Competitive Cyclisation of Singlet and Triplet Nitrenes. Part 6.[1] The Cyclisation of 2-Azidophenyl Thienyl Sulphides

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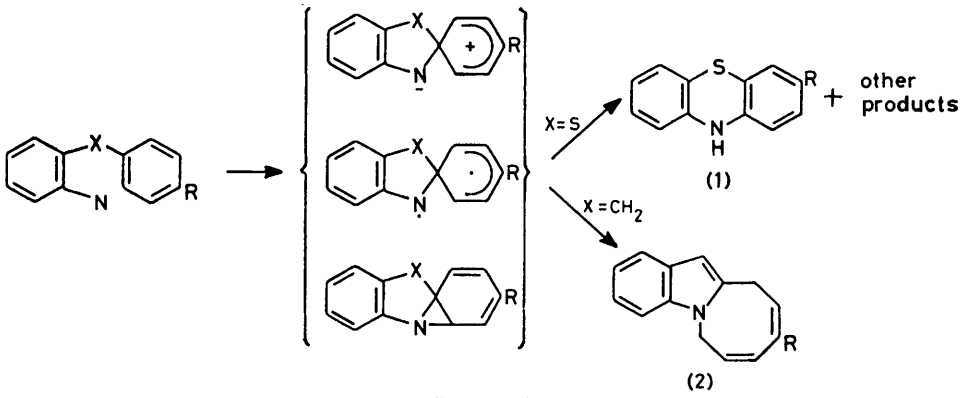
A number of derivatives of the title azides [namely 2-azidophenyl 2-thienyl, 5-methyl-2-thienyl, 3-methyl-2-thienyl, and 3,5-dimethyl-2-thienyl sulphides (5) and 2-azidophenyl 3-thienyl sulphide (6)] have been decomposed thermally and photochemically. The influence of differing solvents and temperatures, of the presence of various dienophiles, of added triethyl phosphite, and of photosensitisation with acetophenone was also studied. Pyrrolo-[2,1-*b*]benzothiazoles were produced in most cases, often in good yield. 2-Azidophenyl 3,5-dimethyl-2-thienyl sulphide gave 2-(3-thienyl)benzothiazole in addition to the pyrrolobenzothiazole. The formation of the products has been rationalised by consideration of a ring-opening–ring-closure mechanism of an intermediate spiro-thieno-benzothiazole, and analogous literature reactions have been reinterpreted in this light.

THE prolific chemistry of aryl *o*-nitrenophenyl sulphides has proved a source of both mechanistic and synthetic diversity, involving ionic or radical spirodienes and/or an azanorcaradiene [2] (Scheme 1) as key intermediates.



SCHEME 1

The corresponding *o*-azidodiphenylmethanes have also been examined yielding, for example, azepinoindoles (2) by a similar pathway.[3] Transformations also resulted from the thermolysis of 2-azidobenzylthiophens which were rationalised by Jones and his co-workers as shown in Scheme 2.[4]

We have investigated a series of 2-azidophenyl thienyl sulphides [5] (5) and (6) as part of our research on singlet

[1] Part 5, J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1977, 2194.

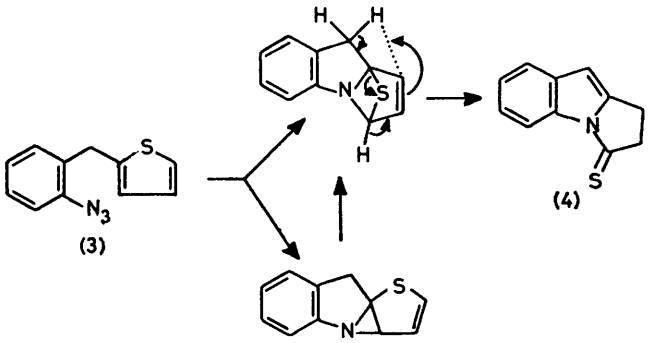
[2] (*a*) J. I. G. Cadogan, *Accounts Chem. Res.*, 1972, **5**, 503; (*b*) *J.C.S. Perkin I*, 1975, 2396; (*c*) I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Research*, 1977, (*S*), 17; (*M*) 0434.

[3] G. R. Cliff, E. W. Collington, and G. Jones, *J. Chem. Soc.* (*C*), 1970, 1490.

[4] G. R. Cliff, G. Jones, and J. McK. Woollard, *J.C.S. Perkin I*, 1974, 2072; *Tetrahedron Letters*, 1973, 2401.

[5] B. Iddon, H. Suschitzky, D. S. Taylor, and K. E. Chippendale, *J.C.S. Perkin I*, 1974, 2500, report that 2-(2-benzo[*b*]-thienylthio)phenyl azide gave only the corresponding amine (22%) on thermolysis in xylene.

and triplet nitrene pathways. Results of both the thermal and photochemical decomposition of the azides

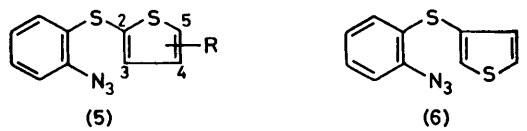


SCHEME 2

(5) and (6) in a variety of solvents and in the presence of sensitisers are summarised in Table 1 and as follows.

(a) In general, pyrrolo[2,1-*b*]benzothiazoles (9) were the major products from the azides (5) (apparently a new ring system) in useful yields.

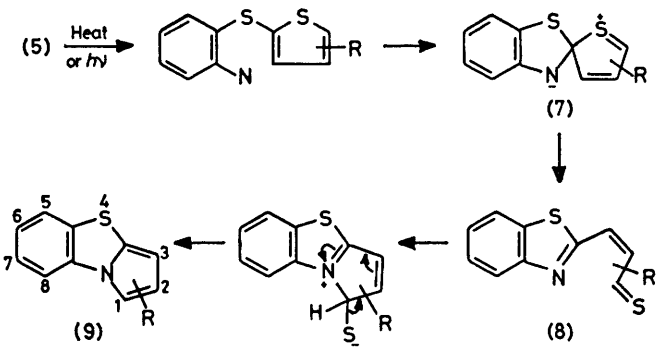
(b) No evidence of attack on an alkyl group was



a; R = H
b; R = 5-Me
c; R = 3-Me
d; R = 3,5-Me_2

observed in the case of (5c) and (5d), unlike the case of 2-(2-azidophenyl)-3-methylthiophen, where this was a major pathway.[1]

We explain the formation of the pyrrolobenzothiazole (9) by attack of the singlet nitrene on the thiophen 2-position to give the spirodiene (7), as in the pheno-



a; R = H
b; R = 1-Me
c; R = 3-Me
d; R = 1,3-Me_2

SCHEME 3

thiazine reaction.[2] However, in the thiophen series this dipolar spiro-species is more readily stabilised by fission of one of the three C-hetero-bonds [*cf.* (7)], yielding in our case, a benzothiazole (8). The unstable thioaldehyde (or ketone) can then eliminate sulphur (in some cases isolated as such) and form the pyrrolobenzothiazole (9). This mechanism, involving cleavage of the thiophen ring is, we believe a better basis for understanding some already well documented reactions. Thus, the action of the highly electrophilic ethoxycarbonylnitrene on thiophen has been argued to involve an unprecedented 1,4-cycloaddition pathway [6] (Scheme 4a). However, a ring-opening–ring-closure process, following electrophilic attack of the nitrene seems more appropriate (Scheme 4b). Furthermore, the formation of the indole (4) from 2-azidobenzylthiophens already mentioned (Scheme 2) seems better explained by analogy with our mechanism rather than the direct or indirect 1,4-cycloaddition route suggested [4] (see Scheme 5).

TABLE 1

Products from thermolysis and photolysis of the azides (5) and (6)

Azide	Decomp. method	Solvent [a]	Temp./°C (time/h)	Products, % Amine	Sulphur	(9)	Purple polymer	Others (%)
(5a)	Δ	$C_6H_3Cl_3$	156 (2)	10	Present		Much	
(6)	Δ	$C_6H_3Cl_3$	156 (2)	3	Present		Much	Azide (6) (20)
(5c)	Δ	$C_6H_3Cl_3$	156 (2)	10	0	63	Little	
(5c)	Δ	$C_6H_3Cl_3$	214 (¼)	3.5	0	63	Little	
(5c)	Δ	PhBr	156 (2)	12.5	0	64.5	Little	
(5b)	Δ	$C_6H_3Cl_3$	214 (2)	8	0	6.5	Much	
(5b)	Δ	C_6H_5Br	156 (¼)	10	0	18.5	Much	
(5b)	*hν*	PhAc	107 (8)	15	0	1.5	Much	
(5b)	*hν*	CH_2Cl_2	20 (24)	13	0	4.5	Much	Azide (3.5)
(5d)	Δ	$C_6H_3Cl_3$	156 (2)	3.5	61.5	68	V. little	(10) (11.5)
(5d)	Δ	$C_6H_3Cl_3$	214 (¼)	3.5	0	5	V. little	(10) (12.5)
(5d)	Δ	PhBr	156 (3)	9	41	74	V. little	(10) (5.5)
(5d)	Δ	$PhCHMe_2$	152 (3)	15.5	0	27	V. little	(10) (14.5)
(5d)	*hν*	PhCl	20 (48)	1	0	19.5	V. little	(10) (16)
(5d)	*hν*	PhAc	20 (40)	6.5	0	0	V. little	(10) (4.5)
(5d)	*hν*	PhAc	107 (8)	11	0	16.5	V. little	(10) (13)

[a] A 2% solution was used in thermolyses and a 1% solution in photolyses.

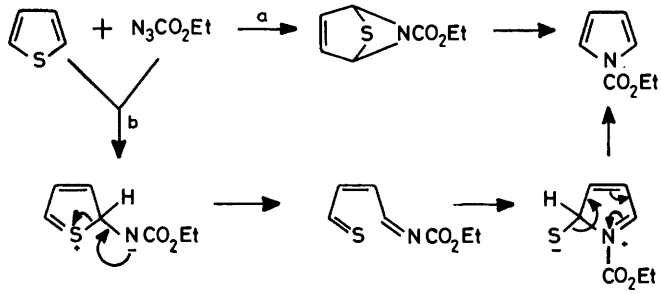
(c) The parent systems (5a) and (6), in particular, gave mainly purple polymers on thermolysis in trichlorobenzene with only traces of amines.

(d) No thiophen analogues of the phenothiazines (1) were found in any of the cases studied.

(e) Sulphur was also isolated.

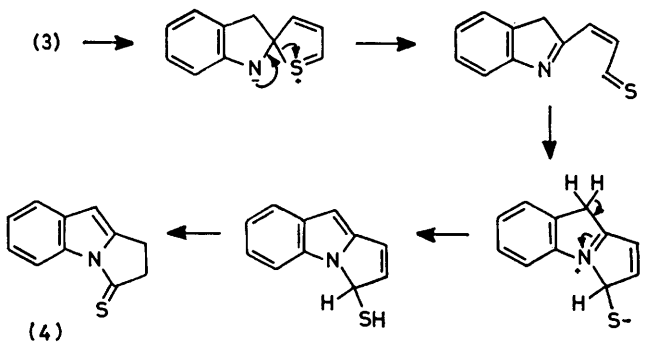
[6] K. Hafner and W. Kaiser, *Tetrahedron Letters*, 1964, 2185.

An alternative pathway is available for the unstable αβ-unsaturated thiones (8) when the 2-azidophenyl 3,5-dimethylthienyl sulphide (5d) is decomposed (Scheme 6).



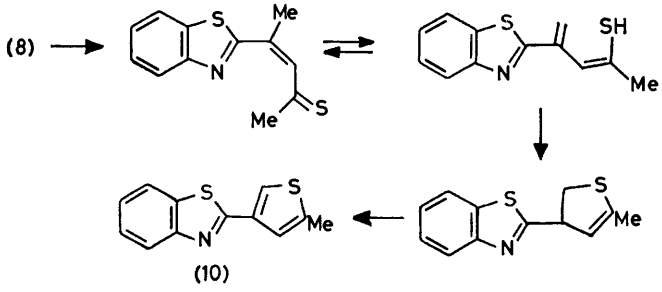
SCHEME 4

Thus, tautomerism of the thione to a dienethiol followed by cyclisation to a dihydrothiophen and subsequent dehydrogenation (possibly by the nitrene [1]) gives the



SCHEME 5

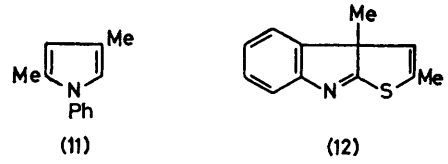
2-(3-thienyl)benzothiophen (10). The fact that this type of product did not arise from the 3-methylthiophen (5c) probably is due to the greater instability of the αβ-unsaturated thioaldehyde intermediate required.



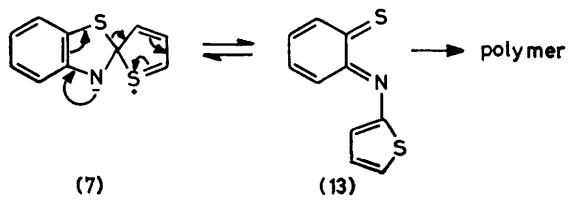
SCHEME 6

The structure of the two types of products from the azides follows from their spectral and other characteristics (see Experimental section). In particular, desulphurisation of the pyrrolobenzothiazole (9d) gave the known [7] (relatively unstable) 2,4-dimethyl-1-phenylpyrrole (11), eliminating isomeric structures such as the thienoindole (12), expected if a Smiles-type rearrangement had occurred followed by sulphur extrusion.[8] The structure of the 2-(3-thienyl)benzothiazole (10) was further confirmed by comparison of its u.v. and ^{13}C n.m.r. spectrum with those of 2-(3-thienyl)benzothiazole, prepared by a literature method.

Surprisingly, the parent thiophens (5a) and (6) which rapidly become purple in daylight, gave only purple polymers and traces of amines on thermolysis. Indeed, good yields of products were obtained only from the systems in which a 3-methyl group was present. By analogy with known reactions in the 2-azidophenyl phenyl sulphide series,[2b,9] it is possible that alternative stabilisation is followed for the spirodiene intermediates (7) in the absence of a 3-thienyl substituent (*e.g.* Scheme



7). This process yields *o*-quinonoid intermediates [*e.g.* (13)], analogues of which are known to polymerise.[10] Since these systems and the previously described intermediates [*e.g.* (8)] are heterodienes we considered the possibility of trapping them with dienophiles. The azides (5a) and (6) were thus decomposed in diethyl



SCHEME 7

maleate and in benzofuran solution (an electron-rich diene) as well as in the presence of *N*-phenylmaleimide

TABLE 2

Attempted trapping experiments, using dienophiles or triethyl phosphite, during thermolysis of the azides (5a) and (6)

		Product(s), %		
Azide [a]	Solvent and additive	Amine	Polymer	Others [%]
(5a)	$C_6H_3Cl_3$	10	(0.49 g)	
(5a)	$C_6H_3Cl_3$ + *N*-phenylmaleimide	1	(0.48 g)	
(5a)	Diethyl maleate	2.5		(14) [2.5]
(5a)	Benzofuran	11	(0.58 g)	(9a) [23]
(5a)	$C_6H_3Cl_3$ + $P(OEt)_3$ (2 mol)			(16) [100]
(6)	$C_6H_3Cl_3$	3	(0.65 g)	(6) [20]
(6)	$C_6H_3Cl_3$ + $P(OEt)_3$ (2 mol)			(16) [100]

[a] The azide (1.0 g) as a 2% solution was thermolysed at 156° for 2 h.

or of triethyl phosphite. The results (Table 2) are disappointing in terms of trapping but none the less of

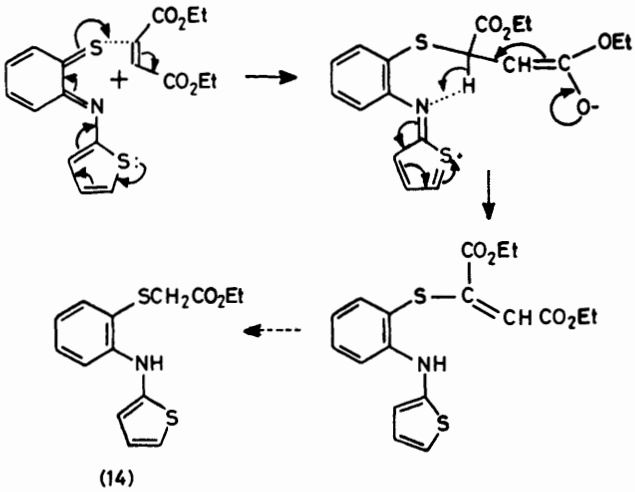
[7] B. Helferich, R. Dhein, K. Geist, H. Jünger, and D. Wiehle, *Annalen*, 1961, **646**, 45.

[8] See ref. 2*b* for an analogy.

[9] J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim, and B. S. Tait, *J.C.S. Perkin I*, 1975, 2376.

[10] D. C. Dittmer, P. L.-F. Chang, F. A. Davis, M. Iwanami, I. K. Stamos, and K. Takahashi, *J. Org. Chem.*, 1972, **37**, 1111.

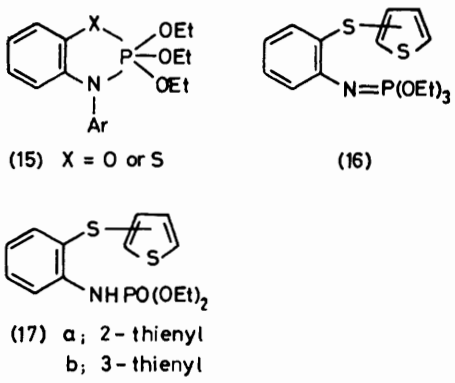
interest. Although *N*-phenylmaleimide proved of little effect, use of diethyl maleate gave a low yield of a compound to which we ascribe the structure (14) on the basis of its spectral characteristics. Thus, the i.r. spectrum showed a non-hydrogen bonded NH absorption (3 370 cm^{-1}) and an aliphatic ester absorption (1 730 cm^{-1}) while the ^1H n.m.r. spectrum revealed an ethoxy group, a singlet methylene absorption (τ 6.10), an NH signal (τ 4.45), and the characteristic high-field signals of an α-substituted thiophen ring. The mass spectrum gave an appropriate molecular ion with losses of CO_2Et and a thiophen ring supported by metastable peaks and accurate mass measurement. A partial explanation for the formation of this system is given in Scheme 8, although the mechanism of the reductive cleavage is unclear. Nevertheless, the formation of this product, in which the thienyl group manifestly has migrated from S to N, lends some support to spirodiene formation followed by breakage of an S–C bond as depicted in Scheme 8.



SCHEME 8

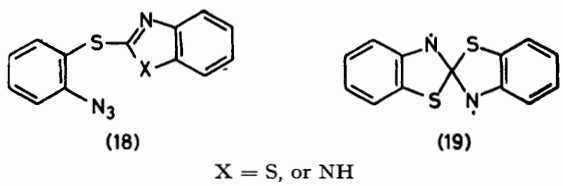
Surprisingly, while benzofuran proved ineffective as a dienophile, it did influence the delicate balance of mechanisms so as to allow formation of the parent pyrrolobenzothiazole (9a) in 23% yield, as well as increasing the yield of the purple polymer.

Ramirez and his co-workers showed that *o*-quinones and related systems gave dioxaphospholes with trialkyl phosphites.[11] Another group isolated related oxazaphospholes [9] and showed the intermediacy of thiazaphospholes,[2b] [*e.g.* (15)] in the reactions of triethyl phosphite with 2-nitrophenyl aryl ethers and sulphides, formed *via* heterodienes analogous to (13). We thus thermolysed the azides (5a) and (6) with triethyl phosphite in trichlorobenzene solution. However, in both cases the colourless reaction mixture yielded quantitatively the corresponding phosphorimidates (16), which on column chromatography gave the phosphoramidates (17) together with some of the parent amine and triethyl phosphate, confirming that no thiazaphosphole had formed. The phosphorimidate formation is probably a reaction of the azide rather than the free nitrene, since



no intramolecular products were isolated and the reaction was extremely clean.[12]

Finally, we have examined the decomposition of some related, π-deficient five-membered analogues (18) of the azidophenyl thienyl azides.



X = S, or NH

The benzothiazole (18; X = S) should be of interest because the possible formation of a degenerate spiro-intermediate such as (19) if the reactions follow related mechanisms. However, as already noted [2b] the π-deficient analogues are disappointing substrates, the above systems giving only the corresponding amines (18; NH_2 in place of N_3) on thermolysis. We have already shown that 2-(2-azidophenyl)-1-methyl-benzimidazole or -benzothiazole can readily undergo attack at the ring nitrogen [13] (or the *N*-methyl group) but once more the reluctance of nitrenes to form six-membered rings would seem to rule out this process with the sulphides (18).

EXPERIMENTAL

The spectroscopic and general experimental conditions are as described in Part 5.[1]

The following compounds were prepared by literature methods: 2-bromothiophen,[14] 3-bromothiophen,[15] 2-aminophenyl 2- and 3-thienyl sulphides,[16] and 2-bromo-3-methylthiophen.[17] Thiophen, and its 2- and 3-methyl and

[11] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, 1963, **85**, 3056.

[12] *Cf.* P. A. S. Smith in 'Nitrenes,' ed. L. Lwowski, Interscience, New York, 1970, p. 113.

[13] I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 929.

[14] H. D. Hartough, 'The Chemistry of Heterocyclic Compounds, Thiophene and its Derivatives,' ed. A. Weissberger, Interscience, New York, 1952, 498.

[15] S. Gronowitz and T. Raznikiewicz, *Org. Synth.*, 1973, Coll. Vol. V, 149.

[16] W. Schindler and A. Zuest, Ger. P. 1,811,824 (1969) (*Chem. Abs.*, 1969, **71**, 81450n).

[17] S. Gronowitz, N. Gjos, R. Kellogg, and H. Wynberg, *J. Org. Chem.*, 1967, **32**, 463.

TABLE 3

Properties of the products from decomposition of the azides (5) and (6)

Product	M.p./°C (from light petroleum)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\lambda_{max.}$(EtOH)/ nm (log ε)	^{1}H N.m.r. τ($CDCl_3$)	^{13} N.m.r. ($CDCl_3$) δ($CDCl_3$)/ p.p.m
(9a)	57—58.5				$C_{10}H_7NS$ [a]				221sh (3.909) 228 (3.953) 248 (4.079) 309 (3.532)	2.5—3.1 (m, 3, 5-, 6-, 7-, 8-H), 3.47 (t, *J* 3.5 Hz, 2-H), 3.79 (dd, J 3.5 and 1 Hz, 1-H)	>C- 127.63, 131.64, 134.66 >CH- 98.82, 110.16, 111.53, 114.75, 123.54, 123.81, 125.30
(9b)	Oil				$C_{11}H_9NS$ [b]				220sh (3.966) 232 (4.027) 249 (3.982) 309 (3.430)	2.1—3.05 (m, 5, 6-, 7-, 8-H), 3.6—3.95 (m, 2-, 3-H), 7.35 (s, Me)	>C- 123.33, 126.16, 132.10 136.02 >CH- 97.66, 112.39, 122.85, 123.71, 124.99 CH_3 14.25
(9c)	110.5—111.5	70.65	5.17	7.48	$C_{11}H_9NS$	70.56	4.85	7.48	220 (3.941) 251 (4.053) 317 (3.434)	2.05—2.95 (m, 3-, 5-, 6-, 7-, 8-H), 3.55 (d, *J* 3.5 Hz, 2-H), 7.80 (s, Me)	>C- 108.57 123.13, 131.53, 135.14 >CH- 109.73, 111.21, 115.90, 123.91, 125.28 CH_3 11.60
(9d)	67.5—68	71.61	5.51	6.96	$C_{12}H_{11}NS$	71.91	5.65	6.98	225 (3.785) 251 (3.826) 313 (3.243)	2.31—3.00 (m, 5-, 6-, 7-, 8-H), 3.97 (s, 2-H), 7.36 (s, 1-Me), 7.87 (3-Me)	>C- 107.40, 122.92, 132.21, 136.61 >CH- 112.19, 115.03, 122.46, 123.81, 124.98 CH_3 11.44, 14.04
(10)	78.5—79.5	62.17	3.91	5.92	$C_{12}H_9NS_2$	62.30	3.92	6.06	226.5 (4.325) 247 (4.006) 256 (3.886) 301.5 (4.245)	1.97—2.72 (m, (6 H) 7.47 (s, Me)	>C- 162.80, 153.82, 141.22, 135.56, 134.58 >CH- 126.16, 124.90, 124.53, 124.03, 122.86, CH_3 15.16
(14)	Oil [c]				$C_{14}H_{15}NO_2S_2$ [c]					2.52—3.61 (m, 7 H), 4.45br (NH), 5.79 (q, CH_2O), 6.10 (s, CH_2), 8.73 (t, Me)	
(16a)	Oil [d]									2.5—3.4 (m, 7 H), 5.80 (q, 3 × CH_2), 8.71 (t, (3 × Me)	
(16b)	Oil [d]									2.6—3.5 (m, 7 H), 5.88 (q, 3 × CH_2), 8.75 (t, 3 × Me)	

[a] M^+, found: *m/e* 173.0298; calc.: 173.0299. [b] M^+, found: *m/e* 187.0438; calc.: 187.0456. [c] I.r. (liquid film) 3 370 (NH) and 1 730 cm^{-1} (CO); *m/e* 293 (M^+, 80%), 220 (M^+ — CO_2Et, 100), 136 (100), 109 (46), 97 (20), and 71 (26); M^+ 293.0547; Calc.: 293,0544. [d] I.r. (liquid film) 1 165 and 970 cm^{-1} (POEt).

2,4-dimethyl derivatives were kindly supplied by Croda Synthetic Chemicals Limited, Four Ashes, Nr. Wolverhampton. (Full spectroscopic details of the intermediates are recorded in the Ph.D. thesis of J. M. Lindley, University

of Salford, 1977.) Light petroleum refers to the fraction of b.p. 40—60°.

3,5-Dimethyl-2-thienyl 2-Nitrophenyl Sulphide.—To a solution of 2,4-dimethylthiophen (11.2 g, 0.1 mol) in dry diethyl ether (50 ml) at ambient temperature under nitrogen was added n-butyl-lithium (0.1 mol) in hexane (from Pfizer, Sandwich, Kent). The resulting solution was stirred for 0.5 h, when sulphur (3.2 g, 0.1 mol) was added. The suspension was stirred for 1 h when ethanol (50 ml) was added and the ether removed by distillation. To the residual solution was added 2-chloronitrobenzene (15.75 g, 0.1 mol) in ethanol (10 ml) and the mixture was boiled under reflux for 3 h. After addition of water (50 ml) and ether extraction (3 × 50 ml), evaporation of the dried ($MgSO_4$) extracts gave a brown oil which was chromatographed on alumina. Elution with light petroleum–diethyl ether (9 : 1) yielded the *3,5-dimethyl-2-thienyl 2-nitrophenyl sulphide* (7.9 g, 30%) as yellow crystals from light petroleum–chloroform, m.p. 121.5—123° (Found: C, 54.3; H, 4.2; N, 5.3. $C_{12}H_{11}NO_2S_2$ requires C, 54.3; H, 4.2; N, 5.3%).

In a similar manner from 2-methylthiophen was obtained *5-methyl-2-thienyl 2-nitrophenyl sulphide* (33%), as yellow crystals from light petroleum, m.p. 103—104° (Found: C, 52.7; H, 3.6; N, 5.5. $C_{11}H_9NO_2S_2$ requires C, 52.6; H, 3.6; N, 5.6%).

3-Methyl-2-thienyl 2-Nitrophenyl Sulphide.—To a stirred solution of 2-bromo-3-methylthiophen (17.7 g, 0.1 mol) in dry ether (50 ml) at −78° under nitrogen, was added n-butyl-lithium (0.1 mol) in hexane. To this solution was added sulphur (3.2 g, 0.1 mol) and the suspension stirred for 10 min at −78° and then allowed to warm to ambient temperature. Addition of water (20 ml) and extraction of the aqueous phase with further ether, gave, on evaporation of the dried ($MgSO_4$) extracts crude 3-methylthiophen-2-thiol. The crude thiol in ethanol (20 ml) was added to a solution of sodium (2.3 g, 0.1 mol) in ethanol (30 ml). To this solution was added 2-chloronitrobenzene (15.75 g, 0.1 mol) in ethanol (10 ml) and the mixture boiled for 5 h. After cooling and addition of water (100 ml), the mixture was ether extracted (3 × 50 ml) and the combined extracts were evaporated after drying ($MgSO_4$) to yield a brown oil purified as above, giving *3-methyl-2-thienyl 2-nitrophenyl sulphide* (9.7 g, 38.5%) as yellow crystals from light petroleum, m.p. 102.5—104° (Found: C, 52.6; H, 3.8; N, 5.55. $C_{11}H_9NO_2S_2$ requires C, 52.5; H, 3.6; N, 5.6%).

Reduction of the Nitrophenyl Thienyl Sulphides.—The nitro-compound (0.02 mol) in ethanol (50 ml), together with reduced iron (5.3 g), ammonium chloride (5.3 g), and water (100 ml) was heated under reflux for 4 h. The hot solution was filtered, the residue washed with ether, and the washings were used to extract the cooled filtrate, which after further extraction gave, on evaporation of the dried ($MgSO_4$) extracts, an oil which was distilled in a Kugelrohr apparatus. By this means was obtained: (a) *2-aminophenyl 3,5-dimethyl-2-thienyl sulphide* (93.5%), b.p. 144° at 0.07 mmHg (Found: C, 61.6; H, 5.7; N, 6.05. $C_{12}H_{13}NS_2$ requires C, 61.2; H, 5.6; N, 6.0%); (b) *2-aminophenyl 5-methyl-2-thienyl sulphide* (74%), b.p. 146° at 0.2 mmHg (Found: C, 59.4; H, 5.2; N, 6.4. $C_{11}H_{11}NS_2$ requires C, 59.7; H, 5.0; N, 6.3%); (c) *2-aminophenyl 3-methyl-2-thienyl sulphide* (92%), b.p. 140° at 0.2 mmHg (Found: C, 59.4; H, 5.15; N, 6.3. $C_{11}H_{11}NS_2$ requires C, 59.7; H, 5.0; N, 6.3%).

Preparation of the 2-Azidophenyl Thienyl Sulphides.—The foregoing amines (0.05 mol) in a mixture of concentrated hydrochloric acid (20 ml) and water (20 ml) was cooled to 0° and diazotised with sodium nitrite (4.8 g, 0.07 mol) in water (30 ml). After 10 min this solution was added dropwise to a solution of sodium azide (6.5 g, 0.1 mol) in saturated aqueous sodium acetate (50 ml). After 1 h the suspension was extracted with ether (3 × 100 ml) and the combined extracts were washed with sodium hydrogen carbonate solution (2 × 50 ml; 5%), then water, and then dried ($MgSO_4$). The residual oil on evaporation was chromatographed on alumina, elution with light petroleum yielding the azides as pale yellow crystals or oils. The following azides, which all darkened in light, particularly rapidly when unsubstituted in the thienyl ring, were obtained: (a) *2-azidophenyl 2-thienyl sulphide* (5a) (75.5%), oil, decomp. 127° (Found: M^+, 233.009 0. $C_{10}H_7N_3S_2$ requires M^+, 233.008 2); (b) *2-azidophenyl 3-thienyl sulphide* (6) (79%), oil, decomp. 122° (Found: M^+, 233.008 2. $C_{10}H_7N_3S_2$ requires M^+, 233.008 2); (c) *2-azidophenyl 3-methyl-2-thienyl sulphide* (5c) (61.5%), m.p. 55—56° (from light petroleum), decomp. 142° (Found: C, 52.95; H, 3.75; N, 17.45. $C_{11}H_9N_3S_2$ requires C, 53.42; H, 3.67; N, 16.99%); (d) *2-azidophenyl 5-methyl-2-thienyl sulphide* (5b) (81%), m.p. 59.5—60° (from light petroleum), decomp. 140° (Found: C, 53.4; H, 3.8; N, 17.55. $C_{11}H_9N_3S_2$ requires C, 53.4; H, 3.7; N, 17.00%); (e) *2-azidophenyl 3,5-dimethyl-2-thienyl sulphide* (5d) (77.5%), m.p. 48.5—49.5° (from light petroleum), decomp. 135° (Found: C, 55.0; H, 4.2; N, 16.5. $C_{12}H_{11}N_3S_2$ requires C, 55.1; H, 4.2; N, 6.1%).

Thermolysis and Photolysis of the Azides.—The methods described previously [1] and the same work-up procedures were employed giving brown residues which were chromatographed on alumina, using firstly light petroleum (which removed sulphur and any unchanged azide) and later increasing proportions fo diethyl ether giving the products recorded in Tables 1—3.

Desulphurisation of 1,3-Dimethylpyrrolo[2,1-b]benzothiazole.—A mixture of the title compound (1.0 g) and freshly prepared Raney nickel (25 g) was heated under reflux in toluene (50 ml) for 1 h, when the inorganic matter was filtered off and washed with toluene and the filtrate evaporated. The residue was eluted through alumina with light petroleum to give 2,4-dimethyl-1-phenylpyrrole (0.48 g, 56%), b.p. 66—75° at 0.1 mmHg (lit.,[7] b.p. 64—73° at 0.1 mmHg); i.r. (liquid film) 755 and 700 cm^{-1} (Ph); ^1H n.m.r. ($CDCl_3$) τ 2.9 (m, Ph), 3.61 (s, pyrrole 5-CH), 4.29 (s, pyrrole 3-CH), and 7.95 (s, 2 × Me); ^{13}C n.m.r. ($CDCl_3$) δ 140.80 (C-1 of Ph), 1.32.13 (C-2 of pyrrole), 128.99 (C-2 and -6 of Ph), 126.44 (C-4 of Ph), 125.57 (C-3 and -5 of Ph), 119.13 (C-5 of pyrrole), 118.73 (C-4 of pyrrole), 110.43 (C-3 of pyrrole), and 12.86 and 11.89 p.p.m. (2 × Me). The compound gave the characteristic red colour with a pine splint dipped firstly in concentrated hydrochloric acid.

2-(3-Thienyl)benzothiazole.[18]—The method employed by Hein and his co-workers [19] to prepare the 2-thienyl analogue was used employing 3-thenoic acid in place of the 2-isomer, giving 2-(3-thienyl)benzothiazole (90%) as white crystals from light petroleum, m.p. 111.5—112.5°. (No data are recorded [18] for this compound.) (Found: C, 60.7; H, 3.3; N, 6.4. $C_{11}H_7NS_2$ requires C, 60.8; H, 3.25; N, 6.45%); u.v. $\lambda_{max.}$ (MeOH) 215sh (log ε 4.255), 225 (4.301), 246sh (3.931), 256 (3.854), and 299 (4.212) nm; ^1H n.m.r. ($CDCl_3$) τ 1.7—2.95 (m); ^{13}C n.m.r. ($CDCl_3$) δ 162.33, 153.82, 135.94,

[18] C. Vernin, J. Metzger, and C. Parkanyi, *J. Org. Chem.*, 1975, **40**, 3183.

[19] D. W. Hein, R. J. Alheim, and J. J. Leavitt, *J. Amer. Chem. Soc.*, 1957, **79**, 427.

and 134.67 (⩾C–); 126.48 (2c); 126.07, 125.89, 124.91, 122.96, and 121.37 (⩾CH–) p.p.m.

Hydrolysis of the Phosphorimidates (16).—The phosphorimidates (16a) and (16b) were adsorbed on to alumina and eluted through a column of alumina with light petroleum admixed with diethyl ether giving firstly 2-aminophenyl thienyl sulphide [49.5% from the 2-thienyl and 40.5% from the 3-thienyl derivatives (16a) and (16b), respectively] followed by a mixture of triethyl phosphate and the phosphoramidates (17). These two mixtures were each separated by distillation giving (a) *diethyl* N-[2-(2-*thienylthio*)*phenyl*]*phosphoramidate* (17a) (34%), b.p. 186° at 0.2 mmHg, m.p. 68—70° (Found: C, 48.5; H, 5.0; N, 3.9. $C_{14}H_{18}NO_3PS$ requires C, 49.0; H, 5.3; N, 4.1%); i.r. (Nujol) 3 100 (NH), 1 245, 1 230 (P=O), 1 160, and 975 cm^{-1} (POEt); ^1H n.m.r. ($CDCl_3$) τ 2.45—2.95 (m, 5 H), 3.0—3.25 (m, 2 H), 3.68br (d, NH, *J ca.* 9 Hz, coupling to P), 6.00 (q, 2 × CH_2), and 8.82 (t, 2 × Me); *m/e* 343 (M^+, 24%), 207 (24), 173 (100), 172 (44), 109 (32), 91 (20), 81 (63), and 71 (36); M^+ *m/e* 343.046 5 (Calc.: 343.046 5) together with triethyl phosphate (20.5%); (b) *diethyl* N-[2-(3-*thienylthio*)*phenyl*]*phosphoramidate* (17b) (59%), b.p. 210° at 0.3 mmHg (Found: C, 48.8; H, 5.35; N, 3.8. $C_{14}H_{18}NO_3PS_2$ requires C, 49.0; H, 5.3; N, 4.1%); i.r. (liquid film) 3 340, 3 200 (NH), 1 260 (P=O), 1 165, and 970 cm^{-1}, (POEt); ^1H n.m.r. ($CDCl_3$) τ 2.4—3.5 (m, 7 H), 3.72br (d, NH, *J ca.* 9 Hz, coupling to P), 6.01 (q, 2 × CH_2), and 8.79 (t, 2 × Me); *m/e* 343 (M^+, 100%), 207 (27), 173 (24), and 172 (30); M^+ *m/e* 343.045 8 (Calc: 343.046 5), together with triethyl phosphate (38.5%).

Benzimidazol-2-yl 2-Nitrophenyl Sulphide and Benzothiazol-2-yl 2-Nitrophenyl Sulphide.—Sodium hydride (2.4 g, 0.1 mol) was added to a stirred solution of either benzimidazole-2-thiol (15.0 g, 0.1 mol) or benzothiazole-2-thiol (16.7 g, 0.1 mol) in dimethyl sulphoxide (50 ml). After 15 min, 2-chloronitrobenzene (15.75 g, 0.1 mol) was added and the mixture heated at 100° for 20 h. The mixture was poured into water (500 ml), and the filtered precipitate recrystallised from aqueous acetic acid to give benzimidazol-2-yl 2-nitrophenyl sulphide (18.7 g, 69%) as yellow crystals, m.p. 210—214° (lit.,[20] m.p. 213—215°) or benzothiazol-2-yl 2-nitrophenyl sulphide (23.6 g, 83.5%), as pale yellow needles, m.p. 109—110° (lit.,[20] m.p. 109—111°).

Reduction of the Nitrophenyl Sulphides.—The foregoing nitro-compounds were reduced by the method utilised for the nitrophenyl thienyl sulphides giving: (a) *2-aminophenyl benzimidazol-2-yl sulphide* (89%) as pale yellow crystals from aqueous ethanol, m.p. 271.5—273° (Found: C, 64.4; H, 4.9; N, 17.4. $C_{13}H_{11}N_3S$ requires C, 64.7; H, 4.6; N, 17.4%) and (b) *2-aminophenyl benzothiazol-2-yl sulphide* (73%) as white plates from chloroform–light petroleum, m.p. 100.5—101.5° (Found: C, 60.2; H, 4.0; N, 11.1. $C_{13}H_{10}N_2S_2$ requires C, 60.4; H, 3.9; N, 10.8%).

2-Azidophenyl Benzimidazol-2-yl Sulphide (18; X = NH) *and 2-Azidophenyl Benzothiazol-2-yl Sulphide* (18; X = S).—The foregoing amines (0.02 mol) in a mixture of concentrated hydrochloric acid (20 ml), water (10 ml), and acetic acid (20 ml) were diazotised at 0—5° with a solution of sodium nitrite (1.4 g, 0.02 mol) in water (10 ml). After 10 min the diazonium solution was added dropwise to a solution of sodium azide (1.5 g) in saturated aqueous sodium acetate (50 ml). The benzimidazole gave the azide as a solid which was filtered, washed with water and dried in a vacuum desiccator (P_2O_5). Crystallisation from aqueous ethanol gave the pure *azide* (18; X = NH) as white needles, m.p. 198.5—200.5° (4.8 g, 90%) (Found: C, 58.3; H, 3.6; N, 26.2. $C_{13}H_9N_5S$ requires C, 58.4; H, 3.4; N, 26.2%); i.r. (Nujol) 2 140 and 2 100 cm^{-1} (N_3). *2-Azidophenyl benzothiazol-2-yl sulphide* (18; X = S) was deposited as an oil which after extraction (CH_2Cl_2) and drying gave an oil, purified by elution through alumina with light petroleum (16%), decomp. 115°; M^+, *m/e* 284.019 2 ($C_{13}H_8N_4S_2$ requires 284.019 7); i.r. (liquid film) 2 140 and 2 100 cm^{-1} (N_3).

Thermolysis of the Azides (18).—The foregoing azides (18) were separately thermolysed by the general method referred to above, as 2% solutions in 1,2,4-trichlorobenzene at 156° for 2 h, when after the usual work-up the residues were chromatographed on alumina. From the benzimidazole by elution with chloroform, 2-aminophenyl benzimidazol-2-yl sulphide (60%) was isolated while the corresponding amine (14.5%) was the sole product recovered from the benzothiazole.

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[20] J. J. D'Amico, Belg. P. 670,434 (1966) (*Chem. Abs.*, 1966, **65**, 15383e).