Condensed Thiophen Ring Systems. Part X.[1] Synthesis and Reactions of 2-Aryl-1*H*-[1]benzothieno[2,3-*b*]pyrroles and 2-Aryl-1*H*-[1]benzothieno[3,2-*b*]pyrroles [2]

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Reductive cyclisation of a *trans*-1-aryl-2-(3-nitro-2-benzo[*b*]thienyl)- or a *trans*-1-aryl-2-(2-nitro-3-benzo[*b*]-thienyl)-ethene, respectively, with triethyl phosphite gave the title compounds. The *trans*-alkenes were prepared by the Wittig reaction from 3-nitrobenzo[*b*]thiophen-2-carbaldehyde or 2-nitrobenzo[*b*]thiophen-3-carbaldehyde, respectively. Improved methods for the preparation of these aldehydes are reported, together with some electrophilic substitution reactions of 2-phenyl-1*H*-[1]benzothieno[3,2-*b*]pyrrole.

REDUCTIVE cyclisation of *cis*- or *trans*-*o*-nitrostilbene or α-nitrostilbene with triethyl phosphite yields 2-phenylindole.[3,4] β-Substituted *o*-nitrostyrenes similarly give the corresponding 2-substituted indoles.[3-6] Indoles may be prepared also by thermal decompositions of *o*-[6,7] or β-azidostyrenes,[8,9] which proceed *via* the intermediacy of a nitrene.[6] Cyclisation of the nitro-compounds may or may not involve a nitrene intermediate.[3-6,10,11]

We now report that the 2-aryl-1*H*-[1]benzothieno-[3,2-*b*]pyrroles (1; R = H, Me, or Cl) and the 2-aryl-1*H*-[1]benzothieno[2,3-*b*]pyrroles (2; R = H, Me, or Cl) may be prepared in yields of 65—80% by reductive cyclisation of the 1-aryl-2-(3-nitro-2-benzo[*b*]thienyl)-ethenes (3; R = H, Me, or Cl) or the 1-aryl-2-(2-nitro-3-benzo[*b*]thienyl)ethenes (4; R = H, Me, or Cl), respectively, with a large excess [5] of triethyl phosphite. The 3-proton of the benzothienopyrroles (1) and (2) gave rise to a doublet in the n.m.r. spectrum at τ 2·95—3·25 ($J_{1,3}$ 1·5—2·0 Hz), collapsing to a singlet on *N*-deuteriation.

1*H*-[1]Benzothieno[3,2-*b*]pyrrole has been prepared

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[2] Presented at the Annual Meeting of The Chemical Society (Heterocyclic Section), Manchester, 10–14 April, 1972, abstract no. 9.9.
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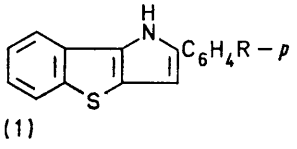
by reductive cyclisation of 3-nitro-2-(β-nitrovinyl)-benzo[*b*]thiophen,[12,13] and by reductive cyclisation of β-(3-nitro-2-benzo[*b*]thienyl)pyruvic acid followed by decarboxylation of the resulting 2-carboxylic acid.[13] It is substituted by electrophiles in the 2-position [14,15] as predicted by molecular orbital calculations.[15] As far as we are aware, compound (5) is the only derivative of 1*H*-[1]benzothieno[2,3-*b*]pyrrole reported. It may be prepared by treatment of the tin double salt of 3-aminobenzo[*b*]thiophen with methyl 1-hydroxy-1-methylethyl ketone in ethanol in the presence of anhydrous zinc chloride.[16] Compound (6) may be prepared similarly.[16]

Successive treatment of an ethereal solution of benzyltriphenylphosphonium chloride with n-butyl-lithium and 3-nitrobenzo[*b*]thiophen-2-carbaldehyde gave *trans*-1-(3-nitro-2-benzo[*b*]thienyl)-2-phenylethene (3; R = H) (27%). The yield of this alkene was increased to 68% by using tetrahydrofuran as solvent. The *trans*-alkenes (3; R = Me or Cl) and (4; R = H, Me, or Cl) were prepared similarly in tetrahydrofuran (50—70% yields). We did not isolate any of the *cis*-isomers of compounds (3) and (4) (R = H, Me, or Cl), presumably because formation of these compounds is sterically hindered by the presence of a bulky nitro-group in the nitro-aldehyde starting materials. The *trans* stereochemistry of compounds (3) and (4) was indicated by strong i.r. absorption near 960 cm^{-1} and by a coupling of 16·0 Hz between the two vinyl protons (*cf.* ref. 5).

3-Nitrobenzo[*b*]thiophen-2-carbaldehyde was prepared by acidic hydrolysis of the anil (7). The latter was obtained by treatment of 2-benzo[*b*]thienyl-lithium with dimethyl sulphate followed by nitration and condensation of the resulting 2-methyl-3-nitrobenzo[*b*]thiophen with *p*-nitroso-*NN*-dimethylaniline. Our procedure allows the aldehyde to be prepared in 57% overall yield from benzo[*b*]thiophen whereas that described by Shkurko and Mamaev [17] gives the aldehyde in only 15% yield from 2-hydroxymethylbenzo[*b*]thiophen. Nitration of benzo[*b*]thiophen-2-carbaldehyde gives a mixture of isomers.[18]

2-Nitrobenzo[*b*]thiophen-3-carbaldehyde was prepared similarly from benzo[*b*]thiophen *via* 3-methylbenzo[*b*]-thiophen. The low overall yield (9%) in this case can be attributed in part to the fact that the methyl group in 3-methyl-2-nitrobenzo[*b*]thiophen is less active towards condensation with *p*-nitroso-*NN*-dimethylaniline than that in its 2-methyl-3-nitro-isomer, and in part to the low yield of 3-methyl-2-nitrobenzo[*b*]thiophen obtained by nitration of 3-methylbenzo[*b*]thiophen.[19] Nitration of benzo[*b*]thiophen-3-carbaldehyde with fuming nitric acid in a mixture of acetic acid and acetic anhydride is reported [20] to give 2-nitrobenzo[*b*]thiophen-3-carbaldehyde, but using this method we obtained only a mixture of nitro-isomers in agreement with others.[21]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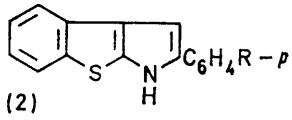
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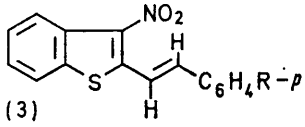
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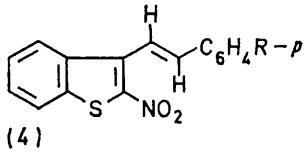
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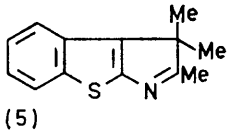
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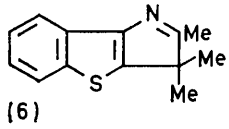
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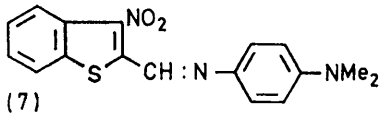
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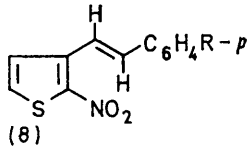
(8)

Since the completion of our work, Srinivasan *et al.*[22] have reported that 2-nitro-3-methylthiophen condenses with benzaldehyde and *p*-anisaldehyde to give the *trans*-alkenes (8; R = H or OMe, respectively). An extension of this reaction to the present work would possibly allow the *trans*-alkenes (4) to be prepared more conveniently.

Since 2-phenyl-1*H*-[1]benzothieno[3,2-*b*]pyrrole (1; R = H) was the most accessible compound, we studied its chemistry briefly. This compound is unstable in the presence of strong acids. Its attempted bromination with bromine in chloroform gave only tar. Successive treatment with n-butyl-lithium and dimethyl sulphate gave a high yield of 1-methyl-2-phenyl[1]-benzothieno[3,2-*b*]pyrrole, which gave 3-bromo-1-methyl-2-phenyl[1]benzothieno[3,2-*b*]pyrrole on bromination with bromine in chloroform. Reaction of the bromo-

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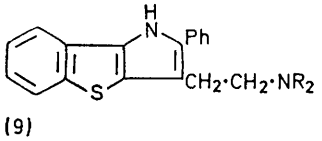
derivative with n-butyl-lithium followed by carboxylation of the product gave 1-methyl-2-phenyl-[1]benzothieno[3,2-*b*]pyrrole-3-carboxylic acid.

Vilsmeier–Haack formylation of the 2-phenyl derivative (1; R = H) gave 2-phenyl-1*H*-[1]benzothieno[3,2-*b*]-pyrrole-3-carbaldehyde, which was reduced by sodium borohydride to the 3-hydroxymethyl compound. Treatment of this compound with thionyl chloride gave only tar.

The tryptamine analogues (9; R = Me or Et) were prepared through treatment of the pyrrole (1; R = H) with oxalyl chloride in ether followed by treatment of the glyoxyloyl chloride (10; R = Cl) with dimethylamine or diethylamine and reduction of the resulting glyoxylamide (10; R = NMe_2 or NEt_2) with lithium aluminium hydride in ether.



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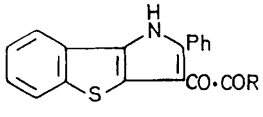

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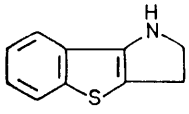

(11)

In an attempt to prepare the 2,3-dihydro-compound (11), we heated a mixture of 2-ethyl-3-nitrobenzo[*b*]-thiophen and an excess of triethyl phosphite under reflux for 7 h. This gave mainly starting material (70% recovery), together with tar. Treatment of 2-ethyl-3-nitrobenzo[*b*]thiophen with triethyl phosphite in refluxing xylene or trimethyl phosphate similarly gave mainly starting material.

EXPERIMENTAL

Molecular weights were determined by mass spectrometry. The spectroscopic instruments used in this work and the experimental precautions taken were the same as described previously.[23] N.m.r. signals were singlets unless stated otherwise. Light petroleum refers to the fraction of b.p. 60—80°.

2-Methyl-3-nitrobenzo[*b*]thiophen (58%), m.p. 96—99° (from ethanol) (lit.,[19] 98—98·5°; lit.,[24] 97—98°), and 3-methyl-2-nitrobenzo[*b*]thiophen (26%), m.p. 146—148° (from ethanol) (lit.,[19] 148—149°), were prepared by literature procedures. For the synthesis of the last compound, 3-methylbenzo[*b*]thiophen was prepared by our procedure.[25]

2-*Ethyl*-3-*nitrobenzo*[b]*thiophen*.—Concentrated nitric acid (12 ml) was added during 5 min to a solution of 2-ethylbenzo[*b*]thiophen [26] (4·0 g, 24·7 mmol) in acetic acid (26 ml) at 0°. The temperature of the mixture was kept at 5—10° during the addition. The mixture was stirred at 5—10° for a further 30 min and then poured on to ice. Extraction with chloroform gave 2-*ethyl*-3-*nitrobenzo*[b]*thiophen* (2·4 g, 48%), m.p. 103—105° (from ethanol), τ ($CDCl_3$) 1·55—1·68 (m, 4-H), 2·15—2·70 (m, aromatic), 6·62 (q, *J* 8·0 Hz, CH_2), and 8·59 (t, *J* 8·0 Hz, CH_3) (Found: C, 58·3; H, 4·4; N, 6·8; S, 15·5%; *M*, 207. $C_{10}H_9NO_2S$ requires C, 57·95; H, 4·4; N, 6·7; S, 15·5%; *M*, 207).

3-*Nitrobenzo*[b]*thiophen*-2-*carbaldehyde*.—(i) A mixture of 2-methyl-3-nitrobenzo[*b*]thiophen (5·0 g, 25·9 mmol), *p*-nitroso-*NN*-dimethylaniline (5·8 g, 38·5 mmol), and ethanol (25 ml) was heated under reflux for 5 h. It was then cooled and the precipitate was filtered off, washed with hot ethanol (25 ml), and recrystallised from light petroleum, to give p-*dimethylamino*-N-(3-*nitrobenzo*[b]-*thiophen*-2-*ylidene*)*aniline* (6·9 g, 82%), m.p. 230—233° (Found: C, 62·3; H, 4·6; N, 12·7%; *M*, 325. $C_{17}H_{15}N_3O_2S$ requires C, 62·75; H, 4·65; N, 12·9%; *M*, 325).

(ii) A mixture of the anil (6·0 g, 18·45 mmol) and concentrated hydrochloric acid (100 ml) was heated under reflux for 1 h. It was then cooled; the precipitate was filtered off, washed with 2N-hydrochloric acid, dried, and recrystallised from benzene–n-hexane (1 : 1), to give 3-nitrobenzo[*b*]thiophen-2-carbaldehyde (3·5 g, 92%), m.p. 125—127° (lit.,[19] 125—127°), $\nu_{max.}$ (Nujol) 1680 cm^{-1} (C:O), τ ($CDCl_3$) 1·40 (q, J_o 9·0, J_m 3·0 Hz, 4-H), 1·85—2·40 (m, aromatic), and −0·75 (CHO).

2-*Nitrobenzo*[b]*thiophen*-3-*carbaldehyde* (77%), prepared similarly, had m.p. 122—124° (sublimed, 120° at 10 mmHg) (lit.,[20] 124°), $\nu_{max.}$ (Nujol) 1680 cm^{-1} (C:O), τ ($CDCl_3$) 1·25 (q, J_o 7·5, J_m 2·0 Hz, 4-H), 2·00—2·75 (m, aromatic), and −0·91 (CHO) (Found: C, 52·1; H, 2·5; N, 6·5%; *M*, 207. $C_9H_5NO_3S$ requires C, 52·2; H, 2·4; N, 6·7; *M*, 207).

p-*Dimethylamino*-N-(2-*nitrobenzo*[b]*thiophen*-3-*ylidene*)-*aniline* (59%) had m.p. 165—167° (from ethanol), τ ($CDCl_3$) 0·33 (CH), 0·5—0·85 (m, 4-H), 2·00—2·68 (m, aromatic), 3·04—3·42 (m, aromatic protons adjacent to *p*-NMe_2), and 6·92 (Me) (Found: C, 62·6; H, 4·8; N, 13·0%; *M*, 325).

trans-1-*Aryl*-2-(3-*nitro*-2-*benzo*[b]*thienyl*)- *and* trans-1-*Aryl*-2-(2-*nitro*-3-*benzo*[b]*thienyl*)-*ethenes*.—*General method*. n-Butyl-lithium (1·0 equiv.) was added dropwise to a stirred suspension of a benzyltriphenylphosphonium chloride (1·0 equiv.) in tetrahydrofuran (10 ml g^{-1}) at room temperature and the mixture was stirred for a further 15 min. A solution of the nitrobenzo[*b*]thiophencarbaldehyde (1·1 equiv.) in tetrahydrofuran (10% w/v) was added dropwise and the mixture was heated under reflux for 2 h. It was then cooled, washed with water, dried ($MgSO_4$), and chromatographed on an alumina column. Ether–light petroleum (1 : 1) eluted the product. Details of the products are given in Table 1.

2-*Aryl*-1H-[1]*benzothieno*[3,2-b]*pyrroles and* 2-*Aryl*-1H-[1]*benzothieno*[2,3-b]*pyrroles*.—*General method*. A mixture of the *trans*-alkene (Table 1) (1·0 equiv.) and triethyl phosphite (12·0 equiv.) was heated under reflux for 20 h under nitrogen. The excess of triethyl phosphite and the triethyl phosphate produced were then distilled off at 0·1 mmHg, and the residue was chromatographed on alumina. The eluant and details of the products are given in Table 2.

1-*Methyl*-2-*phenyl*[1]*benzothieno*[3,2-b]*pyrrole*.—A solution of n-butyl-lithium (8·05 mmol) in hexane (3·5 ml) was added dropwise to a stirred solution of 2-phenyl-1*H*-[1]benzothieno[3,2-*b*]pyrrole (2·0 g, 8·03 mmol) in ether

[23] Part VIII, K. E. Chippendale, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1972, 2023.
[24] J. Cooper and R. M. Scrowston, *J.C.S. Perkin I*, 1972, 265.
[25] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1968, 2733.
[26] E. N. Karaulova, D. Sh. Meĭlanova, and G. D. Gal'pern, *J. Gen. Chem. U.S.S.R.*, 1960, **30**, 3262.

(40 ml) at room temperature, and the mixture was stirred for 15 min. Dimethyl sulphate (1·1 g, 8·7 mmol) in ether (10 ml) was added dropwise during 10 min and the mixture was stirred for a further 1 h. An excess of sodium ethoxide in ethanol was added and the mixture was heated under reflux for 1 h to destroy the excess of dimethyl sulphate. Work-up in the usual way gave the *product* (1·64 g, 78%), m.p. 119—121°, τ ($CDCl_3$) 1·90—2·73 (m, aromatic), 3·41 (3-H), and 5·92 (Me) (Found: C, 77·3; H, 5·1; N, 5·2%; *M*, 263. $C_{17}H_{13}NS$ requires C, 77·5; H, 5·0; N, 5·3%; *M*, 263).

Bromination of 1-*Methyl*-2-*phenyl*[1]*benzothieno*[3,2-b]-*pyrrole*.—Bromine (0·80 g, 5·0 mmol) in chloroform (8·5 ml) was added dropwise during 10 min to a stirred solution of 1-methyl-2-phenyl[1]benzothieno[3,2-*b*]pyrrole (1·2 g, 4·6 mmol) in chloroform (24 ml) at room temperature and the mixture was stirred at room temperature for a further 2 h. 4·5%; *M*, 307. $C_{18}H_{13}NO_2S$ requires C, 70·3; H, 4·3; N, 4·6%; *M*, 307).

Vilsmeier–Haack Formylation of 2-*Phenyl*-1H-[1]*benzothieno*[3,2-b]*pyrrole*.—The benzothienopyrrole (2·0 g, 8·03 mmol) was added in small portions to a mixture of *NN*-dimethylformamide (4·3 g, 59·0 mmol), and phosphoryl chloride (1·6 g, 10·4 mmol) at 0°. The mixture was heated at 55° for 90 min, then cooled and poured on to ice. The resulting mixture was made alkaline with saturated aqueous potassium carbonate and the precipitate was filtered off and crystallised from ethanol, to give 2-*phenyl*-1H-[1]-*benzothieno*[3,2-b]*pyrrole*-3-*carbaldehyde* (1·8 g, 80%), m.p. 248—250°, $\nu_{max.}$ (Nujol) 3200s (NH) and 1620s cm^{-1} (C:O), τ ($CDCl_3$) −0·15 (CHO), 1·78—2·80 (m, aromatic), and 7·38 (exchangeable, NH) (Found: C, 73·6; H, 4·0; N, 5·0%; *M*, 277. $C_{17}H_{11}NOS$ requires C, 73·6; H, 4·0; N, 5·05%; *M*, 277).

TABLE 1

trans-1-Aryl-2-(3-nitro-2-benzo[*b*]thienyl)ethenes and *trans*-1-aryl-2-(2-nitro-3-benzo[*b*]thienyl)ethenes

				Chemical shifts (τ) [c]				Found (%)				Required (%)		
Compound	M.p.[a] (°C)	Yield (%)	$\nu_{max.}$ (CH:CH) [b] (cm^{-1})	Olefinic H [d]	4-H	Me	Other	C	H	N	Formula	C	H	N
(3; R = H)	105—109 [e]	68	965	1·75(d, *J* 16·0 Hz)	1·55(m)		2·10—2·81(m)	68·0	4·1	5·0	$C_{16}H_{11}NO_2S$	68·3	3·95	5·0
(3; R = Me)	129—132	63	955	1·80(d, *J* 16·0 Hz)	1·59(m)	7·66	2·15—3·00(m)	69·1	4·6	4·7	$C_{17}H_{13}NO_2S$	69·1	4·4	4·7
(3; R = Cl)	108—111	72	950		1·52(m)		1·85—2·90(m)	60·8	3·2	4·3	$C_{16}H_{10}ClNO_2S$	60·85	3·2	4·45
(4; R = H)	143—144	59	980				2·10—3·00(m)	68·3	4·1	4·8	$C_{16}H_{11}NO_2S$			
(4; R = Me)	120—125 [e]	50	965			7·60	2·10—2·90(m)	68·9	4·5	4·7	$C_{17}H_{13}NO_2S$			
(4; R = Cl)	147—151 [e]	61	970				2·15—2·90(m)	60·9	3·5	4·3	$C_{16}H_{10}ClNO_2S$			

[a] Recrystallised from ethanol except for compound (3; R = H) which was recrystallised from methanol. [b] Nujol. [c] Solvent $CDCl_3$. [d] In most cases the signals overlapped with those of the aromatic protons and only in the two instances shown was it possible to record the coupling constants. [e] With decomposition.

TABLE 2

2-Aryl-1*H*-[1]benzothieno[3,2-*b*]pyrroles and 2-aryl-1*H*-[1]benzothieno[2,3-*b*]pyrroles

						Chemical shifts (τ) [c]				Found (%)				Required (%)		
Compound	M.p. (°C)	Cryst. from [a]	Eluant [a]	Yield (%)	$\nu_{max.}$(NH) [b] (cm^{-1})	3-H	Me	Other	$J_{1,3}$/Hz	C	H	N	Formula	C	H	N
(1; R = H)	188—190°	A	A	76	3440	3·00(d)		1·70—2·73(m)	2·0	77·1	4·6	5·4	$C_{16}H_{11}NS$	77·1	4·45	5·6
(1; R = Me)	178—180	B	D	79	3430	3·23(d)	7·67	2·10—2·90(m)	2·0	77·5	5·0	5·2	$C_{17}H_{13}NS$	77·5	5·0	5·3
(1; R = Cl)	195—197	B	E	66	3430	3·22(d)		1·85—2·80(m)	2·0	68·05	3·7	4·8	$C_{16}H_{10}ClNS$	67·8	3·5	4·9
(2; R = H)	171—173	B	E	78	3440	2·95(d)		1·90—2·73(m)	2·0	77·5	4·8	5·4	$C_{16}H_{11}NS$			
(2; R = Me)	166—168	C	D	67	3450	3·25(d)	7·62	2·10—3·10(m)	2·0	77·5	4·8	5·2	$C_{17}H_{13}NS$			
(2; R = Cl)	182—184	C	E	64	3420	2·01(d)		2·00—2·80(m)	1·5	67·6	3·7	4·8	$C_{16}H_{10}ClNS$			

[a] A = Ether, B = benzene–light petroleum (1 : 1), C = toluene–light petroleum (1 : 1), D = ether–light petroleum (1 : 2), E = ether–light petroleum (1 : 1). [b] Nujol. [c] Solvent $CDCl_3$.

2N-Sodium hydroxide (50 ml) was added and the organic layer was separated, washed with water, and dried ($MgSO_4$). Removal of the solvent by distillation gave a residue which was chromatographed on alumina. Light petroleum (b.p. 40—60°) eluted 3-*bromo*-1-*methyl*-2-*phenyl*[1]*benzothieno*[3,2-b]*pyrrole* (1·4 g, 89%), m.p. 83—85° (from benzene–light petroleum) [Found: C, 59·9; H, 3·3; N, 3·95%; *M*, 342; *M* + 2, 344 (ratio 1 : 1). $C_{17}H_{12}BrNS$ requires C, 59·65; H, 3·5; N, 4·1%; *M*, 342; *M* + 2, 344 (ratio 1 : 1)].

1-*Methyl*-2-*phenyl*[1]*benzothieno*[3,2-b]*pyrrole*-3-*carboxylic Acid*.—A solution of n-butyl-lithium (4·6 mmol) in hexane (2·0 ml) was added dropwise to a stirred solution of 3-bromo-1-methyl-2-phenyl[1]benzothieno[3,2-*b*]pyrrole (1·4 g, 4·1 mmol) in ether (30 ml) at −70°, and the mixture was stirred at −70° for 1 h. An excess of dry, solid carbon dioxide was then added in small pieces and the mixture was allowed to warm slowly to room temperature. After the addition of 2N-hydrochloric acid, the mixture was worked up in the usual way to give the *acid* (0·5 g, 40%), m.p. 200—202° (from benzene), $\nu_{max.}$ (Nujol) 3100br (OH) and 1670s cm^{-1} (C:O), τ ($CDCl_3$) 1·80—2·69 (m, aromatic and OH) and 6·11 (Me) (Found: C, 69·9; H, 4·3; N,

3-*Hydroxymethyl*-2-*phenyl*-1H-[1]*benzothieno*[3,2-b]*pyrrole*.—A mixture of 2-phenyl-1*H*-[1]benzothieno[3,2-*b*]pyrrole-3-carbaldehyde (3·0 g, 10·8 mmol), sodium borohydride (0·1 g, 2·6 mmol), ethanol (30 ml), and 4N-sodium hydroxide (10 ml) was heated at 50° for 30 min. It was then cooled and filtered, and an excess of water was added. Extraction with ether gave the *product* (1·0 g, 30%), b.p. 120—125° at 0·2 mmHg (Kugelrohr apparatus), $\nu_{max.}$ (film) 3420br cm^{-1} (OH) (Found: C, 73·5; H, 4·7; N, 5·0%; *M*, 279. $C_{17}H_{13}NOS$ requires C, 73·1; H, 4·7; N, 5·0%; *M*, 279).

Reaction of 2-*Phenyl*-1H-[1]*benzothieno*-[3,2-b]*pyrrole with Oxalyl Chloride*.—A mixture of benzothienopyrrole (1·0 g, 4·02 mmol) and oxalyl chloride (0·67 g, 5·3 mmol) in ether (10 ml) was stirred at room temperature for 20 h. The precipitate was filtered off and dried in air to give 2-*phenyl*-1H-[1]*benzothieno*[3,2-b]*pyrrole*-3-*glyoxyloyl chloride* (1·37 g, 100%), m.p. 132—134°, $\nu_{max.}$ (Nujol) 3280s (NH) and 1600 cm^{-1} (C:O) (Found: C, 63·3; H, 3·1; N, 3·9. $C_{18}H_{10}ClNO_2S$ requires C, 63·6; H, 3·0; N, 4·1%).

NN-*Dimethyl*-2-*phenyl*-1H-[1]*benzothieno*[3,2-b]*pyrrole*-3-*glyoxylamide*.—A solution of dimethylamine in ethanol (33%; 28 ml) was added to a solution of the glyoxyloyl chloride (7·0 g, 20·6 mmol) in ethanol (28 ml) and the

mixture was stirred for 2 h at room temperature. It was then filtered; evaporation of the filtrate to dryness under reduced pressure gave the *product* (6·5 g, 93%), m.p. 210—211° (from ethanol), $\nu_{max.}$ (Nujol) 3240s (NH), and 1650s and 1610s cm^{-1} (C:O), τ ($CDCl_3$) 1·90—2·81 (m, aromatic), 7·26 and 7·42 (Me), and 7·49 (exchangeable, NH) (Found: C, 68·9; H, 4·75; N, 8·0%; *M*, 348. $C_{20}H_{16}N_2O_2S$ requires C, 68·9; H, 4·6; N, 8·0%; *M*, 348).

NN-*Diethyl*-2-*phenyl*-1H-[1]*benzothieno*[3,2-b]*pyrrole*-3-*glyoxylamide* (72%), prepared similarly in benzene, had m.p. 218—220° (from ethanol), $\nu_{max.}$ (Nujol) 3180s (NH), and 1630s and 1615s cm^{-1} (C:O), τ ($CDCl_3$) 1·92—2·90 (m, aromatic), 6·78 (q, *J* 8·0 Hz, CH_2), 8·95 (t, *J* 8·0 Hz, CH_3), and 8·65 (exchangeable, NH) (Found: C, 69·95; H, 5·2; N, 7·4%; *M*, 376. $C_{22}H_{20}N_2O_2S$ requires C, 70·2; H, 5·35; N, 7·4%; *M*, 376).

3-(2-*Dimethylaminoethyl*)-2-*phenyl*-1H-[1]*benzothieno*-[3,2-b]*pyrrole*.—A solution of *NN*-dimethyl-2-phenyl-1*H*-[1]benzothieno[3,2-*b*]pyrrole-3-glyoxylamide (5·0 g, 14·4 mmol) in dry ether (100 ml) was added quickly to a stirred suspension of lithium aluminium hydride (0·2 g, 5·70 mmol) in dry ether (50 ml) under nitrogen at room temperature, and the mixture was heated under reflux for 3 h. Ethyl acetate (10 ml) was added cautiously, followed by 5N-sodium hydroxide (15 ml), and the mixture was then heated under reflux for a further 1 h. The precipitate was filtered off, the residue was washed thoroughly with ethyl acetate, and the filtrate and washings were combined and dried ($MgSO_4$). Removal of the solvents by distillation under reduced pressure gave a residue which was crystallised several times from light petroleum to give the *product* (4·2 g, 91%), m.p. 109—111°, τ ($CDCl_3$) 1·29 (exchangeable, NH), 2·10—2·90 (m, aromatic), 6·82—7·52 (m, CH_2), and 7·76 (Me) (Found: C, 74·8; H, 6·5; N, 8·6%; *M*, 320. $C_{20}H_{20}N_2S$ requires C, 75·0; H, 6·3; N, 8·75%; *M*, 320).

3-(2-*Diethylaminoethyl*)-2-*phenyl*-1H-[1]*benzothieno*[3,2-b]-*pyrrole* (76%), prepared similarly, had m.p. 105—107° (from light petroleum), τ ($CDCl_3$) 2·01—3·00 (m, aromatic), 6·80 (exchangeable, NH), 7·16 (CH_2), 7·42 (q, *J* 7·5 Hz, CH_2), and 9·00 (t, *J* 7·5 Hz, CH_3) (Found: C, 75·5; H, 7·0; N, 7·9%; *M*, 348. $C_{22}H_{24}N_2S$ requires C, 75·8; H, 6·9; N, 8·0%; *M*, 348).

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