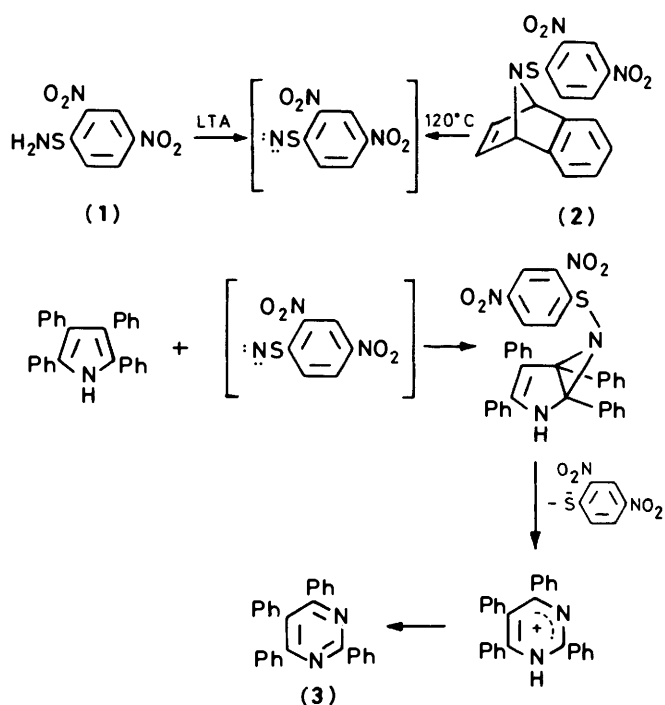


Oxidation of 2,4-Dinitrobenzenesulphenamide in the Presence of 2,3,4,5-Tetraphenylpyrrole.

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Oxidation of the title sulphenamide (1) with lead tetra-acetate in the presence of 2,3,4,5-tetraphenylpyrrole gave 2,4,5,6-tetraphenylpyrimidine (3) and 2-(2,4-dinitrophenylthioamino)-2,3,4,5-tetraphenyl-2*H*-pyrrole (7) as major products. The structure of (7) has been confirmed by X-ray crystallography.

Oxidation of 2,4-dinitrobenzenesulphenamide (1) with lead tetra-acetate (LTA) has been shown to proceed *via* a reactive intermediate having the characteristics of a nitrene.^{1,2} Thus aziridines are isolated when the oxidation is carried out in the presence of alkenes and trapping of the nitrene intermediate by allyl sulphides is particularly efficient. More recently,³ we have found that the same nitrene intermediate is apparently also obtained by thermal decomposition of the bicyclic sulphenamide (2).

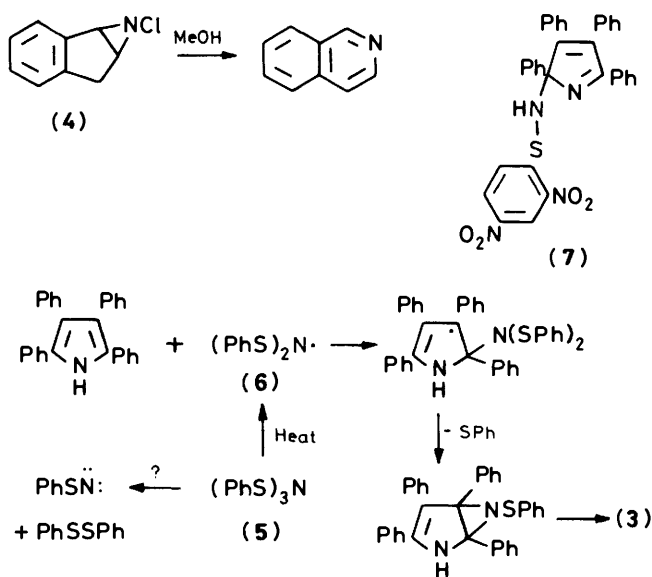


Scheme 1.

We find that oxidation of (1) in the presence of tetraphenylpyrrole gave 2,4,5,6-tetraphenylpyrimidine (3) (47%) after chromatography and fractional crystallisation (to separate from unchanged tetraphenylpyrrole). A likely mechanism for this conversion is shown in Scheme 1.

Analogies for this ring-expansion by concerted loss of the sulphide anion with disrotatory ring-opening are found in the conversion of the *N*-chloroindano[1,2-*b*]aziridine (4) into isoquinoline⁴ and in the conversion of pyrroles into 3-chloropyridines by dichlorocarbene.⁵ Since inversion at nitrogen in *N*-sulphenylated aziridines is known to be rapid at room temperature,⁶ the required *endo*-orientation of the arylthio

substituent is easily accessible even if the *exo*-orientation is that first formed in the nitrene addition.



Scheme 2.

This pyrimidine (3) has been previously obtained by Barton *et al.*⁷ by heating triphenylthioamine (5) with tetraphenylpyrrole and was suggested to be the result of attack of the diphenylthioaminy radical (6) on the heterocyclic ring (Scheme 2). It is possible that heating the amine (5) may give rise, at least in part, to phenylthionitrene which could add directly to the pyrrole ring.[†] In addition to the pyrimidine (3), a yellow crystalline product was isolated by chromatography whose structure was shown to be the 2*H*-pyrrole derivative (7) by X-ray crystallography (Figure). Rotational barriers in dinitrophenylthioamides ArSNR¹R² are known to be significant and the more stable conformation has the Ar-S-N and S-N-R¹(R²) planes orthogonal.⁸ The corresponding angles between these planes in (7) is 114.7° because the thioamide nitrogen is likely to be pyramidal (the attached hydrogen was not located in the X-ray study). It is reasonable to assume that acid catalysed ring-opening of the aziridine can compete with its disrotatory ring-opening (acetic acid is a by-product in the LTA oxidation).

Support for this mechanism comes from oxidation of (1) with

[†] The unsubstituted phenylthionitrene generated by thermolysis of the sulphenamide corresponding to (2) adds to styrene in good yield (ref. 3).

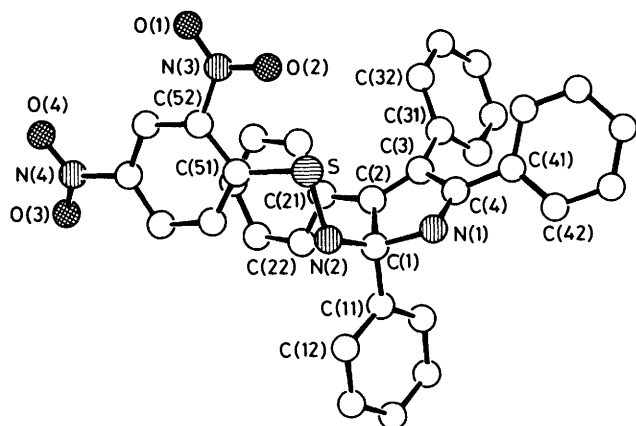


Figure. The molecular structure of (7) showing atomic numbering. H atoms are not shown.

Table 1. Atomic co-ordinates with e.s.d.'s in parentheses

Atom	x	y	z
S	0.099 1(5)	0.037 8(4)	0.355 6(3)
N(1)	0.098 1(14)	-0.085 6(11)	0.494 9(8)
N(2)	-0.007 8(13)	-0.012 8(11)	0.392 9(8)
N(3)	0.214 8(21)	0.110 0(19)	0.222 7(17)
N(4)	-0.107 1(27)	0.039 8(20)	0.046 9(12)
O(1)	0.267 0(17)	0.135 9(16)	0.174 9(11)
O(2)	0.254 3(15)	0.109 1(14)	0.285 6(13)
O(3)	-0.187 8(20)	-0.006 6(14)	0.031 8(10)
O(4)	-0.060 8(17)	0.081 9(13)	0.003 3(9)
C(1)	0.020 6(19)	-0.096 9(15)	0.422 7(11)
C(2)	0.104 9(16)	-0.146 9(12)	0.378 7(10)
C(3)	0.201 4(15)	-0.165 6(12)	0.417 9(9)
C(4)	0.191 6(18)	-0.126 2(14)	0.490 3(11)
C(11)	-0.086 0(11)	-0.142 7(9)	0.440 9(7)
C(12)	-0.194 3(11)	-0.103 6(9)	0.429 5(7)
C(13)	-0.294 4(11)	-0.144 1(9)	0.447 9(7)
C(14)	-0.286 3(11)	-0.223 6(9)	0.477 7(7)
C(15)	-0.178 1(11)	-0.262 6(9)	0.489 1(7)
C(16)	-0.077 9(11)	-0.222 1(9)	0.470 7(7)
C(21)	0.069 0(13)	-0.167 9(10)	0.302 1(6)
C(22)	-0.037 2(13)	-0.205 7(10)	0.279 9(6)
C(23)	-0.065 9(13)	-0.223 0(10)	0.207 2(6)
C(24)	0.011 6(13)	-0.202 5(10)	0.156 8(6)
C(25)	0.117 8(13)	-0.164 7(10)	0.179 0(6)
C(26)	0.146 5(13)	-0.147 4(10)	0.251 7(6)
C(31)	0.294 2(12)	-0.223 9(10)	0.403 5(8)
C(32)	0.382 6(12)	-0.201 6(10)	0.360 9(8)
C(33)	0.469 7(12)	-0.258 7(10)	0.348 4(8)
C(34)	0.468 3(12)	-0.338 0(10)	0.378 4(8)
C(35)	0.379 9(12)	-0.360 3(10)	0.420 9(8)
C(36)	0.292 8(12)	-0.303 3(10)	0.433 5(8)
C(41)	0.280 3(12)	-0.127 6(10)	0.551 7(7)
C(42)	0.244 3(12)	-0.141 1(10)	0.620 1(7)
C(43)	0.326 6(12)	-0.145 5(10)	0.679 6(7)
C(44)	0.444 9(12)	-0.136 3(10)	0.670 7(7)
C(45)	0.480 8(12)	-0.122 8(10)	0.602 4(7)
C(46)	0.398 5(12)	-0.118 4(10)	0.542 8(7)
C(51)	0.038 6(17)	0.041 6(14)	0.267 1(10)
C(52)	0.096 9(21)	0.075 1(16)	0.209 6(12)
C(53)	0.049 9(19)	0.076 5(15)	0.137 6(12)
C(54)	-0.060 5(20)	0.039 1(17)	0.122 1(13)
C(55)	-0.124 4(21)	0.007 4(16)	0.174 4(12)
C(56)	-0.072 0(19)	0.010 9(15)	0.244 5(12)
C(61)	0.360 9(16)	0.371 7(14)	0.276 8(11)
C(62)	0.393 3(16)	0.335 5(14)	0.343 5(11)
C(63)	0.495 4(16)	0.360 7(14)	0.383 4(11)
C(64)	0.565 2(16)	0.422 1(14)	0.356 7(11)
C(65)	0.532 8(16)	0.458 3(14)	0.290 0(11)
C(66)	0.430 7(16)	0.433 1(14)	0.250 0(11)

Table 2. Selected bond lengths and angles with e.s.d.'s in parentheses

(a) Bond lengths (Å)

S-C(51)	1.735(19)	S-N(2)	1.679(16)
C(1)-C(2)	1.55(3)	C(1)-C(11)	1.50(2)
C(1)-N(1)	1.56(2)	C(1)-N(2)	1.49(3)
C(2)-C(3)	1.31(2)	C(2)-C(21)	1.49(2)
C(3)-C(4)	1.51(3)	C(3)-C(31)	1.47(2)
C(4)-C(41)	1.46(2)	C(4)-N(1)	1.27(2)
C(51)-C(52)	1.42(3)	C(51)-C(56)	1.40(3)
C(52)-C(53)	1.40(3)	C(52)-N(3)	1.47(3)
C(53)-C(54)	1.41(3)	C(54)-C(55)	1.37(3)
C(54)-N(4)	1.46(3)	C(55)-C(56)	1.39(3)
N(3)-O(1)	1.20(2)	N(3)-O(2)	1.22(2)
N(4)-O(3)	1.21(3)	N(4)-O(4)	1.22(3)

(b) Bond angles (°)

N(2)-S-C(51)	99.6(0.9)	C(11)-C(1)-C(2)	115.6(1.8)
N(1)-C(1)-C(2)	100.4(1.6)	N(1)-C(1)-C(11)	106.1(1.5)
N(2)-C(1)-C(2)	113.6(1.6)	N(2)-C(1)-C(11)	112.1(1.7)
N(2)-C(1)-N(1)	107.8(1.7)	C(3)-C(2)-C(1)	111.4(1.6)
C(21)-C(2)-C(1)	119.5(1.6)	C(21)-C(2)-C(3)	129.1(1.7)
C(4)-C(3)-C(2)	106.0(1.6)	C(31)-C(3)-C(2)	130.0(1.7)
C(31)-C(3)-C(4)	123.3(1.6)	C(41)-C(4)-C(3)	126.3(1.8)
N(1)-C(4)-C(3)	114.2(1.8)	N(1)-C(4)-C(41)	119.4(1.8)
C(4)-N(1)-C(1)	107.8(1.7)	C(1)-N(2)-S	116.9(1.3)

LTA in glacial acetic acid when the yield of the pyrrole (3) falls almost to zero whereas the yield of (7) is increased. A number of 2*H*-pyrroles have been previously obtained and a characteristic reaction which they undergo on heating is 1,5-sigmatropic rearrangement and regeneration of the aromatic pyrrole ring.^{5,9} When the 2*H*-pyrrole (7) was heated, however, it was converted into the pyrimidine (3) in quantitative yield.

Experimental

Reaction of 2,4-Dinitrobenzenesulphenamide (1) with Tetraphenylpyrrole and LTA.—2,4-Dinitrobenzenesulphenamide (1.2 g, 5.58 mmol) and tetraphenylpyrrole (2.1 g, 5.79 mmol) were stirred in dichloromethane (24 ml) at ambient temperature, powdered LTA (2.5 g, 5.64 mmol) being added over a 10 min period. After a further 30 min, dichloromethane was added, and the mixture filtered and evaporated. The residue was purified by chromatography over Kieselgel (110 g), eluting with light petroleum-dichloromethane (2:1) to give a mixture of two colourless compounds (1.8 g). On fractional crystallisation from dichloromethane-ethanol, 2,4,5,6-tetraphenylpyrimidine (3) was obtained (1.08 g, 48%), m.p. 195–196 °C (lit.,⁷ 195–196 °C) with spectral data identical with those reported. The mother liquors gave unchanged tetraphenylpyrrole (588 mg, 28%).

Further elution with light petroleum-ether (1:1) gave an orange solid (100 mg) which was not identified, followed by a yellow crystalline solid (from dichloromethane-ethanol), m.p. 172–174 °C identified as 2-(2,4-dinitrophenylthioamino)-2,3,4,5-tetraphenyl-2*H*-pyrrole (7) (600 mg, 18%) (Found: C, 70.3; H, 4.3; N, 9.1. C₃₄H₂₄N₄O₄S requires C, 69.85; H, 4.1; N, 9.6%; ν_{\max} 3300w, 3100m, 1600s, and 1520s; δ (CDCl₃) 8.85 (d, *J* 2.5 Hz, Ar 3-H), 8.15 (d, *J* 8 Hz, Ar 6-H), 7.85 (dd, *J* 2.5 and 8.5 Hz, Ar 5-H), 7.7–6.4 (m, 20 × phenyl H), and 4.8 (s, NH).

Crystallographic Studies.—Crystals of the 2-pyrrole (7) were obtained by crystallisation from benzene as the benzene solvate.

Crystal data. C₃₄H₂₃N₄O₄S (+C₆H₆), *M* = 579.6. Space group *P*2₁/*c* *a* = 11.52(1), *b* = 16.10(2), *c* = 18.67(2) Å, β =

95.2(1)°, $U = 3\,477.42\text{ \AA}^3$, $Z = 4$, $F(000) = 1\,380$, $D_c = 1.12\text{ g cm}^{-3}$, $\lambda(\text{Mo-K}\alpha) = 0.7107\text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.99\text{ cm}^{-1}$.

Data collection. Intensity measurements were obtained from a Stadi-2 Stoe diffractometer using monochromatized Mo-K α radiation. Some crystal deterioration occurred during data collection which necessitated the use of two crystals. Integrated relative intensities for 2 703 independent reflexions with $7 < 2\theta < 45^\circ$ were measured by the ω -scan method. After correcting for Lorentz and polarisation effects, scaling and merging, 1 070 reflexions had $I > 3\sigma(I)$.

Structure Solution and Refinement.—The crystal structure was elucidated by direct methods using the EEES option of the SHELX-76¹⁰ suite of programs. Due to the paucity of data, hydrogen atoms were located in calculated positions and the C₆H₅ rings and benzene solvate were refined as rigid groups with D_{6h} symmetry. In the final cycles of least squares refinement, only the sulphur and nitro group atoms were given anisotropic thermal parameters; remaining atoms had isotropic thermal parameters. Refinement converged with $R = 0.099$, $R_w = 0.105$ with $w = 1.787/[\sigma^2(F_o) + 0.006\,59\,F_o^2]$. Final atomic co-ordinates are given in Table 1, and selected bond lengths and angles in Table 2. The following have been treated as a Supplementary Publication: thermal parameters, hydrogen co-ordinates, a full list of non-hydrogen bond lengths and angles, and a list of nearest contact distances; Supp. No. 56286 (11 pp.)*

* For details of the Supplementary Publications scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1. Copies of the structure factors are available on request from the editorial office.

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