The Chemistry of Trisulphenamides [N(SR)$_3$]. Part II.[1] Reactions of Tribenzenesulphenamide with Electron-rich Molecules

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Tribenzenesulphenamide (I) reacts with tetraphenylfuran to give 2,4,5,6-tetraphenylpyrimidine (IV), 2-hydroxy-2,3,4,5-tetraphenyl-2*H*-pyrrole and traces of tetraphenylpyrrole. Similarly the trisulphenamide reacts with tetraphenylpyrrole to give the pyrimidine (IV). Reactions of the trisulphenamide (I) with hydrazones give the phenylthioimine (X) and quinone di-imine (XI).

THE reactions and properties of tribenzenesulphenamide (I),[1] derived from the disulphenamide (II), indicated that its reactions with electron-rich molecules would be interesting.

Tetraphenylfuran (III; X = O) and the trisulphenamide (I) were heated in dichloroethane for 2 h. 2,4,5,6-Tetraphenylpyrimidine [2,3] (IV) (6%) was isolated along with traces (⩽2%) of tetraphenylpyrrole [4] (III; X = NH). 2-Hydroxy-2,3,4,5-tetraphenyl-2*H*-pyrrole [3,5] (V)

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[1] Part I, D. H. R. Barton, I. A. Blair, P. D. Magnus, and R. K. Norris, preceding paper.

[2] R. Kuhn and H. Kainer, *Annalen*, 1952, **578**, 228.

[3] G. Rio, A. Raujon, and O. Pouchot, *Compt. rend.*, 1966, **263**, 634.

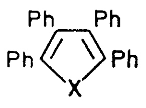
[4] D. Davidson, *J. Org. Chem.*, 1938, **3**, 361.

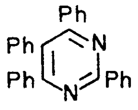
[5] R. E. Lutz and D. W. Boykin, jun., *J. Org. Chem.*, 1967, **32**, 1179.

(*ca.* 24%) was the major product. All these compounds were compared with authentic samples as structure proof. Furthermore since there appears to be some discrepancy concerning the m.p. of 2-hydroxy-2,3,4,5-tetraphenyl-2*H*-pyrrole (V) it was reduced with sodium dithionate to tetraphenylpyrrole (III; X = NH). The preparation of an authentic sample of 2,4,5,6-tetraphenylpyrimidine (IV) deserves comment since to our knowledge this compound has not been fully characterised.[3] Tetraphenylpyrrole (III; X = NH) was oxidised with hydrogen peroxide in acetic acid, and the crude mixture was treated with methanolic ammonia to give *N*-(2-benzoyl-1,2-diphenylvinyl)benzamide (VI).[5] The benzamide (VI) was treated with 60% perchloric acid at 90—95° to give the azapyrylium salt (VII) which was treated with aqueous ammonia to give the pyrimidine (IV) [3] (Scheme 1).

$N(SPh)_3$ (I)

$HN(SPh)_2$ (II)


(III)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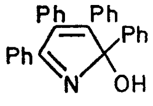
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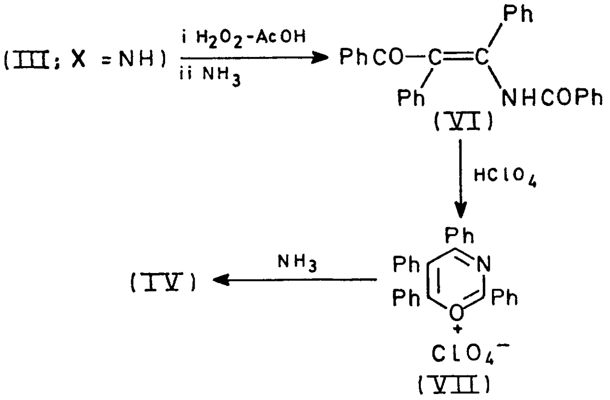


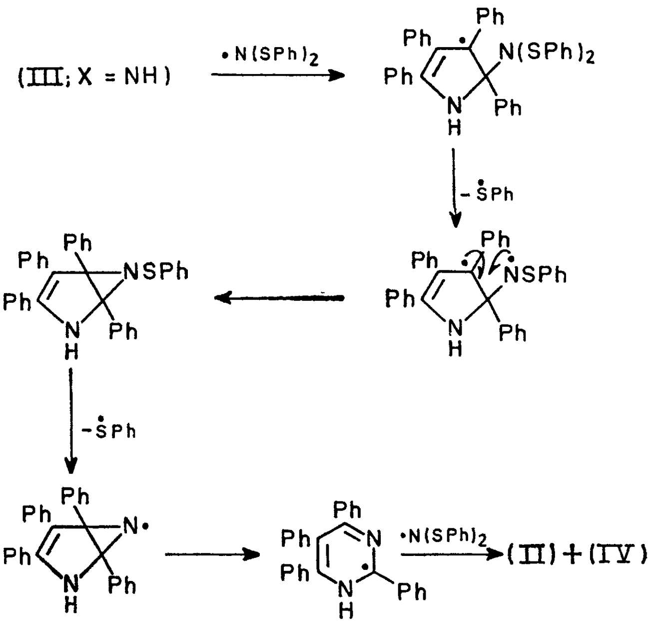
SCHEME 1

Tetraphenylpyrrole (III; X = NH) was treated with the trisulphenamide (I) in dichloroethane at reflux to give 2,3,4,5-tetraphenylpyrimidine (IV) (82%). No 2-hydroxy-2,3,4,5-tetraphenyl-2*H*-pyrrole (V) was formed. Tetraphenylthiophen (III; X = S) did not react with the trisulphenamide (I) in dichloroethane at reflux. A plausible radical mechanism for the formation of the pyrimidine (IV) is outlined in Scheme 2.

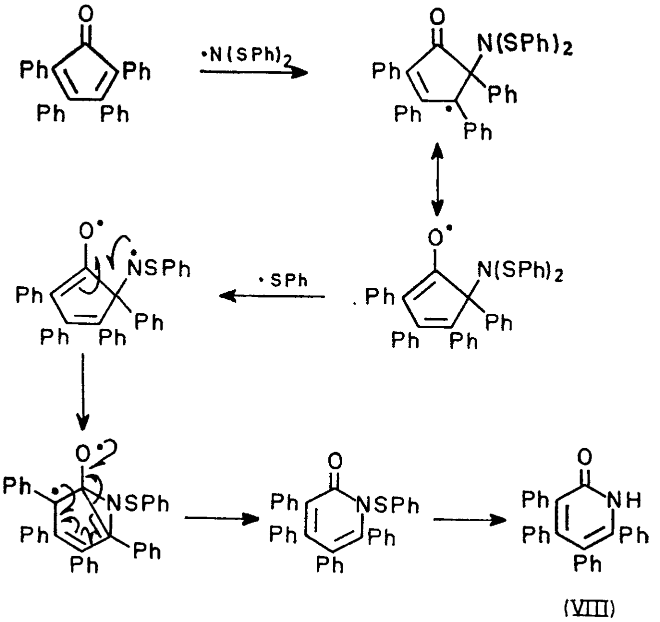
Tetraphenylcyclone reacted with the trisulphenamide (I) to give the pyridone [6] (VIII) (25%). A reasonable mechanism that accounts for this unusual transformation is outlined in Scheme 3.

Indole did not react to any appreciable extent with the trisulphenamide (I), whereas 2-phenylindole reacted to give 2-phenyl-3-phenylthioiminoindolenine (IX) (62%). Reductive acetylation of the imine (IX) gave 3-acetamido-2-phenylindole.[7] This transformation is similar to the reaction of the trisulphenamide (I) with phenols and arylamines.

Benzophenone phenylhydrazone reacted with the trisulphenamide (I) in dichloroethane at reflux to give two compounds (apart from diphenyl disulphide). The less polar component (47%) had $\lambda_{max.}$ 277 and 340 nm and from its molecular weight, 289, was assigned the structure (X). The second component (14%) had $\lambda_{max.}$ 287, 380, and 463 nm and molecular weight 393 and was



SCHEME 2



SCHEME 3

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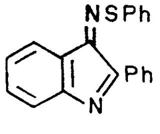
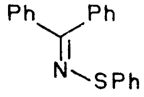
[6] J. F. M. Wajan and J. F. Arens, *Rec. Trav. chim.*, 1957, **76**, 65.

[7] Huang-Hsinmin and F. G. Mann, *J. Chem. Soc.*, 1949, 2111.

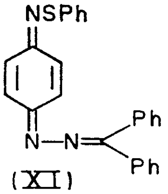
assigned structure (XI). An authentic sample was synthesised from benzophenone hydrazone and 1,4-benzoquinone monophenylthioimine. Benzophenone hydrazone reacted with the trisulphenamide (I) to give diphenylmethylene(phenylthio)amine (X) (10%). Mainly decomposition of the trisulphenamide (I) to diphenyl disulphide took place. Benzophenone *p*-nitrophenylhydrazone reacted with the nitride (I) in dichloroethane at reflux to give the imine (X) (21%), and the quinone di-imine (XI) (5%). Acetone *p*-nitrophenylhydrazone reacted with the trisulphenamide (I) to give the adduct (XII) (52%) as a reasonable stable crystalline compound. Pyrolysis of (XII) at 142 °C gave nitrogen (100%) and *p*-nitrophenyl phenyl sulphide (XIII), identical with an authentic sample. No products from the acetone group could be isolated. Benzophenone oxime on reaction with the trisulphenamide (I) in the usual way gave the imine (X) (48%). All these reactions can be interpreted in radical terms (Scheme 4).



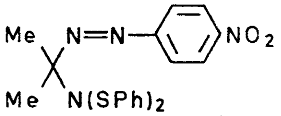
(IX)



(X)

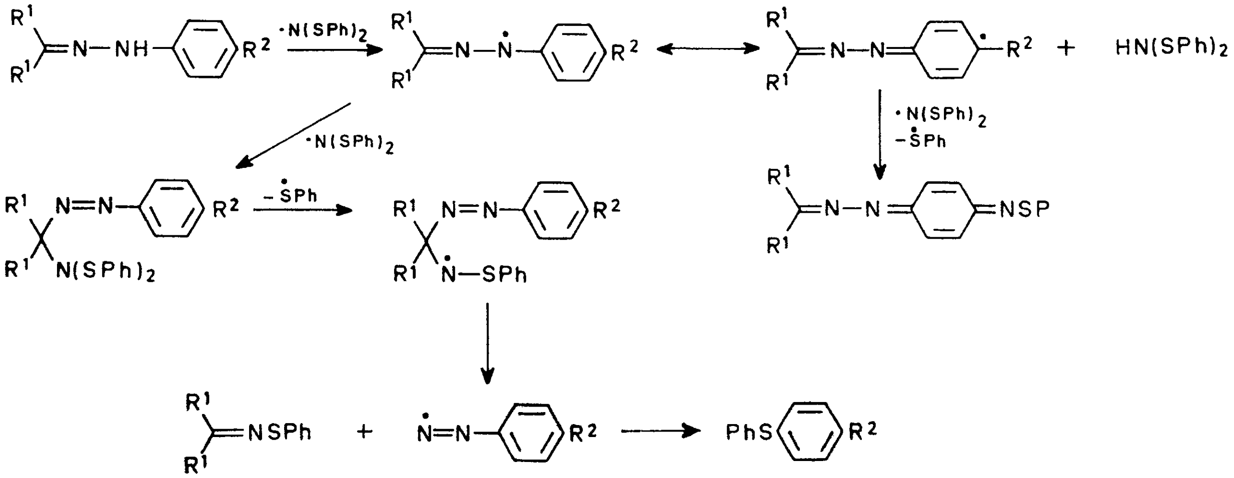


(XI)



(XII)

(XIII)



SCHEME 4

It is clear that tribenzenesulphenamide has many interesting applications.

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. U.v. spectra were measured in ethanol–chloroform unless otherwise stated. N.m.r. spectra were recorded with Varian A60 and HA100 instruments in $[^{2}H]$chloroform with tetramethylsilane as internal standard. Mass spectra were taken with an A.E.I. MS9 high resolution mass spectrometer. All solvents were purified prior to use by standard techniques. Light petroleum refers to the fraction b.p. 40—60 °C.

Reaction of Tribenzenesulphenamide (I) *with Tetraphenylfuran* (III; X = O).—Tetraphenylfuran * (III; X = O) (110 mg) and the trisulphenamide (I) (200 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. The mixture was evaporated and chromatographed (p.l.c.). The first fraction gave 2,4,5,6-*tetraphenylpyrimidine* [3] (IV) (6%), m.p. 194—195° (from benzene–light petroleum), $\nu_{max.}$ 1525, 1495, 1400, 757, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 260 nm (ε 35,000), τ 3·1—2·4 (m) (Found: C, 87·4; H, 5·4; N, 7·2. $C_{28}H_{20}N_2$ requires C, 87·5; H, 5·2; N, 7·3%). The second fraction contained traces ($\leqslant$2%) of tetraphenylpyrrole [4] (III; X = NH). The third fraction gave 2-hydroxy-2,3,4,5-tetraphenyl-2*H*-pyrrole [3,5] (V) (24%), m.p. 170—171° (from benzene–light petroleum), $\nu_{max.}$ 3070, 1630, 1560, 1500, 760, and 700 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 317 nm (ε 6050), τ 3·1—2·4 (20H, m) and 3·57s,br (1H, s, exchanged by D_2O) (Found: C, 86·6; H, 5·4; N, 3·4. Calc. for $C_{28}H_{21}NO$: H, 5·5; N, 3·6%).

Preparation of Authentic Samples of 2-*Hydroxy*-2,3,4,5-*Tetraphenyl*-2H-*pyrrole* (V) [3,5] *and* 2,4,5,6-*Tetraphenylpyrimidine* (IV).[3]—Tetraphenylpyrrole (III; X = NH) was prepared from benzoin in the usual way.[4] The pyrrole (III; X = NH) (500 mg) in acetic acid (50 ml) at 55° was treated with chromium trioxide (100 mg) in water (2 ml) and the mixture stirred at 55° for 10 min. to give the 2*H*-pyrrole (V) (200 mg), m.p. 171° (from benzene–light petroleum) (lit., 170—173,[3] 183—184,[5] and 204—205° [3]), undepressed on admixture with product from reaction with trisulphenamide (I). Treatment of the pyrrole (V) (8 mg) in ethanol (2 ml) with sodium dithionate (20 mg) in water (6 drops) gave tetraphenylpyrrole (III; X = NH), m.p. 213—214°, identical with an authentic sample.

Tetraphenylpyrrole (III; X = NH) (2·0 g) in acetic acid (50 ml) and 30% v/v hydrogen peroxide (1·5 ml) was heated at reflux for 0·5 h. The mixture was poured

* Prepared by heating benzoin with concentrated hydrochloric acid.

into ice–water (100 ml) and the product was filtered off. The crude mixture was dissolved in methanol (800 ml) and heated at reflux whilst ammonia was passed through (10 h). The methanol was evaporated and the residue was crystallised from ethanol (× 3) to give *N*-(2-benzoyl-1,2-diphenylvinyl)benzamide (VI)[6] (800 mg), m.p. 189—190° (lit.,[5] 189—191°). The benzamide (VI) (100 mg) suspended in 60% aqueous perchloric acid (2 ml) was heated at 90—95° for 0·5 h. The mixture was cooled and filtered and the azapyrylium salt (VII) was washed with water, dried, and then suspended in aqueous ammonia (*d* 0·880) solution (5 ml) for 10 min. The mixture was extracted with chloroform and the chloroform layer dried (Na_2SO_4) and evaporated to give 2,4,5,6-tetraphenylpyrimidine (IV) (45 mg), m.p. 194—195° (from ethanol), undepressed on admixture with the sample from the trisulphenamide (I)–tetraphenylfuran reaction.

Reaction of Tribenzenesulphenamide (I) *with Tetraphenylpyrrole* (III; X = NH).—The pyrrole (III; X = NH) (150 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 2,4,5,6-tetraphenylpyrimidine (IV) (82%, corrected for recovered starting material), m.p. 195° (from ethanol), undepressed on admixture with an authentic sample.

Reaction of Tribenzenesulphenamide (I) *with Tetraphenylcyclone*.—The trisulphenamide (I) (228 mg) and tetraphenylcyclone (136 mg) in dichloroethane (10 ml) were heated at reflux for 3 h. Work-up in the usual way gave tetraphenyl-2-pyridone (VIII) (25%), m.p. 260—272° (lit.,[6] 272°), $\nu_{max.}$ 1630, 1595, 760, and 700 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 235, 265, and 342 nm (ε 18,950, 13,000, and 12,700 respectively) (Found: C, 87·2; H, 5·3; N, 3·3. Calc. for $C_{29}H_{21}NO$: C, 87·2; H, 5·3; N, 3·5%).

Reaction of Tribenzenesulphenamide (I) *with* 2-*Phenylindole*.—2-Phenylindole (48 mg) and the trisulphenamide (I) (100 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave 2-*phenyl*-3-*phenylthioimino*-3H-*indole* (IX) (62%), m.p. 86—87° (from light petroleum), $\nu_{max.}$ 1610, 1600, 1570, 1450, 745, 740, and 690 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 267 and 413 nm (ε 31,800 and 17,000) (Found: C, 76·3; H, 4·7; N, 8·7; S, 10·3. $C_{20}H_{14}N_2S$ requires C, 76·4; H, 4·5; N, 8·9; S, 10·2%).

Reductive Acetylation of Imine (IX).—The imine (IX) (5 mg) in acetic anhydride (0·3 ml) and acetic acid (1 drop) was treated with zinc dust (20 mg) and pyridine (1 drop). When the mixture became colourless it was filtered and evaporated. Chromatography of the residue (t.l.c.) eluting with acetone–light petroleum (3 : 7) gave 3-acetamido-2-phenylindole,[7] m.p. 202—204° (from benzene–light petroleum), undepressed on admixture with an authentic sample.

Reaction of Tribenzenesulphenamide (I) *with Benzophenone Phenylhydrazone*.—Benzophenone phenylhydrazone (68 mg) and the trisulphenamide (170 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave *diphenylmethylene*(*phenylthio*)*amine* (X) (47%), m.p. 73° (from light petroleum), $\nu_{max.}$ 1590, 1490, 1450, 1310, 1300, 740, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 277 and 340 nm (ε 8700 and 13,200) (Found: C, 78·8; H, 5·3; N, 4·8; S, 10·9. $C_{19}H_{15}NS$ requires C, 78·9; H, 5·2; N, 4·8; S, 11·0%), and 1,4-*benzoquinone* N-*diphenylmethyleneamine*-N′-*phenylthiodi-imine* (XI) (14%), m.p. 118° (from ethanol), $\nu_{max.}$ 1605, 1580, 1560, 1540, 1490, 1020, 880, 770, 740, and 730 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 287, 380, and 463 nm (ε 15,400, 13,900 and 34,000 respectively) (Found: C, 76·5; H, 5·0; N, 10·6; S, 8·0. $C_{25}H_{19}N_3S$ requires C, 76·3; H, 4·9; N, 10·7; S, 8·1%). Benzophenone phenylhydrazone (30 mg) and 1,4-benzoquinone monophenylthioimine (20 mg) in acetic acid (4 drops) and dimethyl sulphoxide (1 ml) were heated at 90—95° for 2 h. Work-up by p.l.c. gave the quinone di-imine (XI) (8 mg), m.p. 117—118°, undepressed on admixture with the sample from the reaction with trisulphenamide.

Reaction of Tribenzenesulphenamide (I) *with Benzophenone Hydrazone*.—Benzophenone hydrazone (49 mg) and the trisulphenamide (170 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. The imine (X) (10%), m.p. 70° (from light–petroleum), was isolated.

Reaction of Tribenzenesulphenamide (I) *with Benzophenone* p-*Nitrophenylhydrazone*.—Benzophenone *p*-nitrophenylhydrazone (79 mg) and the trisulphenamide (170 mg) in dichloroethane (10 ml) were heated at reflux for 2 h. Work-up in the usual way gave the imine (X) (21%), m.p. 70° (from light–petroleum), undepressed on admixture with an authentic sample. The quinone di-imine (XI) (5%), m.p. 117—118° (from ethanol), undepressed on admixture with an authentic sample, was also isolated.

Reaction of Tribenzenesulphenamide (I) *with Acetone* p-*Nitrophenylhydrazone*.—Acetone *p*-nitrophenylhydrazone (97 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 1-*methyl*-1-p-*nitrophenylazoethylbisphenylthioamine* (XII) (52%), m.p. 102—103° (from light petroleum), $\nu_{max.}$ 1610, 1585, 1530, 1490, 1340, 900, 780, and 720 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 278 nm (ε 19,100), τ 8·27 (6H, s), 2·8—2·4br (12H), and 1·78 (2H, d, *J* 8·5 Hz) (Found: C, 59·3; H, 4·8; N, 13·4; S, 15·0. $C_{21}H_{20}N_4O_2S_2$ requires C, 59·4; H, 4·8; N, 13·2; S, 15·1%).

Thermal Decomposition of Amine (XII).—The adduct (XII) (40 mg) was heated at 142° in a pre-equilibrated microhydrogenator. Nitrogen (2·35 ml corrected) (theoretical 2·33 ml) was evolved over a period of 65 min. The residue was chromatographed (p.l.c.) to give diphenyl disulphide (8 mg) and *p*-nitrophenyl thiophenyl ether (XIII) (10 mg), m.p. 53°, undepressed on admixture with an authentic sample from *p*-nitrochlorobenzene and thiophenol.

Reaction of Tribenzenesulphenamide (I) *with Benzophenone Oxime*.—Benzophenone oxime (49 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 the imine (X) (48%), m.p. 70—72° (from light petroleum), undepressed on admixture with an authentic sample.

We thank the S.R.C. for their support in this work.

[2/2514 *Received*, 6*th November*, 1972]