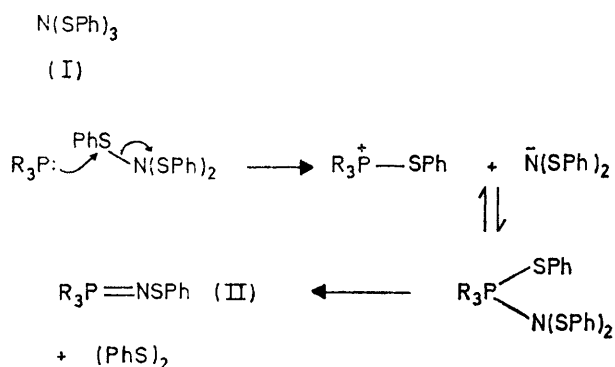


The Chemistry of Trisulphenamides [N(SR)₃]. Part III.¹ Ionic and Radical Reactions of Tribenzenesulphenamide [N(SPh)₃]

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Tribenzenesulphenamide reacts with triphenylphosphine and other P^{III} species to give Wittig-type reagents. These furnish phenylthioimino-derivatives in reactions with unhindered, electrophilic carbonyl groups. Further aspects of the chemistry of the radical (PhS)₂N• have been explored, in particular the formation of new functional group systems in reactions with arylhydrazones and with C-nitroso-compounds.

THE chemistry of tribenzenesulphenamide (I) described so far¹ is radical in character, thermal decomposition at about 80° giving the purple radical (PhS)₂N•. It might, however, be expected that tribenzenesulphenamide (I) would also undergo ionic reactions, at lower temperatures, with appropriate nucleophilic reagents.



SCHEME 1

Treatment of tribenzenesulphenamide (I) with triphenylphosphine at room temperature gave an immediate reaction with formation of the 'ylide' (II; R = Ph) and diphenyl disulphide. The 'ylide' (II; R = Ph) could not be isolated because of its sensitivity to oxygen and moisture. Its formation may be rationalised

TABLE I
ArCH=NSPh (III)

No.	Ar	Yield ^a (%)	M.p. (°) (solvent)
1	Ph	61	44 (isopentane)
2	<i>p</i> -NO ₂ -C ₆ H ₄	84	83–84 (light petroleum)
3	<i>m</i> -NO ₂ -C ₆ H ₄	66 ^b	65 (light petroleum)
4	<i>o</i> -NO ₂ -C ₆ H ₄	77 ^c	41 (ethanol)
5	<i>p</i> -CN-C ₆ H ₄	89	75 (light petroleum)
6	<i>m</i> -BrC ₆ H ₄	78 ^d	38 (ethanol)
7	<i>p</i> -MeO-C ₆ H ₄	25	60–61 (ethanol)
8	Ph-CH=CH	47	60 (isopentane)
9	MeCO·CO ₂ Et	21	(Oil)

^a Yield based on initial (PhS)₂N•. ^b From (II; R = OEt).

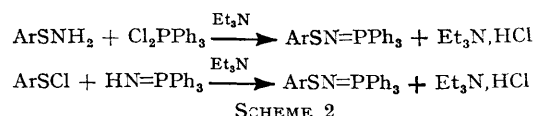
^c From (II; R = Buⁿ). ^d 64% yield from (II; R = OEt); 39% from (II; R = Buⁿ).

as in Scheme 1. Similarly, solutions of the 'ylides' (II; R = Buⁿ or OEt) were prepared from triben-

zenesulphenamide (I) and tri-*n*-butylphosphine or triethyl phosphite, respectively.

Reactions of the 'ylides' (II; R = Ph, Buⁿ, or OEt) with aromatic aldehydes and ethyl pyruvate gave S-phenylthio-oximes (III) (Table I).

The only other reported arylthioiminophosphoranes² have been prepared either from the arylsulphenyl chloride or from the arylsulphenylamine (Scheme 2).



Compound (II; R = Ph) could not be prepared by these methods. The 'ylide' (II; R = Ph) is stable in benzene solution for several days as evidenced by its reaction with *p*-nitrobenzaldehyde to give the thio-oxime (III; Ar = C₆H₄·NO₂-*p*). The 'ylide' did not react with aliphatic aldehydes such as butyraldehyde and phenylacetaldehyde, or with ketones like cyclohexanone and benzophenone. The order of reactivity of the three iminophosphoranes was found to be (II; R = Ph) > (II; R = EtO) > (II; R = Buⁿ) as judged by the yields of (III; Ar = C₆H₄Br-*m*) (78, 63.5, and 39%, respectively).

Further evidence for the formation of the 'ylide' (II; R = Ph) was obtained from its reactions with methyl iodide and benzyl bromide to give the isolable crystalline phosphonium salts³ (IV; R = Me or CH₂Ph), respectively.

Oxidation of the thio-oximes (III; Ar = Ph or C₆H₄Br-*m*) with *m*-chloroperbenzoic acid gave the corresponding sulfoxides (V; Ar = Ph or C₆H₄Br-*m*) in excellent yields.

Treatment of the enamine 1-pyrrolidinocyclohexene with tribenzenesulphenamide (I) at room temperature gave dibenzenesulphenamide (88%) and 2-(phenylthio)-cyclohexanone (VI) (80%). This reaction is clearly a nucleophilic displacement on sulphur by the enamine.

Oxidation of tribenzenesulphenamide (I) with *m*-chloroperbenzoic acid (3 equiv.) gave the sulfoxide (VII) as a crystalline solid that decomposed at room temperature during 1 week. The sulfoxide (VII) did not react with phenols.¹

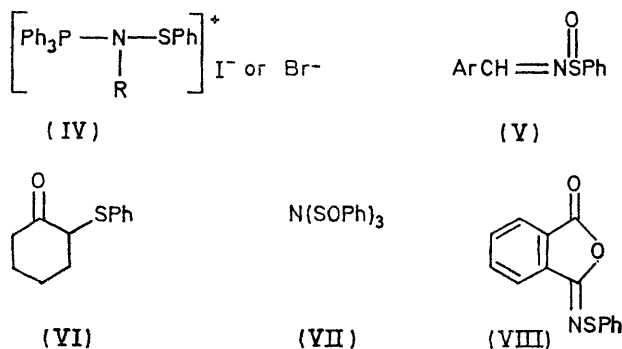
Tribenzenesulphenamide (I) reacted with phthalic

¹ Parts I and II, D. H. R. Barton, I. A. Blair, P. D. Magnus, and R. K. Norris, *J.C.S. Perkin I*, 1973, 1031, 1037.

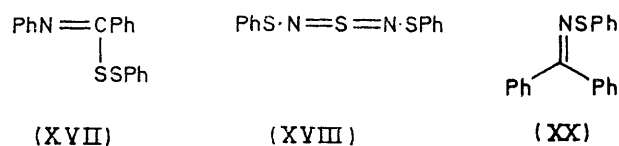
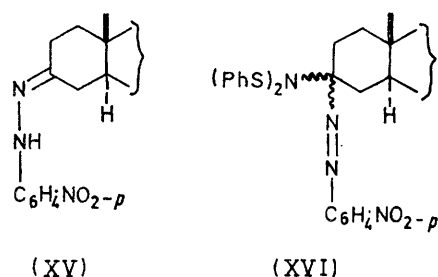
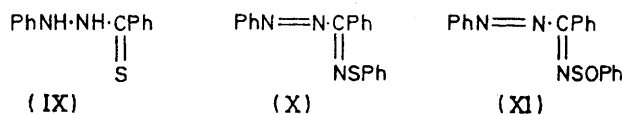
² N. Zhmurova, A. P. Martynyuk, and A. V. Kirsanov, *J. Gen. Chem. (U.S.S.R.)*, 1967, **37**, 1789; see also F. A. Davis, W. A. R. Siegeir, S. Evans, A. Schwartz, D. L. Goff, and R. Palmer, *J. Org. Chem.*, 1973, **38**, 2809.

³ L. Horner and A. Gross, *Annalen*, 1955, **591**, 117; H. Zimmer and G. Singh, *J. Org. Chem.*, 1963, **28**, 483.

anhydride⁴ only in the presence of triphenylphosphine, to give compound (VIII).



Further investigation of the reactions of the radical $\cdot\text{N}(\text{SPh})_2$ formed by thermolysis¹ of tribenzenesulphenamide (I) were carried out. Treatment of the thiohydrazone (IX) with the reagent (I) at 80° gave the phenylazo-thio-oxime (X) as almost black crystals. Reductive acetylation of (X) gave acetanilide as the only isolable product. Oxidation of (X) with hydrogen peroxide in acetic anhydride gave the crystalline sulphoxide (XI).

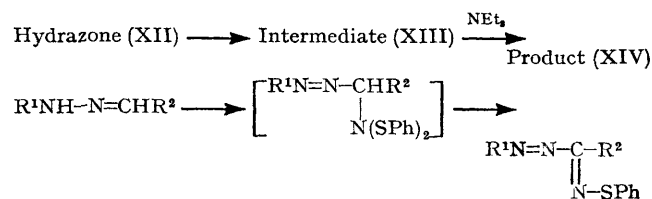


Similarly, reaction of the radical $\cdot\text{N}(\text{SPh})_2$ with aromatic phenylhydrazones (XIIa—d) gave phenylazo-thio-oximes via the intermediates (XIIIa—d) (Scheme 3). In the case of the hydrazone (XIIId) the intermediate (XIIIId) could be isolated and fully characterised. Treatment of this adduct with triethylamine gave the phenylazo-thio-oxime (XIVd). The reaction sequence also applies to aliphatic aldehyde phenylhydrazones [e.g. (XIIe) \rightarrow (XIVe)].

5 α -Cholestan-3-one *p*-nitrophenylhydrazone (XV) re-

acted with tribenzenesulphenamide (I) at 80° to give two isomers of the product (XVI), thermolysis of which gave a complex mixture.

Thiobenzanilide reacted with tribenzenesulphenamide (I) at 80° to give the imino-disulphide (XVII), which on treatment with benzenethiol gave thiobenzanilide and diphenyl disulphide. Thiobenzamide also reacted with the sulphenamide (I) to give a compound $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_3$, identified as (XVIII) by comparison with an authentic specimen kindly provided by Dr. D. A. Armitage (Queen Elizabeth College). This compound is also formed when

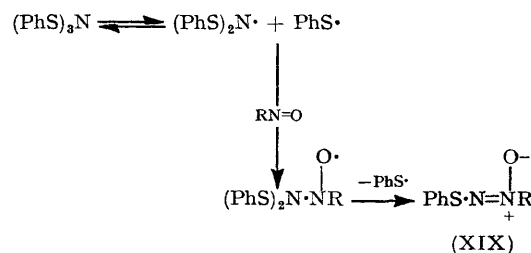


- a; $\text{R}^1 = \text{R}^2 = \text{Ph}$
 b; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{C}_6\text{H}_4\cdot\text{OMe}-p$
 c; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{C}_6\text{H}_4\cdot\text{NO}_2-p$
 d; $\text{R}^1 = \text{C}_6\text{H}_4\cdot\text{NO}_2-p$, $\text{R}^2 = \text{C}_6\text{H}_4\cdot\text{OMe}-p$
 e; $\text{R}^1 = \text{Pr}^n$, $\text{R}^2 = \text{C}_6\text{H}_4\cdot\text{NO}_2-p$

SCHEME 3

the sulphenamide (I) reacts with sulphur, hydrogen sulphide, or thiourea.

Tribenzenesulphenamide (I) reacted with *C*-nitroso-compounds to give the unusual derivatives (XIX) in reasonable yields. The mechanism for their formation is outlined in Scheme 4.



SCHEME 4

Both thiobenzophenone and diphenyldiazomethane react with tribenzenesulphenamide (I) at 80° to give the *S*-phenylthio-oxime of benzophenone (XX) in good yield.

EXPERIMENTAL

M.p.s were determined on 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 CDCl_3 with tetramethylsilane as internal standard. U.v. spectra were measured for solutions in ethanol unless otherwise stated. Rotations were taken for solutions in CHCl_3 (1%).

All solvents were purified prior to use by standard techniques. Light petroleum refers to the fraction of b.p. 40–60°.

Triphenyl(phenylthioimino)phosphorane (II; $\text{R} = \text{Ph}$).—Tribenzenesulphenamide (I) (341 mg) in dry benzene (5 ml)

* F. Ramirez, H. Y. Yamanaka, and O. H. Basedow, *J. Amer. Chem. Soc.*, 1961, **83**, 173; C. W. Bird and D. Y. Wong, *Chem. Comm.*, 1969, 932.

was treated with triphenylphosphine (262 mg) in one portion. The mixture was stirred until the solid had dissolved. The solution contained the phosphorane (II; R = Ph) and diphenyl disulphide.

Triethoxy(phenylthioimino)phosphorane (II; R = OEt) and tributyl(phenylthioimino)phosphorane (II; R = Buⁿ) were prepared in the same way, by use of equivalent amounts of triethyl phosphite and tributylphosphine, respectively.

S-Phenylthio-oximes (III).—*General procedure.* The aromatic aldehyde (2 mmol) was added to a solution of tribenzenesulphenamide (I) (1 mmol) in dry benzene (5 ml). Solid triphenylphosphine (1 mmol) was added and the mixture stirred until all the solid had dissolved. After 1 h at room temperature the mixture was evaporated and the residue was chromatographed on silica plates to give the corresponding *thio-oxime* (III) (Tables 2 and 3).

TABLE 2

Formula (Table 1)	Analysis (%) *				
	C	H	N	S	Br
1 C ₁₃ H ₁₁ NS	(i) 73.3	5.2	6.5	15.2	
	(ii) 73.3	5.2	6.6	15.0	
2 C ₁₃ H ₁₀ N ₂ O ₂ S	(i) 60.6	4.1	11.0	12.6	
	(ii) 60.5	3.9	10.9	12.4	
3 C ₁₃ H ₁₀ N ₂ O ₂ S	(i) 60.4	3.9	10.8	12.7	
	(ii) 60.5	3.9	10.9	12.4	
4 C ₁₃ H ₁₀ N ₂ O ₂ S	(i) 60.8	4.1	10.4		
	(ii) 60.5	3.9	10.9		
5 C ₁₄ H ₁₀ N ₂ S	(i) 70.7	4.3	11.8	13.2	
	(ii) 70.6	4.2	11.8	13.5	
6 C ₁₃ H ₁₀ BrNS	(i) 53.4	3.4	4.9	11.0	27.4
	(ii) 53.4	3.4	4.8	11.0	27.4
7 C ₁₄ H ₁₃ NOS	(i) 69.1	5.2	5.6	13.4	
	(ii) 69.1	5.3	5.8	13.2	
8 C ₁₅ H ₁₃ NS	(i) 75.2	5.5	5.9	13.6	
	(ii) 75.3	5.4	5.9	13.4	
9 C ₁₁ H ₁₃ NO ₂ S	(i) 59.2	5.8	6.3	14.4	
	(ii) 59.2	5.8	6.3	14.4	

* (i) Found; (ii) required.

TABLE 3

Spectral data for *S*-phenylthio-oximes (III)

Compd.	$\lambda_{\max.}/\text{nm}(\epsilon)$	$\nu_{\max.}/\text{cm}^{-1}$	τ
1	331, 227, 233 (16,000, 11,300, 19,500)	870, 970, 1030, 1090, 1220, 1320, 1580	1.6 (1H, s), 2.7 (10H, m)
2	374, 247, 209 (11,000, 10,300, 12,200)	850, 1100, 1350, 1530, 1570, 1590	1.5 (1H, s), 1.95 (4H, ABq, J 8 Hz), 2.4 (5H, m)
3	334, 273, 220 (7700, 9000, 14,600)	850, 960, 1030, 1105, 1350, 1530, 1580	1.5 (2H, s), 2.8—1.6 (2H, m)
4	362, 273, 218 (4800, 7300, 14,300)	858, 870, 1030, 1350, 1525, 1578, 1600	1.35 (1H, s), 2.9—1.75 (9H, m)
5	350, 245, 210 (11,800, 15,900, 14,500)	850, 1570, 1600, 2220	1.58 (1H, s), 2.25 (4H, s), 2.5 (5H, m)
6	336, 276, 240, 218.5 (13,400, 8400, 18,000, 19,400)	890, 1090, 1550, 1578	1.65 (1H, s), 2.5 (9H, m)
7	335.5, 280, 253, 218 (18,200, 14,800, 11,900, 1700)	845, 970, 1110, 1515, 1585, 1600	1.55 (1H, s), 2.6 (5H, m), 2.7 (4H, ABq, J 9 Hz), 6.14 (3H, s)
8	350, 285, 247, 209 (22,000, 19,200, 10,800, 13,600)	985, 1030, 1100, 1578, 1610	1.7 (1H, dd J 7 Hz), 2.7 (10H, m), 2.95 (1H, m), 3.1 (1H, m)
9	320, 229, 210 (7700, 7000, 8000)	1670, 1710	8.66 (3H, t), 7.67 (3H, s), 5.67 (2H, q), 2.5 (5H, m)

Triphenyl-[N-(phenylthio)methylamino]phosphonium Iodide (IV; R = Me).—Tribenzenesulphenamide (I) (1 mmol) in dry ether (3 ml) was treated with triphenylphosphine (262 mg, 1 mmol) in dry benzene (2 ml), followed by methyl iodide (2 ml). After 0.5 h at room temperature ethyl acetate (5 ml) was added and the mixture left for 2 h.

⁵ G. Stork, A. Brizzolara, H. K. Landesman, J. Szmuszkowicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, **85**, 207.

Filtration gave the *iodide* (IV; R = Me) (76%), m.p. 149—150° (from ethyl acetate-chloroform), $\nu_{\max.}$ 975, 1005, 1125, 1310, and 1585 cm⁻¹, $\lambda_{\max.}$ 276, 269, and 225 nm (ϵ 2100, 3200, and 34,000), τ 2.3 (20H, m) and 6.65 (3H, s) (Found: C, 57.1; H, 4.3; I, 24.0; N, 2.6; P, 6.4; S, 6.4. C₂₅H₂₃INPS requires C, 57.0; H, 4.4; I, 24.1; N, 2.7; P, 5.9; S, 6.1%).

Triphenyl-[N-(phenylthio)benzylamino]phosphonium Bromide (IV; R = CH₂Ph).—Triphenyl(phenylthioimino)phosphorane (1 mmol) (prepared as above) was treated with benzyl bromide (2 ml). After 24 h at room temperature the solution was filtered and the crystals washed with ether to give the *bromide* (IV; R = CH₂Ph) (88%), m.p. 118—120° (from ether-chloroform), $\nu_{\max.}$ 1010, 1090, 1125, 1315, and 1580 cm⁻¹, $\lambda_{\max.}$ 276, 269, and 228 nm (ϵ 4000, 5800, and 33,400), τ 2.5 (25H, m) and 5.2 (2H, ABq, J 11 Hz) (Found: C, 66.8; H, 4.7; N, 2.5. C₃₁H₂₇BrNPS requires C, 66.9; H, 4.9; N, 2.5%).

S-Phenylthio-oxime S-Oxides (V; Ar = Ph or C₆H₄Br-*m*).—The *S*-phenylthio-oxime (III; Ar = Ph) (1 mmol) in dry ether (3 ml) was treated with *m*-chloroperbenzoic acid (270 mg) in ether (2 ml). After 1 h at room temperature the mixture was washed with saturated aqueous sodium hydrogen carbonate and water. Evaporation of the dried (Na₂SO₄) ether layer gave the *sulphoxide* (V; Ar = Ph) (93.5%), m.p. 80° (from light petroleum), $\nu_{\max.}$ 1060, 1090, 1210, 1570, and 1600 cm⁻¹, $\lambda_{\max.}$ 263 and 214 nm (ϵ 12,000 and 15,600), τ 1.24 (1H, s) and 2.5 (10H, m) (Found: C, 67.3; H, 4.8; N, 6.1; S, 14.2. C₁₃H₁₁NOS requires C, 68.1; H, 4.8; N, 6.1; S, 14.0%).

Similarly prepared, the *sulphoxide* (V; Ar = C₆H₄Br-*m*) (89%) had m.p. 76° (from light petroleum), $\nu_{\max.}$ 1068, 1108, 1210, 1570, and 1600 cm⁻¹, $\lambda_{\max.}$ 261 and 226 nm (ϵ 16,200 and 14,800), τ 1.3 (1H, s) and 2.45 (9H, m) (Found: C, 50.6; H, 3.5; N, 4.5; S, 10.7. C₁₃H₁₀BrNOS requires C, 50.7; H, 3.2; N, 4.5; S, 10.4%).

Reaction of Tribenzenesulphenamide (I) with 1-Pyrrolidinocyclohexene.—Freshly distilled 1-pyrrolidinocyclohexene ⁶ (150 mg) in dry benzene (2 ml) was treated with tribenzenesulphenamide (I) (341 mg) at room temperature. After 3 h the solution was diluted with light petroleum and filtered to give dibenzenesulphenamide (205 mg, 88%). The filtrate was evaporated and the residue dissolved in ether and shaken with 2N-hydrochloric acid. Evaporation of the dried (Na₂SO₄) ether layer and p.l.c. gave 2-(phenylthio)cyclohexanone (VI) (80%), m.p. 42—43° (lit., ⁶ 53—54°; lit., ⁷ oil). The 2,4-dinitrophenylhydrazone had m.p. 163—165° (lit., ⁶ 158—160°).

Oxidation of Tribenzenesulphenamide (I) with m-Chloroperbenzoic Acid.—Tribenzenesulphenamide (I) (170.5 mg) in dry ether (5 ml) was treated with *m*-chloroperbenzoic acid (3 mmol) in ether (5 ml). After 12 h the crystalline product was filtered off to give *tribenzenesulphinamide* (VII) (150 mg), m.p. 127—128° (from ether), $\nu_{\max.}$ 1130 cm⁻¹ (Found: C, 55.4; H, 3.9; N, 3.6; S, 24.4. C₁₈H₁₅NO₃S₃ requires C, 55.6; H, 3.9; N, 3.6; S, 24.7%).

3-Phenylthioiminophthalide (VIII).—Phthalic anhydride (74 mg) and triphenylphosphine (131 mg) in dichloroethane (5 ml) at 60° were treated with tribenzenesulphenamide (I) (170.5 mg). After 1 h at 60° the solution was evaporated and p.l.c. gave the *imine* (VIII) (23.4 mg, 18%), m.p.

⁶ F. Winternitz, N. J. Antia, M. Tumirova, and R. Lachazette, *Bull. Soc. chim. France*, 1956, 1817.

⁷ M. Mousseron, R. Jacquier, and A. Fontaine, *Bull. Soc. chim. France*, 1952, 767.

158—163° (from benzene–light petroleum), λ_{max} 364 and 220 nm (ϵ 9200 and 19,500) (Found: C, 65.6; H, 3.3; N, 5.7; S, 12.4. $\text{C}_{14}\text{H}_9\text{NO}_2\text{S}$ requires C, 65.9; H, 3.5; N, 5.5; S, 12.6%). This differs from its known isomer *N*-(phenylthio)phthalimide⁸ in its i.r. spectrum [ν_{max} 1660 cm^{-1} (C=N)] and t.l.c. behaviour (direct comparison).

Reaction of Tribenzenesulphenamide (I) with the Thiohydrazide (IX).—The thiohydrazide (IX) (57 mg) in dichloroethane (10 ml) was heated with tribenzenesulphenamide (I) (170 mg) for 2 h. Evaporation and p.l.c. gave dark green crystals of α -phenylazobenzaldehyde *S*-phenylthio-oxime (X) (30 mg), m.p. 119—120° (from light petroleum), ν_{max} 1580, 1260, 770, 745, and 700 cm^{-1} , λ_{max} (CHCl_3) 292 and 453 nm (ϵ 22,000 and 10,600), τ 2.8—2.3 (11H, m) and 2.0—1.65 (4H, m) (Found: C, 71.8; H, 5.0; N, 13.3; S, 10.0. $\text{C}_{19}\text{H}_{15}\text{N}_3\text{S}$ requires C, 71.9; H, 4.8; N, 13.3; S, 10.1%).

Reductive acetylation (Ac_2O – AcOH – $\text{C}_5\text{H}_5\text{N}$ –Zn) of (X) gave acetanilide. Oxidation of the phenylazothio-oxime (X) (16 mg) with hydrogen peroxide (0.2 ml; 30% v/v) in acetic anhydride (0.5 ml) and dichloromethane (0.2 ml) gave the sulphoxide (XI) (11 mg), m.p. 126—127°, ν_{max} 1600, 1495, 1280, 1260, 935, 760, 750, and 690 cm^{-1} , λ_{max} (CHCl_3) 285 nm (ϵ 13,600) (Found: C, 68.8; H, 4.6; N, 12.7; S, 9.9. $\text{C}_{19}\text{H}_{15}\text{N}_3\text{OS}$ requires C, 68.5; H, 4.5; N, 12.6; S, 9.6%).

Reactions of Tribenzenesulphenamide (I) with Arylhydrazones.—**General procedure.** The arylhydrazone (XIIa–d) (1 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (20 ml) and the sulphenamide (I) (1 mmol) were heated at reflux for 1.5 h. Evaporation and p.l.c. gave the arylazodisulphenamide (XIIIa–d), which on treatment with triethylamine gave the arylazothio-oxime (XIVa–d). Compound (XIVa) [\equiv (X)] was already characterised. Compound (XIIIb) had ν_{max} 1610, 1585, 1525, 1490, 1265, 1180, 860, 760, and 705 cm^{-1} , τ 6.37 (3H, s), 3.88 (1H, s), 3.27 (2H, m), and 3.0—2.25 (17H, m); (XIVb) had m.p. 128—128.5° (from benzene–light petroleum), ν_{max} 1600, 1580, 1510, 1305, 1250, 1170, 1155, 1035, 845, 780, 755, and 700 cm^{-1} , λ_{max} (CHCl_3) 275inf, 299, and 464 nm (ϵ 18,200, 23,600, and 8900), τ 6.15 (3H, s), 3.08 (2H, m), 2.8—2.4 (8H, m), and 2.0—1.7 (4H, m) (Found: C, 69.4; H, 4.9; N, 12.0; S, 9.2. $\text{C}_{20}\text{H}_{17}\text{N}_3\text{OS}$ requires C, 69.2; H, 4.9; N, 12.1; S, 9.2%). (XIVc) had m.p. 190° (from benzene–light petroleum), ν_{max} 1600, 1510, 1340, 865, 780, 745, and 690 cm^{-1} , λ_{max} (CHCl_3) 324 and 450 nm (ϵ 18,200 and 15,600), τ 2.8—2.2 (8H, m), 2.0—1.8 (2H, m), and 1.60br (4H, s) (Found: C, 62.8; H, 3.9; N, 15.4; S, 9.0. $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$ requires C, 63.0; H, 3.9; N, 15.4; S, 8.8%); (XIIIId) had m.p. 99—100° (decomp.) (from ether–light petroleum), ν_{max} 1605, 1585, 1515, 1440, 1345, 1250, 1180, 1040, 875, 840, 775, 760, 740, 710, and 700 cm^{-1} , λ_{max} (CHCl_3) 275 nm (ϵ 20,000), τ 6.25 (3H, s), 4.07 (1H, s), 3.27 (2H, m), 2.8—2.6 (12H, m), 2.45 (2H, m), and 1.83 (2H, m) (Found: C, 62.3; H, 4.6; N, 11.1; S, 12.7. $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_3\text{S}_2$ requires C, 62.2; H, 4.4; N, 11.2; S, 12.7%); (XIVd) had m.p. 167° (from benzene–light petroleum), ν_{max} 1605, 1580, 1520, 1515, 1340, 1260, 1175, 1040, 865, 775, 760, and 700 cm^{-1} , λ_{max} (CHCl_3) 280inf, 299, and 509 nm (ϵ 21,600, 22,700, and 8600), τ 6.08 (3H, s), 2.93 (2H, m), 2.7 (5H, m), and 2.0—1.4 (6H, m) (Found: C, 61.7; H, 4.2; N, 14.3; S, 8.3. $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_3\text{S}$ requires C, 61.3; H, 4.1; N, 14.3; S, 8.2%); (XIVe) had m.p. 70° (from benzene–light petroleum), ν_{max} 1610, 1580, 1520, 1340, 865, 850, 765, 745, and 695 cm^{-1} , λ_{max} (CHCl_3) 295 and 436 nm (ϵ 16,900 and 11,700). τ 8.95

(3H, t), 8.20 (2H, m), 7.17 (2H, t), 2.9—2.2 (5H, m), 1.97 (2H, m), and 1.61 (2H, m) (Found: C, 58.7; H, 5.1; N, 17.3; S, 10.0. $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ requires C, 58.5; H, 4.9; N, 17.1; S, 9.8%).

Reaction of Tribenzenesulphenamide (I) with 5 α -Cholestane-3-one *p*-Nitrophenylhydrazone (XV).—The hydrazone (XV) (260 mg) and tribenzenesulphenamide (I) (360 mg) in dichloroethane (20 ml) were heated at reflux for 2 h. The mixture was evaporated and the major product isolated (p.l.c.) as an orange gum. This was stored in ethanol (5 ml) to give a yellow powder (315 mg), m.p. 115—137°, $[\alpha]_{\text{D}}^{25}$ 37°. Fractional crystallisation from light petroleum followed by manual separation of the two crystalline forms (orange prisms and yellow needles) gave the two isomers of 3-*p*-nitrophenylazo-3-bis(phenylthio)amino-5 α -cholestane (XVI): orange prisms, m.p. 140° (from light petroleum), ν_{max} 1615, 1585, 1530, 1345, 870, 860, 750, and 695 cm^{-1} , λ_{max} (CHCl_3) 275inf nm (ϵ 17,600), $[\alpha]_{\text{D}}^{25}$ +45.5° (Found: C, 72.1; H, 8.1; N, 7.5; S, 8.7. $\text{C}_{45}\text{H}_{60}\text{N}_4\text{O}_2\text{S}_2$ requires C, 71.8; H, 8.0; N, 7.4; S, 8.5%); yellow needles, m.p. 151—152° (from light petroleum), ν_{max} 1615, 1590, 1525, 1350, 870, 760, 750, and 695 cm^{-1} , λ_{max} (CHCl_3) 281 nm (ϵ 19,600), $[\alpha]_{\text{D}}^{25}$ +43° (Found: C, 72.0; H, 8.0; N, 7.4; S, 8.8%).

Reaction of Tribenzenesulphenamide (I) with Thiobenzanilide.—Thiobenzanilide (54 mg) and tribenzenesulphenamide (170 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Evaporation and p.l.c. gave the α -phenyliminobenzyl phenyl disulphide (XVII) (47 mg), m.p. 79° (from ethanol), ν_{max} 1605, 1590, 1180, 780, 760, and 600 cm^{-1} , λ_{max} 240 nm (ϵ 23,000) (Found: C, 71.0; H, 4.6; N, 4.3; S, 20.1. $\text{C}_{19}\text{H}_{15}\text{NS}_2$ requires C, 71.0; H, 4.7; N, 4.4; S, 20.0%).

The imino-disulphide (XVII) (10 mg) and benzenethiol (10 mg) in benzene (0.2 ml) were heated under reflux for 5 min. Evaporation followed by chromatography gave thiobenzanilide (5.3 mg, 80%), m.p. 101—102°.

Reaction of Tribenzenesulphenamide (I) with Thiobenzamide.—Thiobenzamide (68 mg) and tribenzenesulphenamide (340 mg) in dichloroethane (20 ml) were heated under reflux for 2 h. Evaporation and rapid chromatography gave orange plates of bis(phenylthioimino)sulphur(IV) (XVIII) (20 mg), m.p. 106° (from light petroleum), ν_{max} 1580, 1440, 1140, 1075, 1025, 905, 740, and 695 cm^{-1} , λ_{max} 256 and 447 nm (ϵ 14,100 and 12,200) (Found: C, 51.7; H, 3.8; N, 10.3; S, 34.0. Calc. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_2$: C, 51.8; H, 3.6; N, 10.1; S, 34.5%), identical with an authentic sample.

Reactions of Tribenzenesulphenamide (I) with Hydrogen Sulphide and with Sulphur.—Tribenzenesulphenamide (I) (170 mg) in dichloroethane (20 ml) was heated at reflux while a stream of hydrogen sulphide gas passed through the solution. Work-up as before gave (XVIII) (20 mg). Similarly, heating tribenzenesulphenamide (170 mg) in dichloroethane (20 ml) with sulphur (120 mg) gave the compound (XVIII) (6 mg), and (I) with thiourea gave (XVIII) (29%).

***N*-Phenylthio-azoxy-compounds (XIX).**—**General procedure.** The nitroso-compound (RNO) (0.5 mmol) in dichloroethane (5 ml) was added to a solution of tribenzenesulphenamide (I) (0.5 mmol) in dichloroethane (5 ml). The solution was refluxed for 2 h, cooled, and evaporated and the residue was chromatographed on thick silica plates. *N*-(Phenylthioimino)aniline *N*-oxide (XIX; R = Ph) (50%), was an oil, ν_{max} 1295 cm^{-1} , λ_{max} 339 and 225 nm (ϵ 9200 and 9300)

* M. Behforouz and J. E. Kerwood, *J. Org. Chem.*, 1969, **34**, 51.

(Found: C, 62.6; H, 4.4; N, 12.2; S, 13.9. $C_{12}H_{10}N_2OS$ requires C, 62.6; H, 4.4; N, 12.2; S, 13.9%). *p*-Methyl-N-(phenylthioimino)aniline N-oxide (XIX; R = C_6H_4Me-p) (51%) had m.p. 104–105° (from benzene–light petroleum), ν_{max} 1295 cm^{-1} , λ_{max} 384, 240, and 210 nm (ϵ 15,200, 8300, and 10,200) (Found: C, 61.5; H, 5.4; N, 15.5; S, 11.6. $C_{14}H_{15}N_3OS$ requires C, 61.1; H, 5.5; N, 15.4; S, 11.7%). N-(Phenylthioimino)-*t*-butylamine N-oxide (XIX; R = Bu^t) (64%) had m.p. 35° (from light petroleum), ν_{max} 1315 cm^{-1} , λ_{max} 302 and 216 nm (ϵ 8800 and 9200) (Found: C, 57.0; H, 6.6; N, 13.1. $C_{10}H_{14}N_2OS$ requires C, 57.2; H, 6.7; N, 13.3%).

Benzophenone S-Phenylthio-oxime (XX).—Tribenzenesul-

phenamide (I) (170.5 mg) was added to diphenyldiazomethane (97 mg) in dichloroethane (5 ml). The solution was refluxed for 1.5 h, cooled, and evaporated. Chromatography (p.l.c.) of the residue gave the *S*-phenylthio-oxime ¹ (83%). Similarly thiobenzophenone gave the *S*-phenylthio-oxime (45%).

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⁹ von J. Weiss and H. Piechaczek, *Z. Naturforsch.*, 1963, **18b**, 1139.