The Chemistry of Trisulphenamides [N(SR)$_3$]. Part I. Preparation, Thermal Decomposition, and Reactions of Tribenzenesulphenamide [N(SPh)$_3$]

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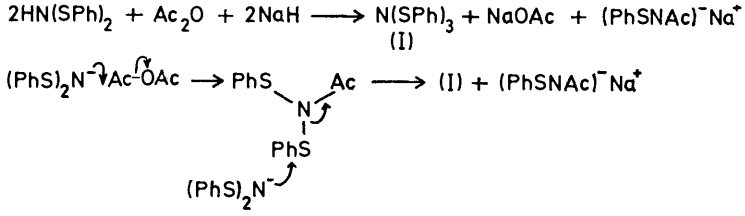
Treatment of the sodium salt of dibenzenesulphenamide with acetic anhydride gave tribenzenesulphenamide [N(SPh)$_3$]. Decomposition of this substance at *ca.* 80° gave nitrogen and diphenyl disulphide in quantitative yields. Phenols react with tribenzenesulphenamide to give quinone phenylthioimines. Where both *ortho*- and *para*-positions in the phenol are available for substitution, *ortho*-substitution predominates. The mechanism of this reaction involves initial H· abstraction from the phenol by the ·N(SPh)$_2$ radical to give *e.g.* species (XVI). Subsequent decomposition of such intermediates gives the isolated product. Amines give less specific reactions compared with phenols.

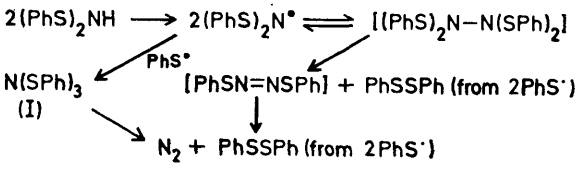
WHILST engaged on a programme designed to examine the preparation and properties of new nitrogen radicals (·NR$_2$) we examined some aspects of the chemistry of dibenzenesulphenamide (PhS)$_2$NH.[1,2] Reaction of dibenzenesulphenamide with sodium hydride in tetrahydrofuran (see Experimental section) gave the sodium salt. Treatment of this salt with acetic anhydride at −20° gave not the expected *N*-acetyl derivative but tribenzenesulphenamide (I) (87%) as a reasonably stable crystalline compound. As confirmation of its structure treatment of the sodium salt of (PhS)$_2$NH with benzenesulphenyl chloride gave (I) albeit in much lower yield (35%). The major product was diphenyl disulphide. The mechanism suggested for this unusual reaction is based on the observed stoicheiometry (Scheme 1). Acetylation of (PhS)$_2$NH gives the *N*-acetyl intermediate, which reacts with another molecule of the sodium dibenzenesulphenamide by displacement on sulphur to give (I). The other product *N*-phenylthioacetamide (sodium salt) was only observed as a transient intermediate and rapidly decomposes. Other experiments carried out in these laboratories have indicated that this compound is extremely unstable.



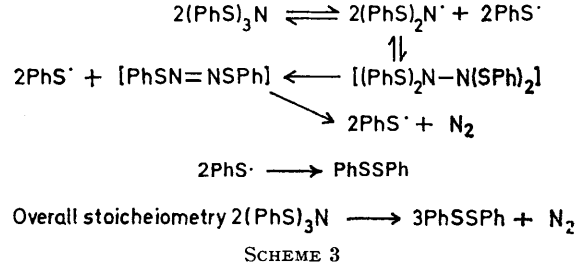
SCHEME 1

Tribenzenesulphenamide (I) is a pale yellow crystalline compound melting at 68 °C with the formation of a purple solution and the evolution of a gas. Quantitative examination of its thermal decomposition at 78° gave nitrogen (94%) and analytically pure diphenyl disulphide (100%). When the above decomposition was carried out in 1,1,2,2-tetrachloroethane the nitrogen evolution was 96%. The purple colouration of the reaction mixture fades as nitrogen evolution approaches completion. The radical (PhS)$_2$N· is thought to be responsible for the purple colour. This is substantiated by a closer study of Lecher's [1] attempted preparation of tetrakisphenylthiohydrazine. Treatment of dibenzenesulphenamide with lead dioxide gave a purple solution (same visible spectrum). From this solution tribenzenesulphenamide (24%) and diphenyl disulphide (51%) could be isolated. The hydrazine (PhS)$_2$N–N(SPh)$_2$ may be an intermediate (Scheme 2). A mechanism for the thermal decomposition of the trisulphenamide (I) is outlined in Scheme 3. The e.s.r. spectrum of a solution of (I) in cyclohexane at 70° gave a nitrogen triplet with a splitting of 11·4 G. This is consistent with the formation of a radical on nitrogen attached to two sulphur atoms.

The trisulphenamide (I) decomposed photochemically at room temperature to give a purple solution. From this solution nitrogen (77·5%) was evolved; dibenzenesulphenamide (21%) and diphenyl disulphide along with several polymeric sulphides (derived from PhS· radicals) were formed.



SCHEME 2



SCHEME 3

The only other compound with three divalent sulphur

[1] H. Lecher, F. Holschneider, K. Koberle, W. Speer, and P. Stocklin, *Ber.*, 1925, **58**, 409.

[2] T. Mukaiyami and T. Taguchi, *Tetrahedron Letters*, 1970, 3411.

atoms attached to a single nitrogen atom is tris(trifluoromethylsulphen)amide which similarly decomposes to nitrogen and the corresponding disulphide.[3,4]

Since thermal decomposition of tribenzenesulphenamide (I) gives, initially, the radical $\cdot N(SPh)_2$, it was felt that this radical ought to undergo reactions with phenols analogous to Frémy's salt.[5] A 2 : 1 equimolar mixture of the trisulphenamide (I) and phenol in dichloroethane at reflux gave two main products (apart from diphenyl disulphide *). The major product, a dark red crystalline substance (*ca.* 35%), $\lambda_{max.}$ 460 and 260 nm, was assigned structure (II) on the basis of its reductive acetylation (Zn–HOAC–Ac_2O–pyridine) to give 2-acetamidophenyl acetate.[6] The minor component (12%), $\lambda_{max.}$ 440 and 278 nm, is the *para*-isomer (III). Again its structure was assigned on the basis of its reductive acetylation to give 4-acetamidophenyl acetate.[7] An authentic sample of (III) was prepared from *p*-aminophenol and an excess of benzenesulphenyl chloride.[8] The configuration of the phenylthioimino-group (=NSPh) in (II) and subsequent compounds where geometrical isomers are possible is not known, but only one stereoisomer has been detected in every case where stereoisomerism is possible.

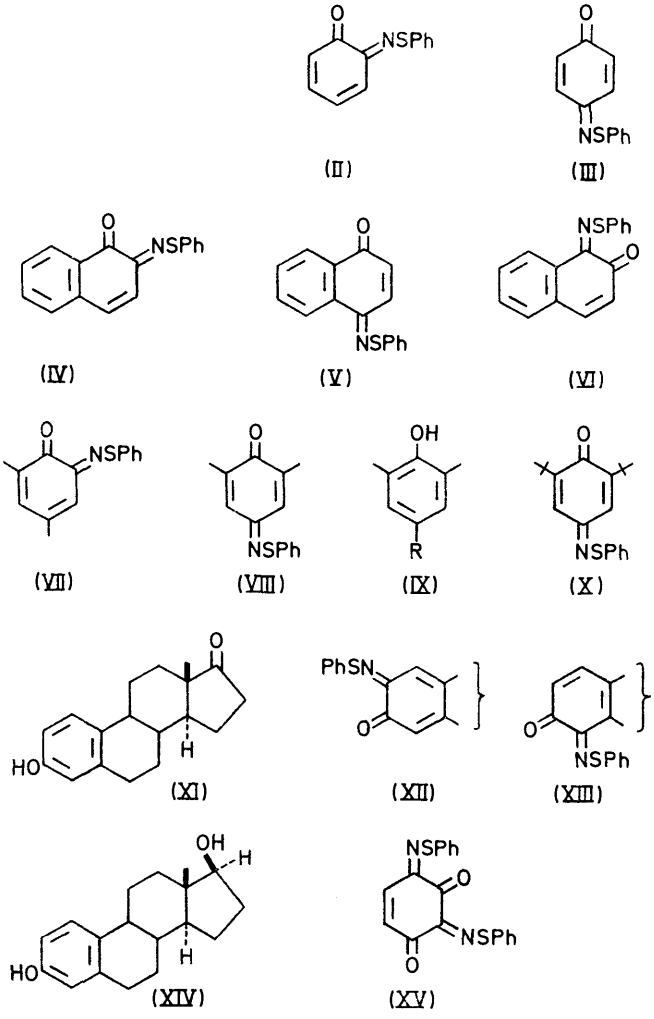
The predominance of *ortho*-attack was also observed in the case of α-naphthol. Reaction of α-naphthol with the trisulphenamide (I) in dichloroethane at reflux gave two products. The major product (64% from u.v., 50% isolated) is assigned structure (IV). 2-Amino-1-naphthol hydrochloride, on treatment with benzenesulphenyl chloride gave compound (IV). The minor product (10% from u.v., 3% isolated) is the *para*-isomer, (V). The structure of the latter was confirmed by preparation of an authentic sample from 4-amino-1-naphthol hydrochloride and benzenesulphenyl chloride.

β-Naphthol, on reaction with the trisulphenamide (I) under the usual conditions, gave the phenylthioimine (VI) (85%). Its structure was confirmed by reductive acetylation to 1-acetamido-2-naphthyl acetate.[9]

2,4-Dimethylphenol reacted with the trisulphenamide (I) in dichloroethane at reflux to give a deep red crystalline compound (VII) (80%). Reductive acetylation of (VII) gave 2-acetamido-3,5-dimethylphenyl acetate. The authentic sample was prepared by reductive acetylation of 2,4-dimethyl-6-nitrophenol.[10]

2,4,6-Trimethylphenol on reaction with the trisulphenamide (I) in the usual way gave (VIII), and only traces of (VII) (<1%). The structure of (VIII) was confirmed by reductive acetylation to give 4-acetamido-3,5-dimethylphenyl acetate.[11] Furthermore 2,6-dimethylphenol on reaction with the trisulphenamide (I) in dichloroethane at reflux gave (VIII) (85%). The reaction was not affected by the presence of oxygen.

2,6-Dimethyl-4-nitrophenol[11] (IX; R = NO_2) on treatment with (I) under the usual conditions gave (VIII) (55%) and traces (*ca.* 2%) of 2,6-dimethyl-1,4-benzoquinone. Fries rearrangement of 2,6-dimethylphenyl benzoate[12] gave 2,6-dimethyl-4-benzoylphenol



(IX; R = COPh). Whilst (IX; R = COPh) was unreactive towards the nitride (I),† the derived product (IX; R = CH_2Ph)[13] reacted in the usual way to give (VIII) (*ca.* 50%). Benzyl phenyl sulphide[14] was also isolated from this reaction in amounts approaching complete capture of the $PhCH_2\cdot$ group by PhS· radicals.

2,6-Dimethyl-4-methoxyphenol (IX; R = OMe)[15]

* All reactions of (I) with phenols and amines gave diphenyl disulphide as one of the products.

† The phenyl compound (IX; R = Ph) was also unreactive.

[3] A. Haas, M. E. Peach, and P. Schott, *Angew. Chem.*, 1965, **77**, 458.

[4] A. Haas and P. Schott, *Chem. Ber.*, 1968, **101**, 3407.

[5] H. Zimmer and D. C. Lankin, *Chem. Rev.*, 1971, **71**, 229.

[6] R. Meldola, G. H. Woolcatt, and E. Wray, *J. Chem. Soc.*, 1896, 1323.

[7] W. O. Emery and C. D. Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 2323.

[8] N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, 1946, **39**, 269.

[9] R. Meldola and G. T. Morgan, *J. Chem. Soc.*, 1889, 121.

[10] W. R. Hodgkinson and L. Limpach, *J. Chem. Soc.*, 1893, 105.

[11] (*a*) F. M. Rowe, S. H. Bannister, and R. C. Storey, *J. Chem. Soc. Ind.*, 1931, **50**, 79 (*Chem. Abs.*, 1930, 2424); (*b*) K. Von Auwers and T. Markovitz, *Ber.*, 1908, **41**, 2335.

[12] K. Von Auwers and E. Janssen, *Annalen*, 1930, **483**, 44.

[13] M. E. Hey and W. A. Waters, *J. Chem. Soc.*, 1955, 2753.

[14] R. L. Shriner, H. C. Struck, and W. J. Jonson, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.

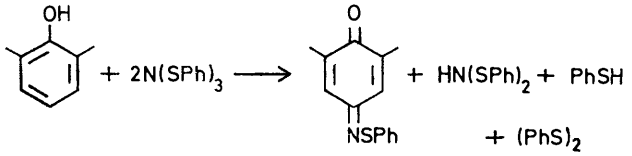
[15] E. Bamberger, *Ber.*, 1903, **36**, 2028.

gave, on reaction with the trisulphenamide (I) in the usual way, (VIII) (64%). 2,6-Di-t-butylphenol gave (X) (37%) on reaction with the trisulphenamide (I).

Estrone (XI) reacted with the trisulphenamide (I) to give two products. The major product (XII) (51%) was assigned its structure from n.m.r. spectroscopy, τ 3·85br (1H, s, 4-H) and 3·07br (1H, s, 1-H). The minor component is (XIII) (28%), τ 3·48 (1H, d, J 10 Hz, 2-H). Estradiol (XIV) on reaction with the trisulphenamide (I) gave two compounds corresponding to (XII) (36%) and (XIII) (15%) in the 17β-hydroxy-series.

Resorcinol reacted with the trisulphenamide (I) to give the di-imine (XV) (73%), τ 3·2 (1H, d, J 10 Hz), the other vinyl proton being hidden under the aromatic envelope. Hydroquinone reacted with the trisulphenamide (I) to give benzoquinone as the only product.

The mechanism of the reactions between phenols and the trisulphenamide (I) was studied. The reactions of the 2,6-dimethylphenol derivatives (IX; R = Me, NO_2, OMe, and CH_2Ph) to give (VIII) indicate a radical rather than electrophilic mechanism. The overall stoicheiometry (see Experimental section), as seen from the curves (1) and (2), requires two equivalents of the trisulphenamide (I) to each of phenol [equation (1)].



The dibenzenesulphenamide produced in equation (1) was detected, as was the thiophenol, both in low yields.

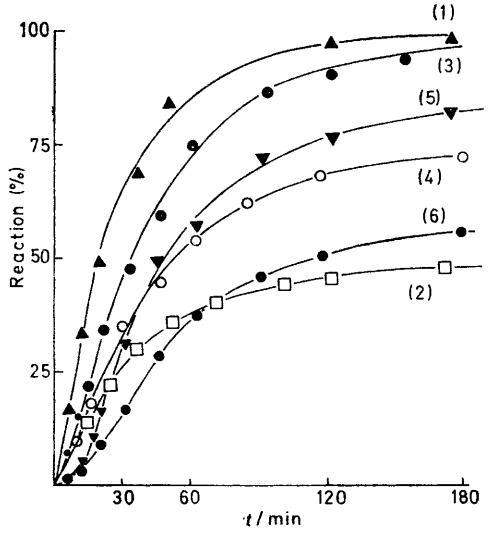


FIGURE 1 (1), (IX; R = H) + 2(I) ⟶ (VIII) at 80·0°; (2), (IX; R = H) + (I) ⟶ (VIII) at 77·0°; (3), (IX; R = H) + 2(I) ⟶ (VIII) at 76·0° in the presence of H_2O; (4), (IX; *O*-D, R = H) + 2(I) ⟶ (VIII) at 76·0° in the presence of D_2O; (5), (IX; R = D) + 2(I) ⟶ (VIII) at 76·0° in the presence of H_2O; (6), (IX; *O*-D, R = H) + 2(I) ⟶ (VIII) at 76·0° in the presence of D_2O

Thiophenol does not react with dibenzenesulphenamide, but ·SPh radicals presumably do [more diphenyl disulphide was isolated than equation (1) indicates]. A plausible mechanism for typical phenol reactions is outlined in Scheme 4. The trisulphenamide (I) dissociates thermally into ·N(SPh)$_2$ and ·SPh radicals. The ·SPh

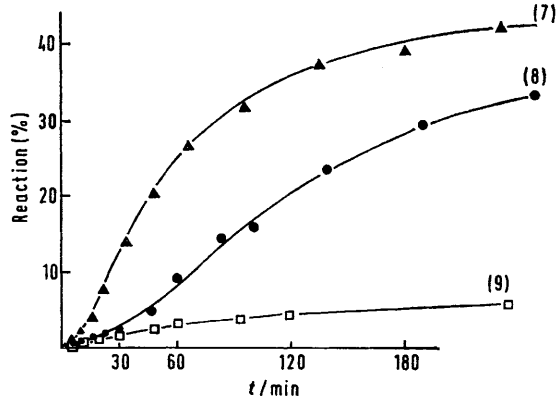
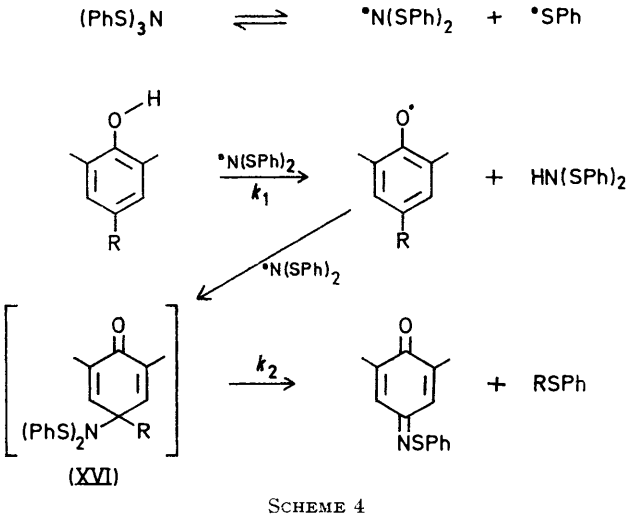


FIGURE (2) (7), 2,6-Di-t-butylphenol + 2(I) ⟶ (X) at 76·0° in the presence of H_2O; (8), [4-^{2}H]-2,6-di-t-butylphenol + 2(I) ⟶ (X) at 76·0° in the presence of H_2O; (9), [4, *O*-$^2H_2$]-2,6-di-t-butylphenol + 2(I) ⟶ (X) at 76·0° in the presence of D_2O



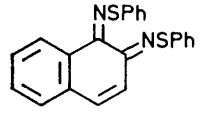
SCHEME 4

radicals are extremely poor hydrogen atom abstractors. The ·N(SPh)$_2$ radicals abstract a hydrogen atom in a rate-determining step from the H–O bond of the phenol, producing a phenoxyl radical. The phenoxyl radical is rapidly captured by the ·N(SPh)$_2$ radical to give the cyclohexadienone intermediate (XVI). Since the highest electron density for the unsubstituted phenoxyl radical is at C-2 and C-6,[16] this would account for the predominance of *ortho*-substitution in the case of phenol, and α-naphthol. No dimerisation or capture of the phenoxyl radicals by oxygen is observed. This is consistent with a low concentration of phenoxyl radicals.[17] The cyclohexadienone intermediate (XVI) decomposes to the product (VIII) and R·. The fate of R· is seen in the case of (IX; R = CH_2Ph); benzyl phenyl sulphide

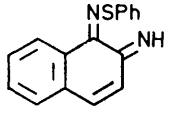
[16] T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 1962, 253.
[17] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968, p. 281.

is formed. To confirm this picture the following kinetic experiments were performed. Reaction of 2,6-dimethylphenol with the trisulphenamide (I) in the presence of an excess of D_2O [curve (4)] caused a diminution in rate [compare blank, curve (3)]. The *para*-deuterio-2,6-dimethylphenol–trisulphenamide (I) reaction [curve (5)] in the presence of water showed that the initial rate was slower by a factor of 8. Repeating this experiment in the presence of D_2O [curve (6)] again demonstrated the isotope effect exerted by the initial step k_1. Therefore k_1 and k_2 are comparable in magnitude, k_2 being the smaller in this particular example. A more clearly defined distinction is obtained from work with 2,6-di-t-butylphenol. The *para*-deuterio-2,6-di-t-butylphenol–trisulphenamide (I) reaction [curve (8)] shows a diminution in initial rate by a factor of 5, with respect to the protium compound [curve (7)]. The *O*-deuterio-2,6-di-t-butylphenol reaction, however, shows an extremely large decrease in rate because of the steric hindrance of the t-butyl groups on the abstraction of the H–O hydrogen [curve (9)]. Clearly in this case k_2 is larger than k_1 and is approximately the same as in the 2,6-dimethylphenol–trisulphenamide (I) reaction. The unusual shape of the initial parts of the curves (4)—(6) and (8) is interpreted as implying that the cyclohexadienone intermediate (XVI; R = D or H) accumulates in the reaction and then decomposes to the product. Scheme 1 is, therefore, supported by the preliminary kinetic results.

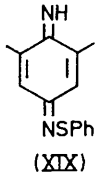
Aniline and *N*-methylaniline reacted slowly with the trisulphenamide (I) in dichloroethane at reflux to give an intractable mixture. β-Naphthylamine reacted with the trisulphenamide (I) in the usual way to give the diimine (XVII) (33—38%). Presumably the monosubstituted compound (XVIII) is an intermediate. Reductive acetylation of (XVIII) gave 1,2-diacetamido-



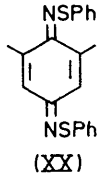
(XVII)



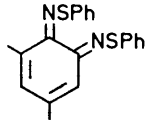
(XVIII)



(XIX)



(XX)



(XXI)

naphthalene.[18] 2,6-Dimethylaniline reacted with the trisulphenamide (I) to give (VIII), derived from hydrolysis of (XIX), and (XX). The configuration of the phenylthioimino-groups is not known. 2,4-Dimethylaniline on similar treatment with (I) gave (XXI) in modest yield.

[18] (*a*) A. Kaufmann, *Ber.*, 1909, **42**, 3482; (*b*) C. Liebermann and P. Jacobson, *Annalen*, 1882, **211**, 36; (*c*) T. A. Lawson, *Ber.*, 1885, **18**, 796.

[19] V. Krafft, *Ber.*, 1893, **26**, 2815.

The trisulphenamide (I) provides a simple method of *ortho*-aminating phenols.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage and are uncorrected. 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 [^{2}H]chloroform 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 b.p. 40—60 °C.

Dibenzenesulphenamide.—The sulphenamide was prepared by the method of Lecher [1] in 62% yield after crystallisation from benzene–light petroleum. It had m.p. 129° (lit.,[1] 129°), $\nu_{max.}$ 3250, 1590, 870, 750, and 700 cm^{-1}, $\lambda_{max.}$ 224 and 270 nm (ε 14,620 and 8450 respectively), τ 2·70br (10H, s) and 3·70 (1H, m, exchanged by D_2O).

Tribenzenesulphenamide (I).—Sodium hydride (1·8 g; 50% dispersion in mineral oil) in dry tetrahydrofuran (180 ml) was treated with a solution of dibenzenesulphenamide (7·0 g) in tetrahydrofuran (75 ml) at −10 to −18° with stirring. When hydrogen evolution was complete the solution was cooled to −20° and acetic anhydride (3·0 g) in tetrahydrofuran (40 ml) was added dropwise over 40 min. The mixture was worked up by two alternative procedures. The precipitated sodium acetate was filtered and the filtrate was evaporated at room temperature. Alternatively, dilution of the mixture with water was followed by ether extraction. Recrystallisation of the residue (from evaporation of the ether or tetrahydrofuran phase) from ethanol gave equivalent yields of *tribenzenesulphenamide* (I) (4·45 g, 87%), m.p. 68° (to give a purple solution), $\nu_{max.}$ 1580, 1440, 760, 750, and 700 cm^{-1}, $\lambda_{max.}$ 235 and 368 nm (ε 21,250 and 860 respectively), τ 2·6 (s) (Found: C, 63·1; H, 4·7; N, 4·0; S, 28·0. $C_{18}H_{15}NS_3$ requires C, 63·3; H, 4·4; N, 4·1; S, 28·1%).

It is advisable to check the sodium hydride by conducting a small-scale experiment first. The rate of addition of acetic anhydride to the sodium salt of dibenzenesulphenamide was such that the solution never became red.

Sulphenation of Dibenzenesulphenamide.—The sulphenamide (0·466 g) in dry glyme (10 ml) was added to a stirred suspension of sodium hydride (0·96 g) in glyme (10 ml) under nitrogen at −20°. After 5 min (hydrogen evolution complete) benzenesulphenyl chloride (0·289 g) in dry glyme (5 ml) was added. A purple colouration immediately developed and faded after 1 h. The mixture was filtered and evaporated to give a residue that was chromatographed on thick silica plates (Merck MFG 254). Diphenyl disulphide (0·398 g, 61%), m.p. 60° (lit.,[19] 61°), was isolated and tribenzenesulphenamide (I) (0·228 g, 35%), m.p. 68·5°, undepressed on admixture with an authentic sample.

Pyrolysis of Tribenzenesulphenamide (I).—The nitride (I) (0·073 g) in a hydrogenation tube connected to a microhydrogenator filled with nitrogen was equilibrated at 78° in a thermostatically controlled oil-bath. Gas evolution was complete after 5 h when 94% of the nitrogen had been evolved. The residue was pure diphenyl disulphide, m.p. 61° (Found: C, 66·0; H, 4·8; N, 0·0. Calc. for $C_{12}H_{10}S_2$: C, 66·1; H, 4·6%).

Pyrolysis of Tribenzenesulphenamide (I) *in* 1,1,2,2-*Tetrachloroethane.*—The nitride (I) (0·0822 g) in 1,1,2,2-tetra-

chloroethane (5 ml) in a micro-hydrogenator was equilibrated at 80°. Gas evolution was complete after 3 h when 96% of the nitrogen had been evolved. The residue was diphenyl disulphide, m.p. 61° (100%).

Pyrolysis in Cyclohexane.—The nitride (I) (0·100 g) in cyclohexane (25 ml) was heated at reflux under nitrogen. A purple colour developed, $\lambda_{max.}$ 531 nm, which disappeared after 2 h. The solvent was evaporated to give diphenyl disulphide (0·094 g, 98·7%).

Identification of the Gas from Tribenzenesulphenamide Pyrolysis.—The nitride (I) (0·0687 g) was heated in a vacuum of 10^{-5} cmHg at 80° in an apparatus connected to the gas inlet of an MS9 mass spectrometer. The spectrometer was evacuated up to the tap of the pyrolysis apparatus and a background spectrum run. The tap was opened and a spectrum of the gas in the pyrolysis apparatus was obtained. The ratio of the *m/e* 28 (N_2) and 32 (O_2) peaks in each spectrum was recorded.

Sample	*m/e* 28 : 32	*m/e* 28	*m/e* 32
Background	4·3	13	3
Pyrolysis gas	10·3	36	3·5

Reaction of Dibenzenesulphenamide with Lead Dioxide.[20]—The sulphenamide (6·5 g) in dry ether (50 ml) was treated with lead dioxide (1·5 g) and anhydrous potassium carbonate (1·5 g) at room temperature under nitrogen. An intense purple colour, $\lambda_{max.}$ (Et_2O) 531 nm, was observed which slowly disappeared over 6 h. The mixture was filtered and the filtrate evaporated to give, after thick layer chromatography, diphenyl disulphide (0·213 g, 51%) and tribenzenesulphenamide (I) (0·060 g, 24%).

Photolysis of Tribenzenesulphenamide (I) *in a Microhydrogenator.*—The nitride (I) (0·089 g) in cyclohexane (5 ml) in a hydrogenation flask attached to a micro-hydrogenator was equilibrated at 6° under nitrogen. The sample was irradiated using a medium pressure mercury lamp. A purple-blue solution was formed, $\lambda_{max.}$ 531 nm. After 2 h nitrogen evolution had ceased (77·5% nitrogen evolved). The solution was evaporated and three major products were separated by t.l.c. using 10% acetone–light petroleum as eluant. Diphenyl disulphide (0·048 g, 60%), a diphenyl disulphide dimer (0·009 g, 16%) (M^+, 432), and dibenzenesulphenamide (0·013 g, 21%) were formed.

Reaction of Tribenzenesulphenamide (I) *with Phenol.*—The trisulphenamide (I) (0·34 g) and phenol (0·047 g) in dichloroethane (DCE; 20 ml) were heated at reflux (*ca.* 82°) under nitrogen for 2 h. The mixture was evaporated and the residue was chromatographed on silica gel. Elution with light petroleum gave diphenyl disulphide (0·185 g), m.p. 61°. Elution with benzene–light petroleum (1 : 1) gave 1,2-*benzoquinone monophenylthioimine* (II) (0·041 g), m.p. 98—99° (from benzene–light petroleum), $\nu_{max.}$ 1630, 1590, 1420, 740, and 680 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 460 and 260 nm (ε 12,000 and 6100 respectively), τ 3·2 (2H, t) and 2·0—2·9 (7H, m) (Found: C, 66·8; H, 4·1; N, 6·5; S, 14·8. $C_{12}H_9NOS$ requires C, 67·0; H, 4·2; N, 6·5; S, 14·9%). Elution with ether gave the 1,4-*isomer* (III) (0·014 g), m.p. 98° (from benzene–light petroleum) [mixed m.p. with (II) was 65°], $\nu_{max.}$ 1640, 860, 750, 720, and 695 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 440 and 278 nm (ε 20,000 and 13,500 respectively), τ 3·4 (2H, m), 2·5 (7H, m) (Found: C, 66·8; H, 4·4; N, 6·4%).

Reductive Acetylation of the Benzoquinone Imine (II).—The imine (II) (0·032 g) in acetic anhydride (2 ml) was treated with zinc dust (0·060 g), acetic acid (3 drops), and pyridine (1 drop). The mixture was stirred at room temperature for 0·5 h. Dilution with dichloromethane, filtration, and evaporation gave a residue that was chromatographed (p.l.c.) to give 2 acetamidophenyl acetate [6] (0·015 g), m.p. 123—124° (from benzene–light petroleum) (lit.,[6] 123°), undepressed on admixture with an authentic sample.

Reductive Acetylation of the Benzoquinone Imine (III).—The imine (III) (10 mg) in acetic anhydride (1 ml) and acetic acid (2 drops) was treated with zinc dust (20 mg) and pyridine (1 drop). After a few minutes the mixture was diluted with chloroform, filtered, and evaporated. The residue was chromatographed (p.l.c.) to give 4-acetamidophenyl acetate, m.p. 153—154° (lit.,[7] 150—151°), undepressed on admixture with an authentic sample.

1,4-*Benzoquinone Monophenylthioimine* (III).—*p*-Aminophenol (1·0 g) in benzene (10 ml) and pyridine (1·5 ml) was treated with benzenesulphenyl chloride (1·5 g). After 0·5 h at room temperature the mixture was poured onto a silica gel column (100 g) and eluted with benzene–light petroleum (1 : 1). Further elution with ether–benzene (1 : 9) gave a deep orange band which on evaporation gave the imine (III) (200 mg), m.p. 97—98°, undepressed on admixture with an authentic sample.

Reaction of Tribenzenesulphenamide (I) *with α-Naphthol.*—α-Naphthol (36 mg) in dichloroethane (10 ml) was heated under reflux with the trisulphenamide (I) (170 mg) for 2 h. The mixture was evaporated and chromatographed (p.l.c.). Analysis of the eluates (u.v.) gave 64% 1,2-*naphthoquinone 2-phenylthioimine* (IV) (35 mg, 50% isolated), m.p. 148—149° (from light petroleum), $\nu_{max.}$ 1640, 1610, 1595, 830, 810, 750, 700, and 690 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 455—480 and 270 nm (ε 15,000 and 20,850 respectively), τ 1·66 (1H, m), 2·0—2·8 (8H, m), 2·91 (2H, s) (Found: C, 72·3; H, 4·4; N, 5·1; S, 12·3. $C_{16}H_{11}NOS$ requires C, 72·5; H, 4·2; N, 5·3; S, 12·1%). An authentic sample was prepared from α-naphthol as follows. Hydrogenation of 2-nitro-1-naphthol [21] over 10% Pd–C in ethanol followed by treatment with hydrogen chloride in ether to give 2-amino-1-naphthol hydrochloride. Treatment of 2-amino-1-naphthol hydrochloride (0·5 g) in benzene (10 ml) and pyridine (0·5 ml) with benzenesulphenyl chloride (0·6 g) at 30—40° for 0·5 h followed by chromatography on silica gel (100 g) gave the imine (IV) (0·28 g), m.p. 148—149°, undepressed on admixture with the product from α-naphthol and the trisulphenamide (I).

Further elution of the products from the α-naphthol–trisulphenamide (I) reaction gave 1,4-*naphthoquinone monophenylthioimine* (V) (10% u.v., 3% isolated), m.p. 137—139° (from light petroleum), $\nu_{max.}$ 1645, 1595, 1330, 1305, 765, 720, and 700 cm^{-1}, $\lambda_{max.}$ 453, 337, and 275 nm (ε 16,000, 4100, and 17,000 respectively), τ 3·35 (1H, d, *J* 10 Hz), 2·8—2·2 (8H, m), 2·0—1·6 (2H) (Found: C, 72·7; H, 4·4; N, 5·2; S, 12·0%). This compound was identical with an authentic sample prepared from 4-amino-1-naphthol hydrochloride and benzenesulphenyl chloride in the usual way (m.p. and mixed m.p.).

Reaction of Tribenzenesulphenamide (I) *with β-Naphthol.*—β-Naphthol (72 mg) and the trisulphenamide (I) (341 mg) in dichloroethane (20 ml) were heated at reflux for 2 h. The mixture was evaporated and the residue chromatographed on silica gel. Elution with light petroleum gave diphenyl disulphide. Elution with benzene–light petroleum (1 : 1) gave 1,2-*naphthoquinone* 1-*phenylthioimine* (VI) (85%), m.p. 124—125° (from benzene–light petroleum), $\nu_{max.}$ 1630, 1580,

[20] H. Lecher, K. Koberle, and P. Stocklin, *Ber.*, 1925, **58**, 423.
[21] H. H. Hodgson and E. W. Smith, *J. Chem. Soc.*, 1935, 672.

830, 750, 690, and 670 cm^{-1}, $\lambda_{max.}$ (EtOH) 445, 271, and 227 nm (ε 15,000, 10,000, and 26,800 respectively), τ 1·7 (1H, d), 2·2 (1H, m), 2·6 (8H, m), and 3·4 (1H, d *J* 10 Hz) (Found: C, 72·6; H, 4·1; N, 5·2; S, 12·2%). Dibenzenesulphenamide (33%), m.p. 129°, was also isolated.

Reductive Acetylation of Imine (VI).—The imine (VI) (30 mg) in acetic anhydride (1·5 ml) was treated with zinc dust (100 mg), acetic acid (3 drops), and pyridine (1 drop). After 2 h the mixture was filtered and the residue was washed with chloroform. The combined filtrate and washings were evaporated and the residue crystallised from ethanol to give 1-acetamido-2-naphthyl acetate (15 mg), m.p. 205—206° (lit.,[9] 206°), undepressed on admixture with an authentic sample.

Reaction of Tribenzenesulphenamide (I) *with* 2,4-*Dimethylphenol*.—The trisulphenamide (I) (341 mg) and 2,4-dimethylphenol (61 mg) in dichloroethane (20 ml) were heated at reflux for 1 h. The mixture was evaporated and the residue chromatographed on silica gel. Benzene–light petroleum elution gave 4,6-*dimethyl*-1,2-*benzoquinone monophenylthioimine* (VII) (96 mg, 80%), m.p. 129° (from light petroleum), $\nu_{max.}$ 1610, 1590, 765, 740, and 690 cm^{-1}, $\tau_{max.}$ (CH_2Cl_2) 465, 410, and 270 nm (ε 11,500, 9200, and 5900 respectively), τ 7·86 (6H, m), 3·21 and 3·11 (1H each, m), 2·7—2·4 (3H, m), 2·3—2·0 (2H, m) (Found: C, 68·8; H, 5·5; N, 5·5; S, 13·3. $C_{14}H_{13}NOS$ requires C, 69·1; H, 5·4; N, 5·8; S, 13·2%). Reductive acetylation of the imine (VII) in the usual way gave 2-*acetamido*-3,5-*dimethylphenyl acetate*, m.p. 161—162° (from benzene–light petroleum), $\nu_{max.}$ 3395, 1747, 1695, 1620, 1605, 1540, 1220, 1190, 905, and 855 cm^{-1}, τ 7·91 and 7·88 (6H, s), 7·72 and 7·68 (6H, s), 3·13 (1H, m), 2·78br (1H, exchanged by D_2O), and 2·33 (1H, m) (Found: C, 65·1; H, 6·7; N, 6·3. $C_{12}H_{15}NO_3$ requires C, 65·1; H, 6·8; N, 6·3%). An authentic sample was prepared by reductive acetylation of 2,4-dimethyl-6-nitrophenol [10] in the usual way.

Reaction of Tribenzenesulphenamide (I) *with* 2,4,6-*Trimethylphenol*.—The trisulphenamide (I) (341 mg) and 2,4,6-trimethylphenol (68 mg) in dichloroethane (20 ml) were heated at reflux for 4 h. Work-up in the usual way, followed by chromatography over silica gel gave imine (VII) (<1%) and 2,6-*dimethyl*-1,4-*benzoquinone monophenylthioimine* (VIII) (30 mg), m.p. 152—153° (from light petroleum), $\nu_{max.}$ 1620, 1580, 820, 740, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 443, 345, and 280 nm (ε 19,800, 2850, and 11,900 respectively), τ 2·3—2·8 (6H, m), 3·0 (1H, m), and 7·9 (6H, d) (Found: C, 69·4; H, 5·4; N, 5·7; S, 13·1. $C_{14}H_{13}NOS$ requires C, 69·1; H, 5·4; N, 5·8; S, 13·2%). Reductive acetylation of (VIII) in the usual way gave 4-acetamido-3,5-dimethylphenyl acetate, m.p. 161° (lit.,[11] 160°), identical with an authentic sample (m.p. and mixed m.p.).

Reaction of Tribenzenesulphenamide (I) *with* 2,6-*Dimethylphenol*.—2,6-Dimethylphenol (61 mg) and the trisulphenamide (I) (341 mg) were heated in dichloroethane (20 ml) at reflux for 1 h. Work-up in the usual way gave the *imine* (VIII) (103 mg, 85%), m.p. 152—153° (from benzene–light petroleum), identical with the product from 2,4,6-trimethylphenol (m.p. and mixed m.p.). The above reaction was repeated under a stream of oxygen. No change in yield or products was observed.

Reaction of Tribenzenesulphenamide (I) *with* 2,6-*Dimethyl*-4-*nitrophenol* (IX; R = NO_2).—The nitrophenol [11] (IX; R = NO_2) (42 mg) and the trisulphenamide (I) (170 mg) in dichloroethane (10 ml) were heated at reflux for 1·5 h. Work-up in the usual way gave the imine (VIII) (27 mg, 55%), m.p. 153°, undepressed on admixture with an authentic sample. Traces (3—5 mg) of 2,6-dimethyl-1,4-benzoquinone were also present.

Reaction of Tribenzenesulphenamide (I) *with* 4-*Benzyl*-2,6-*dimethylphenol* (IX; R = CH_2Ph).[12,13]—The phenol (IX; R = CH_2Ph) (57 mg) and the trisulphenamide (I) (170 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave imine (VIII) (30 mg), m.p. 153°, undepressed on admixture with an authentic sample and benzyl phenyl sulphide (22 mg), m.p. 38—40°, identical with an authentic sample (lit.,[14] 40—41°) and further characterised as benzyl phenyl sulphoxide, m.p. 124° (lit.,[14] 122—123°), undepressed on admixture with an authentic sample.

Reaction of Tribenzenesulphenamide (I) *with* 4-*Methoxy*-2,6-*dimethylphenol* (IX; R = OMe).[15]—The phenol (IX; R = OMe) (34 mg) and the sulphenamide (I) (170 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave imine (VIII) (39 mg, 64%), m.p. 153°, undepressed on admixture with an authentic sample.

Reaction of Tribenzenesulphenamide (I) *with* 2,6-*Di-t-butylphenol*.—The trisulphenamide (I) (170 mg) and 2,6-di-t-butylphenol (52 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave 2,6-*di-t-butyl*-1,4-*benzoquinone monophenylthioimine* (X) (30 mg, 37%), m.p. 111—112° (from ethanol), $\nu_{max.}$ 1650, 1620, 1360, 1315, 1255, 1085, 1030, 915, 887, 818, 760, 740, and 690 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 434, 340, and 278 nm (ε 19,200, 3350, and 13,300 respectively), τ 2·8—2·2 (6H, m), 3·07 (1H, d, *J* 2·5 Hz), 8·70 and 8·67 (18H, *anti*- and *syn*-Bu^t groups) (Found: C, 73·2; H, 7·7; N, 4·1; S, 10·0. $C_{20}H_{25}NOS$ requires C, 73·4; H, 7·7; N, 4·3; S, 9·8%).

Reaction of Tribenzenesulphenamide (I) *with Estrone* (XI).—Estrone (136 mg) and the trisulphenamide (I) (341 mg) in dichloroethane (20 ml) were heated at reflux for 2 h. Work-up in the usual way gave 2-*phenylthioiminoestra*-1(10),4-*diene*-3,17-*dione* (XII) (101 mg, 51%), m.p. 153° (from benzene–light petroleum), $\nu_{max.}$ 1745, 1640, 1605, 755, and 690 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 462, 410, and 265 nm (ε 9100, 9800, and 6500 respectively), τ 9·06 (3H, s), 8·7—7·0br (15H), 3·58br (1H, s), 3·07br (1H, s), 2·7—2·4 (3H, m), and 2·3—2·0 (2H, m) (Found: C, 73·8; H, 6·7; N, 3·4. $C_{24}H_{25}NO_2S$ requires C, 73·6; H, 6·4; N, 3·6%), and 4-*phenylthioiminoestra*-1,5(10)-*diene*-3,17-*dione* (XIII) (54 mg, 28%), m.p. 183° (from methanol), $\nu_{max.}$ 1745, 1630, 1600, 745, and 680 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 467, 415, and 269 nm (ε 8800, 9800, and 8700 respectively), τ 9·07 (3H, s), 8·9—6·7br (15H), 3·48 (1H, d, *J* 10 Hz), 2·7—2·4 (4H, m), 2·3—2·0 (2H, m) (Found: C, 73·7; H, 6·5; N, 3·4%).

Reaction of Tribenzenesulphenamide (I) *with Estradiol* (XIV).—Estradiol (137 mg) and the trisulphenamide (350 mg) in dichloroethane (20 ml) were heated at reflux for 2 h. Work-up in the usual way gave 2-*phenylthioimino*-17β-*hydroxyestra*-1(10),4-*dien*-3-*one* (70 mg, 36%), m.p. 158—159° (from benzene–light petroleum), $\nu_{max.}$ 3450, 1625, 1585, 900, 765, and 715 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 462, 408, and 270 nm (ε 10,400, 12,000, and 6500 respectively), τ 9·20 (3H, s), 9·0—7·1br (16H), 6·30 (1H, m), 3·65br (1H, s), 3·12br (1H, s), 2·9—2·4 (3H, m), and 2·3—2·0 (2H, m) (Found: C, 73·5; H, 7·0; N, 3·6; S, 7·9. $C_{24}H_{27}NO_2S$ requires C, 73·3; H, 6·9; N, 3·6; S, 8·1%), and 4-*phenylthioimino*-17β-*hydroxyestra*-1,5(10)-*dien*-3-*one* (40 mg, 15%), m.p. 104—105° (from benzene–light petroleum), $\nu_{max.}$ 3480, 1620, 1585, 770, and 700 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 468, 413, and 260 nm (ε 9300, 10,100, and 6600 respectively), τ 9·20 (3H, s), 9·0—6·8br (16H), 6·30 (1H, m), 3·49 (1H, d, *J* 10 Hz),

2·9—2·4 (10H, m), and 2·3—2·05 (2H, m) (Found: C, 76·3; H, 6·9; N, 2·8; S, 7·0%).

Reaction of Tribenzenesulphenamide (I) *with Resorcinol.*—The trisulphenamide (I) (228 mg) and resorcinol (18 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave *2,6-bisphenylthioimino-cyclohex-4-ene-1,3-dione* (XV) (43 mg, 73%), m.p. 198° (from acetone–light petroleum), $\nu_{max.}$ 1650, 1620, 1580, 780, 760, 740, and 690 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 421 and 270 nm (ε 32,000 and 12,000 respectively), τ 3·2 (1H, d) and 1·8—2·8 (11H, m) (Found: C, 62·2; H, 3·8; N, 7·6; S, 18·1%; M^+, 352·0334. $C_{18}H_{12}N_2O_2S_2$ requires C, 61·4; H, 3·4; N, 8·0; S, 18·2%; *M* 352·0340).

Kinetic Studies on the Reaction of Tribenzenesulphenamide (I) *with Phenols.*[22]—*Curve* (1). 2,6-Dimethylphenol (IX; R = H) (30·4 mg, 0·25 mmol) in dichloroethane (15 ml) and the trisulphenamide (I) (170 mg, 0·5 mmol) in dichloroethane (5 ml) were heated at 80·0 ± 0·5° in a vapour (benzene) heated flask. Aliquot portions (1 ml) were removed and analysed by observing the u.v. absorbance at 443 nm for the formation of product (VIII). The results are presented in curve (1).

Curve (2). As above, but using a 1 : 1 proportion of trisulphenamide (I) to phenol (IX; R = H) and n-butyl chloride in the solvent at 77°.

Curve (3). As for (1) but adding water (1·5 ml) to the reaction mixture.*

Curve (4). As for (1) but adding deuterium oxide (1·5 ml).

Curve (5). [4-^{2}H]-2,6-Dimethylphenol (IX; R = D), prepared from (IX; R = H), D_2O (98%), and triethylamine in the standard way,[23] was treated as for (4).

Curve (6). As for (5) but adding D_2O (1·5 ml).

Curve (7). 2,6-Di-t-butylphenol (51·5 mg, 0·25 mmol) and the trisulphenamide (I) (170 mg, 0·5 mmol) in dichloroethane (20 ml) and water (1 ml) as for (3).

Curve (8). [4-^{2}H]-2,6-Di-t-butylphenol (prepared in the standard manner [23]), was treated as for (7).

Curve (9). As for (7), but using D_2O (1 ml).

Reaction of Tribenzenesulphenamide (I) *with β-Naphthylamine.*—β-Naphthylamine (71 mg) and the nitride (I) (350 mg) in dichloroethane (20 ml) were heated at reflux for 2 h. Work-up in the usual way gave *1,2-naphthoquinone bisphenylthioimine* (XVII) (62 mg), m.p. 138° (from benzene–light petroleum), $\nu_{max.}$ 1580, 820, 750, and 700 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 489, 440, and 267 nm (ε 12,200, 10,900, and 12,200), τ 1·6—3·4 (m) (Found: C, 70·8; H, 4·5; N, 7·4. $C_{22}H_{16}N_2S_2$ requires C, 71·0; H, 4·3; N, 7·5%).

Reductive acetylation of the di-imine (XVII) in the usual way gave 1,2-diacetamidonaphthalene, m.p. 234—235° (lit.,[18] 235—236°), identical by m.p. and mixed m.p. with an authentic sample.

Reaction of Tribenzenesulphenamide (I) *with 2,6-Dimethylaniline.*—2,6-Dimethylaniline (61 mg) and the trisulphenamide (I) (341 mg) in dichloroethane (20 ml) were heated at reflux for 2 h. Work-up in the usual way gave the *imine* (VIII) (16 mg), m.p. 153°, undepressed on admixture with an authentic sample, and *2,6-dimethyl-1,4-benzoquinone bisphenylthioimine* (XX) (20 mg), m.p. 137—138° (from light petroleum), $\nu_{max.}$ 1580, 1080, 1020, 870, 740, and 695 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 468 and 280 nm (ε 47,500 and 13,100 respectively), τ 7·60br (6H, m), 3·37 (1H, m), 3·15 (1H, m), and 2·8—2·2 (10H, m) (Found: C, 68·6; H, 5·4; N, 7·8; S, 18·2. $C_{20}H_{18}N_2S_2$ requires C, 68·6; H, 5·2; N, 8·0; S, 18·3%).

Reaction of Tribenzenesulphenamide (I) *with 2,4-Dimethylaniline.*—2,4-Dimethylaniline (30 mg) and the trisulphenamide (I) (340 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave *3,5-dimethyl-1,2-benzoquinone bisphenylthioimine* (XXI) (11 mg), m.p. 137—138° (from light petroleum), $\nu_{max.}$ 1630, 1575, 1320, 1020, 820, 730, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 430 and 500 nm (ε 9700 and 13,200 respectively), τ 7·83br (3H, s), 7·65br (3H, s), 3·57 (1H, m), 3·28 (1H, m), and 2·8—1·9 (10H, m) (Found: C, 68·4; H, 5·0; N, 8·1; S, 18·3%).

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* Azeotrope temperature 76·0 ± 0·5° for all wet reactions.

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