Studies of Heterocyclic Compounds. Part XIII.[1] Pyrrolo[2,1-*b*]thiazole Thioaldehydes: Synthesis and Spectral Studies

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Pyrrolo[2,1-*b*]thiazole-5- and 7-thiocarbaldehydes, a class of stable heterocyclic thioaldehydes, have been synthesised by a modification of the Vilsmeier reaction. 6-Methyl- and 2,3,6-trimethylpyrrolo[2,1-*b*]thiazole-5-[^{2}H]-thiocarbaldehyde have been obtained by using [$^2H_7$]dimethylformamide in the Vilsmeier reaction. ^{1}H N.m.r. spectral data for the thioaldehydes in $CDCl_3$ are recorded. Restricted rotation about the ring–CHS bond was detected in 6-methyl-, 2,6-dimethyl-, and 6,7-dimethyl-pyrrolo[2,1-*b*]thiazole-5-thiocarbaldehyde, by using the change in shape of the 3-H and CHS signals with temperature as a probe. The coalescence temperatures for solutions in $(CD_3)_2SO$ lie in the range 78—86°. ^{1}H N.m.r. spectral data indicate that pyrrolo[2,1-*b*]thiazole-5-thiocarbaldehydes exist either in a *syn*-configuration (6-methyl-, 2,6-dimethyl-, 6,7-dimethyl-, and 3-methyl-6-t-butyl-) or in an *anti*-configuration (3,6-dimethyl- and 2,3,6-trimethyl-), and that the 7-thiocarbaldehydes exist in a *syn*-configuration. Normal ranges for the thioformyl proton chemical shifts are: 5-*syn* CHS, δ 10·2—10·4; 5-*anti* CHS, 11·0—11·1; 7-*syn* CHS, 10·5—10·8 p.p.m. The preparation of some new pyrrolo[2,1-*b*]thiazoles is described.

We have briefly reported the isolation of stable thioaldehydes from indolizines, pyrrolo[2,1-*b*]thiazoles, and indoles.[2] Details of the preparation of indolizine thioaldehydes were subsequently given[3] with u.v. and ^{1}H n.m.r. spectral data. At the beginning of our work only one authentic stable thioaldehyde was known; consequently knowledge of the properties and reactivity of thioaldehydes is scanty. We have extended our synthetic and spectral studies, examined the reactivity of stable heterocyclic thioaldehydes, and carried out crystallographic structure determinations of selected compounds. This paper describes synthetic and spectral studies of pyrrolo[2,1-*b*]thiazole thioaldehydes.

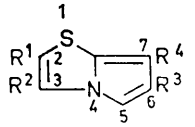
Synthesis and Structure of Pyrrolo[2,1-b]*thiazole Thioaldehydes.*—Thioformylation was carried out by a novel application[2,3] of the Vilsmeier reaction. Treatment of the pyrrolo[2,1-*b*]thiazoles (1)—(9) in dimethylformamide with phosphoryl chloride produced the corresponding Vilsmeier salts (10) and (11), which, when solvolysed with aqueous sodium hydrogen sulphide, gave the orange or red pyrrolo[2,1-*b*]thiazole thioaldehydes (12)—(22). The crude products from the pyrrolo[2,1-*b*]-thiazoles (1)—(3) and (6)—(9) were homogeneous or contained only traces of a yellow impurity (t.l.c.). Compounds (1)—(3) and (6) gave the 5-thioformyl derivatives (12)—(14) and (17), respectively, whereas the 5,6-dimethyl (7), 3,5,6-trimethyl (8), and 2,3,5,6-tetramethyl (9) compounds afforded the 7-thioformyl derivatives

[1] Part XII, D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1972, 1447.

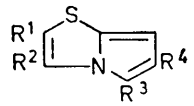
[2] S. McKenzie and D. H. Reid, *Chem. Comm.*, 1966, 401.

[3] S. McKenzie and D. H. Reid, *J. Chem. Soc.* (*C*), 1970, 145.

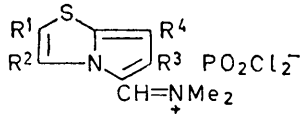
(18)—(20). In contrast, 3,6-dimethylpyrrolo[2,1-*b*]-thiazole (5) produced in high yield a 4 : 1 mixture



	R^1	R^2	R^3	R^4
(1)	H	H	Me	H
(2)	Me	H	Me	H
(3)	H	H	Me	Me
(4)	H	Me	Bu^t	H
(5)	H	Me	Me	H
(6)	Me	Me	Me	H



	R^1	R^2	R^3	R^4
(7)	H	H	Me	Me
(8)	H	Me	Me	Me
(9)	Me	Me	Me	Me



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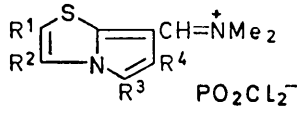

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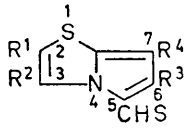
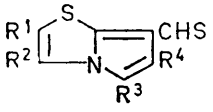
(n.m.r.) of the 5- (16) and 7-thioaldehydes (22). 3-Methyl-6-t-butylpyrrolo[2,1-*b*]thiazole (4) also gave a mixture from which the 5-thioformyl (15) (12%) and



	R^1	R^2	R^3	R^4
(12)	H	H	Me	H
(13)	Me	H	Me	H
(14)	H	H	Me	Me
(15)	H	Me	Bu^t	H
(16)	H	Me	Me	H
(17)	Me	Me	Me	H

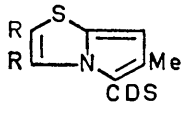


	R^1	R^2	R^3	R^4
(18)	H	H	Me	Me
(19)	H	Me	Me	Me
(20)	Me	Me	Me	Me
(21)	H	Me	H	Bu^t
(22)	H	Me	H	Me

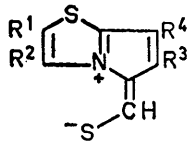
7-thioformyl (21) (17%) derivatives were isolated by preparative t.l.c.

Although 6-methylpyrrolo[2,1-*b*]thiazole (1) is known to undergo electrophilic substitution,[4] including Vilsmeier formylation, exclusively at position 5, we decided to obtain definite evidence of structure for each thioaldehyde as far as possible, especially since compounds (4) and (5) give two thioformylation products. The thioaldehyde from 6-methylpyrrolo[2,1-*b*]thiazole (1) is compound (12) since it is produced from the same Vilsmeier salt (10; $R^1 = R^2 = R^4 = H$, $R^3 = Me$) as 6-methylpyrrolo[2,1-*b*]thiazole-5-carbaldehyde (12; CHO for CHS) of established structure.[4] The structure of the 2,3,6-trimethyl-5-thiocarbaldehyde (17), obtained from the base (6), was confirmed by reduction[5] with lithium aluminium hydride–aluminium chloride to 2,3,5,6-tetramethylpyrrolo[2,1-*b*]thiazole (9), whose synthesis is described in this paper. Structures (14) and (18) for the thioformylation products of the bases (3) and (7) follow from the presence of an AB pattern of signals, arising from 2-H and 3-H, in the aromatic regions of their ^{1}H n.m.r. spectra. Reduction[5] of the major thioformylation product of 3,6-dimethylpyrrolo[2,1-*b*]thiazole (5) gave a trimethylpyrrolo[2,1-*b*]thiazole, which was different from 3,6,7-trimethylpyrrolo[2,1-*b*]thiazole[6] and from 2,3,6-trimethylpyrrolo[2,1-*b*]thiazole (6) whose synthesis is described in this paper. It must therefore be the remaining possible methyl homologue of 3,6-dimethylpyrrolo[2,1-*b*]thiazole, namely, 3,5,6-trimethylpyrrolo[2,1-*b*]thiazole (8), and its precursor is therefore the 5-thioaldehyde (16). The identification of 3-methyl-6-t-butylpyrrolo[2,1-*b*]thiazole-5-thiocarbaldehyde (15) rests securely on an *X*-ray diffraction structure determination.[7] The second thioformylation products of 3,6-dimethyl- (5) and 3-methyl-6-t-butylpyrrolo[2,1-*b*]-thiazole (4) can be safely assumed to be the 7-thioformyl compounds (22) and (21), respectively, since pyrrolo-[2,1-*b*]thiazoles are known to undergo electrophilic substitution in the 7-position when the 5-position is blocked.[4]

The deuteriated thioaldehydes (23) and (24) were prepared from the bases (1) and (6) by the Vilsmeier reaction, by using [$^2H_7$]dimethylformamide and phosphoryl chloride in 1,2-dichloroethane, followed by solvolysis with aqueous sodium hydrogen sulphide.



(23) R = H
(24) R = Me



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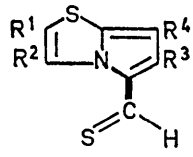

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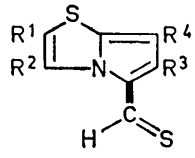

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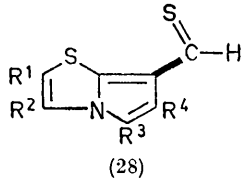

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^1H *N.m.r. Spectra and Geometry of Pyrrolo*[2,1-b]-*thiazole Thioaldehydes.*—All attempts to isolate alkyl and aryl thioaldehydes have until now led to cyclic or linear polymers by opening of the transient C=S bond. However, in pyrrolo[2,1-*b*]thiazole-5- and -7-thiocarbaldehydes, conjugation of the thioformyl group with the nitrogen atom results in polarisation of the C=S bond, indicated in the case of the 5-thioaldehydes by the dipolar structure (25). The attendant decrease in double-bond character of the C=S bond reduces the tendency of these thioaldehydes to polymerise. This polarisation also sets up a barrier to rotation about the

[4] S. McKenzie, B. B. Molloy, and D. H. Reid, *J. Chem. Soc.* (*C*), 1966, 1908.
[5] D. H. Reid and R. G. Webster, unpublished data.
[6] B. B. Molloy, D. H. Reid, and F. S. Skelton, *J. Chem. Soc.*, 1965, 65.
[7] D. F. Grant, R. C. G. Killean, D. H. Reid, A. Sharma, and R. G. Webster, unpublished data.

ring–CHS bond [represented by a thickened line in formulae (26)—(28)] which allows in principle the existence of *syn* (26) and *anti* (27) geometrical isomers. temperatures (*ca.* 80 °C). Although the coexistence of *syn*- and *anti*-forms was not observed the spectral data (see Table) are consistent with the 5-thioaldehydes

Chemical shifts in the 100 MHz ^{1}H n.m.r. spectra of (A) the pyrrolo[2,1-*b*]thiazole thioaldehydes (12)—(24) in $CDCl_3$ (0·4M; +31·4 °C) and (B) the pyrrolo[2,1-*b*]thiazole thioaldehydes (12)—(14) in $(CD_3)_2SO$ (0·1M) at various temperatures (J in Hz)

	Proton signals (δ in p.p.m.)										
	2-Me	3-Me	5-Me	6-Me	7-Me	6-Bu^t	2-H	3-H	5-H	7-H	CHS
(A)											
(12)				2·40 (d) $J_{6\text{-Me},7}$ 0·8			6·93(d) $J_{2,3}$ 4·0	9·67(dd) $J_{3,2}$ 4·0 $J_{3,7}$ 0·5		6·33(m)	10·37
(13)	2·43(d) $J_{2\text{-Me},3}$ 1·3			2·36(d) $J_{6\text{-Me},7}$ 0·7				9·38(m) $J_{3,2\text{-Me}}$ 1·3 $J_{3,7}$ 0·5		6·24(m) $J_{7,6\text{-Me}}$ 0·7 $J_{7,3}$ 0·5	10·28
(14)				2·30	2·13		6·93(d) $J_{2,3}$ 4·0	9·69(d) $J_{3,2}$ 4·0			10·23
(15)		2·73(d) $J_{3\text{-Me},2}$ 1·2				1·52	6·53(q) $J_{2,3\text{-Me}}$ 1·2			6·48	10·88
(16)		2·65(d) [a] $J_{3\text{-Me},2}$ 1·2		2·64(d) $J_{6\text{-Me},7}$ 0·8			6·53(q) $J_{2,3\text{-Me}}$ 1·2			6·39(quint) $J_{7,6\text{-Me}}$ 0·8 $J_{7,\text{CHS}}$ 0·8	11·06br [b]
(16) [c]		1·56(d) $J_{3\text{-Me},2}$ 1·2		2·72(d) $J_{6\text{-Me},7}$ 0·8			5·29(q) $J_{2,3\text{-Me}}$ 1·2			5·82(quint) $J_{7,6\text{-Me}}$ 0·8 $J_{7,\text{CHS}}$ 0·8	11·09br
(17)	2·36br,w	2·55br,w [a]		2·65(d) $J_{6\text{-Me},7}$ 0·8						6·34(quint) $J_{7,6\text{-Me}}$ 0·8 $J_{7,\text{CHS}}$ 0·8	11·05br [b]
(18)			2·27 or 2·33(q) $J_{5\text{-Me},6\text{-Me}}$ 0·8	2·33 or 2·27(q) $J_{6\text{-Me},5\text{-Me}}$ 0·8			7·03(d) $J_{2,3}$ 4·0	7·41(d) $J_{3,2}$ 4·0			10·62
(19)		2·61(d) $J_{3\text{-Me},2}$ 1·2	2·48(q) $J_{5\text{-Me},6\text{-Me}}$ 0·8	2·28(q) $J_{6\text{-Me},5\text{-Me}}$ 0·8			6·57(q) $J_{2,3\text{-Me}}$ 1·2				10·62
(20)	2·33 [d]	2·49 [d]	2·46 [d]	2·25 [d]							10·55
(21)		2·47(d) $J_{3\text{-Me},2}$ 1·2				1·48	6·63(q) $J_{2,3\text{-Me}}$ 1·2		6·94		11·11
(22)		2·43 or 2·39(d) $J_{3\text{-Me},2}$ 1·2		2·39 or 2·43 $J_{6\text{-Me},5}$ 1·2			6·63(q) $J_{2,3\text{-Me}}$ 1·2		6·95(q) $J_{5,6\text{-Me}}$ 1·2		10·78
(22) [c]		1·46(d) $J_{3\text{-Me},2}$ 1·2		1·99(d) $J_{6\text{-Me},5}$ 1·2			5·57 or 6·12(q) $J_{2,3\text{-Me}}$ 1·2		6·12 or 5·57(q) $J_{5,6\text{-Me}}$ 1·2		11·04
(23)				2·40(d) $J_{6\text{-Me},7}$ 0·8			6·92(d) $J_{2,3}$ 4·0	9·68(dd) $J_{3,2}$ 4·0 $J_{3,7}$ 0·5		6·32(m)	
(24)	2·36(q)	2·54(q)		2·64(d) $J_{6\text{-Me},7}$ 0·8						6·36(q) $J_{7,6\text{-Me}}$ 0·8	
(B)											
(12) [e]				2·41			7·52(d) $J_{2,3}$ 4·0	9·56(d) $J_{3,2}$ 4·0		6·63	10·27
(12) [f]				2·40			7·46(d)	9·53br [g]		6·59	10·32br [h]
(12) [i]				2·40			7·42(d)	9·49(d)		6·56	10·34
(13) [j]	2·47			2·37				9·34(m)		6·55	10·23
(13) [k]	2·47			2·38				9·32br [l]		6·53	10·29br [m]
(13) [i]	2·46			2·38				9·27(m)		6·49	10·30
(14) [l]				2·30	2·11		7·52(d) $J_{2,3}$ 4·1	9·56(d) $J_{3,2}$ 4·1			10·15
(14) [n]				2·32	2·12		7·47(d)	9·54br [o]			10·22br [h]
(14) [p]				2·32	2·13		7·45(d)	9·53(d)			10·27

Unless otherwise stated values refer to singlet absorptions. Multiplicity refers to the appearance of spectra on the 100 Hz scale; w = weakly split.

[a] Weakly coupled to CHS. [b] Weakly coupled to 3-Me. [c] [$^2H_6$]Benzene solution. [d] Me assignments uncertain. [e] 31·4 °C. [f] Coalescence temp. 82°. [g] $W_{\frac{1}{2}}$ *ca.* 10 Hz. [h] $W_{\frac{1}{2}}$ *ca.* 5 Hz. [i] 100 °C. [j] 40 °C. [k] Coalescence temp. 78°. [l] $W_{\frac{1}{2}}$ *ca.* 8 Hz. [m] $W_{\frac{1}{2}}$ *ca.* 4 Hz. [n] Coalescence temp. 86°. [o] $W_{\frac{1}{2}}$ *ca.* 12 Hz. [p] 110 °C.

We have established by variable temperature ^{1}H n.m.r. spectral studies the occurrence of restricted rotation in the thioaldehydes (12)—(14) which, at the normal probe temperature (31·4 °C), are well below their coalescence existing either in the *syn*-configuration (26) [compounds (12)—(15)] or in the *anti*-configuration (27) [compounds (16) and (17)], and with the 7-thioaldehydes in the *syn*-configuration (28).

The characteristic thioformyl proton signal of pyrrolo-[2,1-*b*]thiazole thioaldehydes occurs at lower field than the formyl proton signal of the corresponding aldehydes [4] (Δδ 0·65—0·80 p.p.m.). The normal range for the 5-*syn*-thioaldehydes is δ 10·20—10·40 p.p.m. [compounds (12)—(14)]. The anomalously large deshielding of the thioformyl proton in 3-methyl-6-t-butylpyrrolo[2,1-*b*]-thiazole-5-thiocarbaldehyde (15) (δ 10·87 p.p.m.) is attributed to van der Waals deshielding by the t-butyl group.*

The thioformyl proton signals of the 5-*anti*-thioaldehydes (16) (δ 11·06 p.p.m.) and (17) (δ 11·05 p.p.m.) occur at much lower field than those of the 5-*syn*-compounds (12)—(14) (Δδ 0·7—0·8 p.p.m.). We attribute this to a combination of van der Waals deshielding by the 3-Me substituent and the increased ring-current deshielding by the thiazole ring in structure (27).

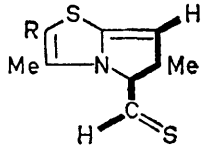
With the exception of the 3-methyl-6-t-butyl derivative (21) the 7-thioaldehydes show thioformyl proton resonances over a narrow range (δ 10·55—10·78 p.p.m.). The anomalously large thioformyl proton chemical shift of compound (21) (δ 11·11 p.p.m.) is attributed here also to van der Waals deshielding by the t-butyl group.

Evidence in support of the geometry assigned to the thioaldehydes now follows. The 5-*syn*-thioformyl group exerts a strong diamagnetic anisotropic deshielding of 3-H (Δδ *ca.* 2 p.p.m.), which is seen by comparing the chemical shift of 3-H in the 5,6-dimethyl-7-thioformyl compound (18) (δ 7·41 p.p.m.) with that of 3-H in the 5-thioaldehydes (12) (δ 9·67), (13) (9·38), and (14) (9·69 p.p.m.). The large deshielding of 3-H is evidence for the 5-*syn*-geometry assigned to these thioaldehydes.

The use of the [^{2}H]thioformyl compounds (23) and (24) and the determination of weak couplings between methyl substituents and adjacent ring protons ($J_{2,3\text{-Me}} = J_{5,6\text{-Me}} = 1{\cdot}2$; $J_{7,6\text{-Me}} = 0{\cdot}8$ Hz) assisted in the identification of closely spaced Me signals and in establishing the 5-*anti*-geometry of the thioaldehydes (16) and (17). The spectra of these thioaldehydes showed an additional long-range 7-H,CHS coupling (*J* 0·8 Hz) not displayed by the 5-thioaldehydes (12)—(14). In the spectrum of the 3,6-dimethyl-5-thioaldehyde (16) the 6-Me signal appears as a doublet (*J* 0·8 Hz), the 7-H signal as a quintet (*J* 0·8 Hz), and the CHS signal as a doublet (*J* 0·8 Hz) whose components are broadened. Irradiation at the 6-Me frequency caused the 7-H quintet to collapse to a doublet (*J* 0·8 Hz) but left the CHS signal unchanged. Irradiation at the 7-H frequency caused the 6-Me doublet to collapse to a singlet and the CHS signal to become a broadened singlet. Irradiation at the CHS frequency caused the 7-H quintet to be replaced by a quartet (*J* 0·8 Hz). Thus, 7-H is coupled to 6-Me and the thioformyl proton to the same degree (*J* 0·8 Hz). The thioformyl proton is also, surprisingly, very weakly coupled to the 3-Me protons. This was seen clearly in spin-decoupling experiments on the thioaldehyde (16) in [$^2H_6$]benzene solution. The normal spectrum (100 Hz) showed the CHS signal as a broad singlet which was resolved into a sharp doublet ($J_{7,\text{CHS}}$ 0·8 Hz) by irradiation at the 3-Me frequency. Irradiation at the CHS frequency caused no change in the 6-Me signal, but the slight splitting of the 3-Me doublet ($J_{2,3\text{-Me}}$ 1·2 Hz) became more pronounced.

The long-range 7-H,CHS coupling (*J* 0·8 Hz) in the 2,3,6-trimethyl-5-thioaldehyde (17) was determined by similar procedures. The 7-H quintet was replaced by a quartet (*J* 0·8 Hz) either upon irradiation at the CHS frequency or when CHS was replaced by CDS [compound (24)]. The existence of a weak 3-Me,CHS interaction was also demonstrated by comparing the spectrum of the thioaldehyde (17) with that of its deuteriated analogue (24), The 3-Me signal in the spectrum of the thioaldehyde (17) is an unresolved broad signal, whereas that of the deuteriated thioaldehyde (24) is a sharp quartet (coupling with the 2-Me group).

The presence of long-range 7-H,CHS coupling in the thioaldehydes (16) and (17) is evidence for their formulation as 5-*anti*-structures (26). In these structures the 7-H and CHS protons are arranged in the W-configuration (29), which is the most favourable for effective coupling through a conjugated system.



(29) R = H or Me

The 7-H and CHS signals in the spectrum of the 3-methyl-6-t-butyl-5-thioaldehyde (15) were both singlets, whence it is concluded that this thioaldehyde has 5-*syn*-geometry. The fact that the 3-Me signal (δ 2·72 p.p.m.) of the thioaldehyde (15) occurs at lower field than the 3-Me signal of the 3,6-dimethyl-5-thioaldehyde (16) (δ 2·64 p.p.m.) is consistent with this conclusion.

The thioformyl proton signals in the spectra of the 3-methyl-6-t-butyl- (21) and 3,6-dimethyl-7-thioaldehyde (22) were sharp singlets. The 5-H signal of compound (21) was also a singlet, and that of the thioaldehyde (22) was a quartet ($J_{5,6\text{-Me}}$ 1·2 Hz). The absence of a long-range 5-H,CHS coupling is taken as evidence for 7-*syn*-geometry in these thioaldehydes and, by extrapolation, in the 7-thioaldehydes (18)—(20). Corroborative evidence comes from the anomalously large deshielding of the thioformyl proton in the thioaldehyde (21) [δ(CHS) (21) − δ(CHS) (22) = 0·33 p.p.m.]. In the 7-*syn*-configuration of compound (21) the thioformyl proton is subject to van der Waals deshielding by the t-butyl group.

Variable Temperature ^{1}*H N.m.r. Spectral Studies.*— Restricted rotation about the ring–CHS bond was detected in the 5-thioaldehydes (12)—(14), by using the temperature-dependence of the shapes of the 3-H and

* A similar deshielding of the thioformyl proton by the adjacent t-butyl group has been observed in the spectrum of 2-t-butylindolizine-3-thiocarbaldehyde.[3]

CHS signals as a probe. No change was observed in the pattern of the spectra of the thioaldehydes (12)—(14) in $CDCl_3$ over the range −60 to +60 °C. Studies were then carried out on solutions of the thioaldehydes in $(CD_3)_2SO$. Below 60 °C the signals from 3-H and CHS in the 6-methyl-5-thioaldehyde (12) consist of a doublet ($J_{2,3}$ 4·0 Hz) * and a sharp singlet, respectively. At higher temperatures the doublet collapses to a broad singlet ($W_{\frac{1}{2}}$ *ca.* 10 Hz) (coalescence temp. 82 ± 4 °C) and the thioformyl signal broadens ($W_{\frac{1}{2}}$ *ca.* 5 Hz). Further rise in temperature causes the 3-H doublet to reappear, and the components of the doublet and the thioformyl singlet become progressively sharper above 100 °C.

The spectrum of the 6,7-dimethyl-5-thioaldehyde (14) changed with temperature in the same manner as that of compound (12). The 3-H doublet ($J_{2,3}$ 4·0 Hz) collapsed to a broad singlet ($W_{\frac{1}{2}}$ *ca.* 12 Hz) in the region of the coalescence temperature (86 ± 4 °C) and reappeared at higher temperatures. The 3-H signal of the 2,6-dimethyl-5-thioaldehyde (13) consists of a weakly split quartet ($J_{3,2\text{-Me}}$ 1·2 Hz) which, at higher temperatures, changes into a broad singlet ($W_{\frac{1}{2}}$ *ca.* 8 Hz) (coalescence temp. 78 ± 4 °C) and reappears above 100 °C. The thioformyl signal broadens ($W_{\frac{1}{2}}$ *ca.* 4 Hz). in the temperature range over which the 3-H signal is broad.

Ring protons become more shielded (Δδ −0·03 to −0·12 p.p.m.) and thioformyl protons become more deshielded (Δδ 0·09 — 0·12 p.p.m.) in the thioaldehydes (12)—(14) with increase in temperature from +30 to +120 °C. These changes are consistent with the transition from restricted to free rotation.

We suggest that the greater stability of the 5- and 7-*syn*-thioformyl structures relative to the *anti*-structures arises from an intramolecular electrostatic attraction between the fractional charges on the thioformyl sulphur atom and on the thiazole ring [see structure (25)]. In the exceptional cases of the 3,6-dimethyl- (16) and 2,3,6-trimethyl-5-thioaldehyde (17) the preference for the *anti*-structure is attributed to the steric effect of the 3-Me substituent which directs the thioformyl sulphur atom away from the thiazole ring. In the case of the 3-methyl-6-t-butyl-5-thioaldehyde (15) the large t-butyl group adjacent to the thioformyl group over rides the steric effect of the 3-Me group and causes the thioformyl group to revert to the 5-*syn*-configuration.

Preparation of Some Pyrrolo[2,1-b]*thiazoles*.—The previously unknown pyrrolo]2,1-*b*]thiazoles (6) and (9) were prepared by established procedures.[6] Quaternisation of 2,4,5-trimethylthiazole with bromoacetone gave the bromide (30a), which was cyclised with sodium acetate in acetic anhydride. Protodeacetylation of the resulting mixture of mono- and di-acetyl-2,3,6-trimethylpyrrolo[2,1-*b*]thiazoles gave the base (6). Similarly quaternisation of 2,4,5-trimethylthiazole with 3-bromobutan-2-one gave the thiazolium bromide (31) and thence 2,3,5,6-tetramethylpyrrolo[2,1-*b*]thiazole (9).

Cyclisation of the bromide (32), obtained by quaternisation of 2,4-dimethylthiazole with bromopinacolone, with sodium acetate in acetic anhydride gave a mixture of mono- and di-acyl derivatives of both 3-methyl-6-t-butyl- (4) and 3,6-dimethyl-pyrrolo[2,1-*b*]thiazole (5) (acyl = acetyl or pivaloyl). However, cyclisation of the bromide (32) with triethylamine in pivalic anhydride gave a mixture of mono- and di-pivaloyl 3-methyl-6-t-butylpyrrolo[2,1-*b*]thiazoles, protodeacylation of which afforded 3-methyl-6-t-butylpyrrolo[2,1-*b*]thiazole (4). The bases (4), (6), and (9) were characterised, *inter alia*, by their ^1H n.m.r. spectra in trifluoroacetic acid, in which they form the 5*H*-pyrrolo[2,1-*b*]thiazolium cations (33)—(35), respectively.[8]

(30a) R = H, X = Br
(30b) R = H, X = ClO_4
(31) R = Me, X = Br

(32)

	R^1	R^2	R^3	R^4
(33)	H	Me	H	Bu^t
(34)	Me	Me	H	Me
(35)	Me	Me	Me	Me

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured with a Unicam SP 800 spectrophotometer. Light absorption data refer to solutions in cyclohexane; principal maxima are italicised. ^1H N.m.r. spectra of thioaldehydes were obtained with a Varian HA100 spectrometer operating at 100 MHz. Spectra were recorded at 31·4° for 0·4M-solutions in $CDCl_3$. Variable temperature studies were carried out with 0·1M-solutions in $CDCl_3$ and $(CD_3)_2SO$. Spectra of other compounds were obtained with a Perkin-Elmer R10 spectrometer operating at 60 MHz (tetramethylsilane as internal reference); *J* values were measured on the 100 Hz scale. Complex signals were resolved and coupling constants obtained with the aid of spin-decoupling procedures. Unless otherwise stated values refer to singlet absorptions.

Procedures.—Solutions were dried over sodium sulphate and evaporated at reduced pressure. Column chromatography was carried out with Spence grade H alumina. Solvent mixtures are described in ratios by volume.

Materials.—Perchloric acid refers to 70—72% (w/w) perchloric acid. Dimethylformamide was dried for *ca.* 1 week over powdered calcium hydride, then distilled at 15 mmHg. Light petroleum was of boiling range 40—60°.

* The weak 3-H,7-H coupling observed in the spectrum of the thioaldehyde (12) in $CDCl_3$ (see Table) was ignored in this study.

[8] B. B. Molloy, D. H. Reid, and S. McKenzie, *J. Chem. Soc.*, 1965, 4368.

6-Methyl- (1), 2,6-dimethyl- (2), 6,7-dimethyl- (3), 3,6-dimethyl- (5), and 5,6-dimethyl-pyrrolo[2,1-*b*]thiazole (7) were prepared by the method of ref. 6.

3-*Methyl*-6-*t*-*butylpyrrolo*[2,1-b]*thiazole* (4).—A mixture of 2,4-dimethylthiazole (22·6 g, 21·4 ml, 200 mmol) and bromopinacolone (43 g, 32·4 ml, 240 mmol) was heated at 75° for 5 days. Digestion of the cooled crystalline mass with ether, filtration, and washing with ether gave 3-(3,3-*dimethyl*-2-*oxobutyl*)-2,4-*dimethylthiazolium bromide* (32) (52·09 g, 88%), needles (ethanol), m.p. 225—226° (Found: C, 45·3; H, 6·2; N, 4·7. $C_{11}H_{18}BrNOS$ requires C, 45·2; H, 6·2; N, 4·8%); δ(CF_3·CO_2H) 1·43 (9H, Bu^t), 2·49 (3H, d, $J_{4\text{-Me},5}$ 1·2 Hz, 4-Me), 2·90 (3H, 2-Me), 5·69 (2H, CH_2), and 7·56br (1H, 5-H).

A mixture of the bromide (14·61 g, 50 mmol), pivalic anhydride (100 ml), and triethylamine (34·4 ml, 250 mmol) was heated at 150° for 2 h, cooled, and poured into water (500 ml). After 12 h the mixture was extracted with dichloromethane, and the extracts were washed with water (×4), dried, and evaporated. The residue and water (750 ml) were warmed to 60°, then basified with sodium carbonate to remove pivalic acid, and the resulting mixture was cooled before being extracted with dichloromethane. The extracts were washed with water (×3), dried, and evaporated. The residual oil, consisting of a mixture of pivaloyl derivatives of the base (4), was boiled for 3 h with acetic acid (67 ml), water (200 ml), and concentrated hydrochloric acid (67 ml). The cooled mixture was basified by gradual addition of solid sodium hydroxide and steam-distilled. The distillate was extracted with ether, and the extracts were washed with water, dried, and evaporated. The residual oil was chromatographed (silica; 45 × 2·5 cm) with benzene. Fractions (50 ml) were collected and their composition was monitored by t.l.c. Evaporation of fractions (vi) and (vii) and distillation of the residue at 110—115° and 0·2 mmHg afforded 3-*methyl*-6-*t*-*butylpyrrolo*[2,1-b]*thiazole* (2·555 g, 26%) as an oil (Found: C, 68·0; H, 7·7; N, 7·0. $C_{11}H_{15}NS$ requires C, 68·3; H, 7·8; N, 7·3%); δ($CDCl_3$; 100 MHz) 1·30 (9H, Bu^t), 2·29 (3H, d, $J_{3\text{-Me},2}$ 1·3 Hz, 3-Me), 6·13 (1H, q, $J_{2,3\text{-Me}}$ 1·3 Hz, 2-H), 6·15 (1H, d, $J_{7,5}$ 1·2 Hz, 7-H), and 6·85 (1H, d, $J_{5,7}$ 1·2 Hz, 5-H); δ{CF_3·CO_2H; 100 MHz; spectrum of the 3-methyl-6-t-butyl-5*H*-pyrrolo[2,1-*b*]thiazolium cation (33)} 1·42 (9H, Bu^t), 2·60 (3H, d, $J_{3\text{-Me},2}$ 1·2 Hz, 3-Me), 5·12 (2H, d, $J_{5,7}$ 1·2 Hz, 5-H_2), 7·00 (1H, t, $J_{7,5}$ 1·2 Hz, 7-H), and 7·33 (1H, q, $J_{2,3\text{-Me}}$ 1·2 Hz, 2-H).

2,3,6-*Trimethylpyrrolo*[2,1-b]*thiazole* (6).—A solution of 2,4,5-trimethylthiazole (12·72 g, 100 mmol) and bromoacetone (8·4 ml, 100 mmol) in acetone (20 ml) was kept at room temperature for 3 days. The crystalline 3-acetonyl-2,4,5-trimethylthiazolium bromide (30a) (21·65 g, 82%) was filtered off, washed with ether, and dried *in vacuo*. Attempts to recrystallise the bromide were unsatisfactory, and for characterisation a sample of the bromide (1·25 g, 4·5 mmol) in ethanol (5 ml) was treated with perchloric acid (1 ml). Addition of ether precipitated 3-*acetonyl*-2,4,5-*trimethylthiazolium perchlorate* (30b). Two recrystallisations from ethanol gave needles (850 mg, 67%), m.p. 131—131·5° (Found: C, 38·3; H, 5·1; N, 4·8. $C_9H_{14}ClNO_5S$ requires C, 38·1; H, 5·0; N, 4·9%); δ(CF_3·CO_2H) 2·37 (3H, COMe), 2·52 (3H, 5-Me), 2·59 (3H, 4-Me), 2·84 (3H, 2-Me), and 5·56 (2H, CH_2).

The bromide (26·42 g, 100 mmol), sodium acetate (16·4 g, 200 mmol), and acetic anhydride (240 ml) were boiled for 2 h, cooled, and poured into water (1 l). After 12 h the mixture was extracted with dichloromethane. The extracts were washed successively with water, aqueous potassium carbonate, and water, dried, and evaporated. The residual brown solid (18·96 g), comprising mono- and di-acetyl 2,3,6-trimethylpyrrolo[2,1-*b*]thiazoles, was boiled with acetic acid (184 ml), water (184 ml), and concentrated hydrochloric acid (92 ml) for 3 h. The cooled mixture was basified with solid sodium hydroxide, then steam-distilled. The distillate was extracted with ether, and the extracts were dried and evaporated. Sublimation of the residue at 80—85° and 1 mmHg gave 2,3,6-*trimethylpyrrolo*[2,1-b]-*thiazole* (5·633 g, 34%), needles (from methanol), m.p. 53—54° (Found: C, 65·4; H, 6·9; N, 8·4. $C_9H_{11}NS$ requires C, 65·5; H, 6·7; N, 8·5%); δ($CDCl_3$) 2·18 (3H, 6-Me), 2·23 (6H, 2-Me + 3-Me), 5·98 (1H, 7-H), and 6·77 (1H, 5-H); δ{CF_3·CO_2H; spectrum of the 2,3,6-trimethyl-5*H*-pyrrolo[2,1-*b*]thiazolium cation (34)} 2·46 (3H, d, $J_{6\text{-Me},7}$ 1·6 Hz, 6-Me), 2·50 (3H, 2-Me), 2·56 (3H, 3-Me), 4·97 (2H, 5-H_2), and 6·92 (1H, q, $J_{7,6\text{-Me}}$ 1·6 Hz, 7-H).

2,3,5,6-*Tetramethylpyrrolo*[2,1-b]*thiazole* (9).—A solution of 2,4,5-trimethylthiazole (6·36 g, 50 mmol) and 3-bromobutan-2-one (7·55 g, 5·2 ml, 50 mmol) in chloroform (5 ml) was boiled for 8 h. Solvent was then evaporated off and the residual oil, containing the bromide (31), was washed thoroughly with ether before being boiled with sodium acetate (8·2 g, 100 mmol) and acetic anhydride (120 ml) for 2 h. Work-up of the mixture as in the preceding experiment gave crude 7-acetyl-2,3,5,6-tetramethylpyrrolo[2,1-*b*]-thiazole (8·73 g) as an oil which slowly solidified. This oil, acetic acid (90 ml), water (90 ml), and concentrated hydrochloric acid (45 ml) were boiled for 3 h. The cooled mixture was basified with solid sodium hydroxide, then steam-distilled. The distillate was extracted with ether, and the extracts were dried and evaporated. Sublimation of the residual solid at 105—110° and 0·1 mmHg afforded 2,3,5,6-*tetramethylpyrrolo*[2,1-b]*thiazole* (2·956 g, 33% from 2,4,5-trimethylthiazole), pale yellow needles (from hexane), m.p. 114·5—115·5° (Found: C, 67·0; H, 7·6; N, 7·7. $C_{10}H_{13}NS$ requires C, 67·0; H, 7·3; N, 7·8%); δ($CDCl_3$) 2·09 (3H, 6-Me), 2·19 (3H, 2-Me), 2·38 (3H, 5-Me), 2·46 (3H, 3-Me), and 5·85 (1H, 7-H); δ{CF_3·CO_2H; spectrum of the 2,3,5,6-tetramethyl-5*H*-pyrrolo[2,1-*b*]thiazolium cation (35)} 1·79 (3H, d, $J_{5\text{-Me},5}$ 7·1 Hz, 5-Me), 2·38 (3H, d, $J_{6\text{-Me},7}$ 1·5 Hz, 6-Me), 2·59 (6H, 2-Me + 3-Me), 5·17 (1H, q, $J_{5,5\text{-Me}}$ 7·1 Hz 5-H), and 6·86br (1H, 7-H).

Preparation of Pyrrolo[2,1-b]*thiazole Thioaldehydes: General Procedure.*—A solution of phosphoryl chloride (1·69 g, 1·0 ml, 11 mmol) in dimethylformamide (10 ml) was added dropwise during 30 min to a stirred solution of the pyrrolo[2,1-*b*]thiazole (10 mmol) in dimethylformamide (15 ml). The temperature was kept at −35° during the addition in the case of pyrrolo[2,1-*b*]thiazoles unsubstituted at both positions 5 and 7, in order to avoid disubstitution, and at room temperature in the case of 5- or 7-substituted pyrrolo[2,1-*b*]thiazoles. The reaction mixture, from which the Vilsmeier salt crystallised in some cases, was stirred at this temperature for a further 30 min before being poured into aqueous 2M-sodium hydrogen sulphide (50 ml). The resulting mixture was diluted with water and the orange-red precipitate was extracted with ether or benzene. The extracts were washed with water (×6), dried, and evaporated. The residue was chromatographed (alumina; 12 × 2·5 cm) with benzene. Evaporation of the eluates and recrystallisation gave the following thioaldehydes: 6-*methylpyrrolo*[2,1-b]*thiazole*-5-*thiocarbaldehyde* (12) (1·614 g,

89%), red needles (from cyclohexane), m.p. 101—103°, $\lambda_{max.}$ 579infl (log ε 1·33), *539*br (1·78), 514br (1·75), *426* (4·52), 417 (4·51), 407sh (4·42), *328*br (3·89), and *222* nm (4·21) [Found: C, 53·2; H, 3·9; N, 7·6; S, 35·5%; *M*, 181 (osmometric; benzene), 181 (mass spec.). $C_8H_7NS_2$ requires C, 53·0; H, 3·9; N, 7·7; S, 35·4%; *M*, 181·3]; 2,6-*dimethylpyrrolo*[2,1-b]*thiazole*-5-*thiocarbaldehyde* (13) (1·746 g, 89%), orange dendritic crystals (from cyclohexane), m.p. 127—128°, $\lambda_{max.}$ 578infl (log ε 1·41), *536*br (1·84), *510*br (1·84), *428* (4·51), 420 (4·49), 410sh (4·42), *335*br (3·91), and *224* nm (4·21) (Found: C, 55·7; H, 4·5. $C_9H_9NS_2$ requires C, 55·4; H, 4·6%); 6,7-*dimethylpyrrolo*-[2,1-b]*thiazole*-5-*thiocarbaldehyde* (14) (1·379 g, 71%), orange-yellow prisms (from cyclohexane), m.p. 165—167·5°, $\lambda_{max.}$ 573infl (log ε 1·38), *536*br (1·89), *508*br (1·89), *437* (4·52), 428 (4·49), 417sh (4·41), *331*br (3·93), and *220* nm (4·27) (Found: C, 55·1; H, 4·3%); 2,3,6-*trimethylpyrrolo*[2,1-b]-*thiazole*-5-*thiocarbaldehyde* (17) (1·610 g, 77%), orange needles (from benzene), m.p. 169—170°, $\lambda_{max.}$ 570—500, plateau with broad maximum at 535 (log ε 1·74), *418* (4·62), 410sh (4·59), *336*br (3·99), *227* (4·11), and 205 nm (4·06) (Found: C, 57·6; H, 5·4; N, 6·9. $C_{10}H_{11}NS_2$ requires C, 57·4; H, 5·3; N, 6·7%); 5,6-*dimethylpyrrolo*[2,1-b]*thiazole*-7-*thiocarbaldehyde* (18) (1·275 g, 65%), orange cubes [from benzene–cyclohexane (1 : 1)], m.p. 162·5—164·5°, $\lambda_{max.}$ 530—500, plateau (log ε 1·81), 425 (4·12), *413* (4·29), *297*br (3·73), and *228* nm (4·39) (Found: C, 55·4; H, 4·5%).

3,5,6-*Trimethylpyrrolo*[2,1-b]*thiazole*-7-*thiocarbaldehyde* (19).—Thioformylation was carried out according to the general procedure. Recrystallisation (× 2) of the sparingly soluble crude product from benzene, without chromatographic purification, gave the 7-*thioaldehyde* as orange needles, m.p. 195—199° (decomp.), $\lambda_{max.}$ † 429 (log ε 4·26), *416* (4·29), 409sh (4·21), 289br (3·69), 260br (3·71), and *229* nm (4·34) (Found: C, 57·5; H, 5·5; N, 6·8%). Chromatography of the residue from the mother liquors (alumina; 12 × 2·5 cm) with benzene afforded a further quantity of the thioaldehyde (total yield to 1·919 g, 92%).

2,3,5,6-*Tetramethylpyrrolo*[2,1-b]*thiazole*-7-*thiocarbaldehyde* (20).—The procedure was identical with that of the preceding experiment. The 7-*thioaldehyde* (1·663 g, 75%) was obtained as orange needles, m.p. 224—226° (decomp.), $\lambda_{max.}$ † 431 (log ε 4·24), *418* (4·27), 410sh (4·17), 283br (3·66), 263br (3·78), and *230* nm (4·28) (Found: C, 59·4; H, 6·1; N, 6·5. $C_{11}H_{13}NS_2$ requires C, 59·1; H, 5·9; N, 6·3%).

Thioformylation of 3-*Methyl*-6-*t*-*butylpyrrolo*[2,1-b]*thiazole* (4).—A solution of phosphoryl chloride (0·20 ml, 2·2 mmol) in dimethylformamide (3 ml) was added dropwise during 10 min to a stirred solution of the base (4) (387 mg, 2 mmol) in dimethylformamide (5 ml) at room temperature. The mixture was stirred for 2 h, then poured into aqueous 2M-sodium hydrogen sulphide (10 ml). The mixture was diluted with water and extracted with benzene, and the extracts were washed with water (× 6), dried, and evaporated. The residue, in benzene (3·5 ml), was divided into seven portions. Preparative t.l.c. of each portion (silica gel; 20 × 20 cm, 1 mm thickness) with benzene gave two yellow bands. The slower-moving band from each plate was collected and the combined material was extracted with boiling benzene–acetone. The residue from the extracts was chromatographed (silica; 12·5 × 1·9 cm) with benzene. The initial pale yellow eluates were discarded. The succeeding red eluates afforded 3-*methyl*-6-*t*-*butylpyrrolo*-[2,1-b]*thiazole*-5-*thiocarbaldehyde* (15) (55 mg, 12%), red prisms (from hexane), m.p. 117—118°, $\lambda_{max.}$ 546br (log ε 2·18), *530*br (2·20), *420* (4·46), *326*br (3·79), *224* (4·16), and 204 nm (4·16) (Found: C, 60·8; H, 6·5; N, 5·9. $C_{12}H_{15}NS_2$ requires C, 60·7; H, 6·4; N, 5·9%). The faster-moving band from each plate was processed in the same manner as the slower-moving band. The residue from the extracts was chromatographed (alumina; 5 × 1·9 cm) with benzene. The yellow eluates gave 3-*methyl*-6-*t*-*butylpyrrolo*[2,1-b]-*thiazole*-7-*thiocarbaldehyde* (21) (80 mg, 17%), orange spars (from hexane), m.p. 156—158°, $\lambda_{max.}$ 564sh (log ε 1·14), 531br (1·81), *513*br (1·84), 506br (1·78), 416 (4·31), *405* (4·34), 397sh (4·22), 281br (3·80), 261br (3·83), and *226* nm (4·34) (Found: C, 60·7; H, 6·5; N, 6·1%).

Thioformylation of 3,6-*Dimethylpyrrolo*[2,1-b]*thiazole* (5).—3,6-Dimethylpyrrolo[2,1-*b*]thiazole (1·51 g, 10 mmol) was thioformylated according to the general procedure. The crude product was a mixture (n.m.r.) of 5-thioformyl (80%) and 7-thioformyl derivatives (20%) which could not be separated efficiently by column chromatography. Recrystallisation of the crude product from cyclohexane–benzene (1 : 1; 40 ml) and then from cyclohexane–benzene (3 : 1; 50 ml) gave 3,6-*dimethylpyrrolo*[2,1-b]*thiazole*-5-*thiocarbaldehyde* (16) (962 mg, 49%) as red prisms, m.p. 152—154°, $\lambda_{max.}$ 615infl (log ε 1·19), 570—500, plateau with broad maximum at *539* (1·71), *417* (4·65), 408sh (4·62), *326*br (3·52), *225* (4·11), and 204 nm (4·09) (Found: C, 55·0; H, 4·8; N, 7·1. $C_9H_9NS_2$ requires C, 55·4; H, 4·6; N, 7·2%). The combined mother liquors were evaporated and the residue was divided into six portions (each *ca.* 120 mg). Each portion was subjected to preparative t.l.c. (silica gel; 20 × 20 cm, 1 mm thickness) with benzene. Separation of the faster-moving yellow 7-isomer from the orange-red 5-isomer was incomplete. The leading edge of the yellow band was removed and extracted with boiling benzene–acetone, and the combined extracts from the six plates were evaporated. The residue, in benzene, was chromatographed (alumina; 8 × 1·9 cm) with benzene–acetone (199 : 1). The yellow eluates afforded 3,6-*dimethylpyrrolo*-[2,1-b]*thiazole*-7-*thiocarbaldehyde* (22) (83 mg, 4·5%), golden yellow needles (from cyclohexane), m.p. 161—162°, $\lambda_{max.}$ *540—500*, plateau (log ε 1·81), 416 (4·31), *405* (4·36), 397sh (4·16), *284*br (3·74), 254infl (3·67), and *227* nm (4·32) (Found: C, 55·7; H, 4·8; N, 7·0%).

6-*Methylpyrrolo*[2,1-b]*thiazole*-5-[^{2}H]*thiocarbaldehyde* (23).—Phosphoryl chloride (0·23 ml, 2·5 mmol) was added to a solution of [$^2H_7$]dimethylformamide (0·23 ml, 3 mmol) in 1,2-dichloroethane (2 ml) at 0°. After 10 min a solution of 6-methylpyrrolo[2,1-*b*]thiazole (1) (274 mg, 2 mmol) in 1,2-dichloroethane (1 ml) was added, and the deep red solution was kept at room temperature for 1 h. The solution was shaken with aqueous 2M-sodium hydrogen sulphide (20 ml) diluted with water, and extracted with benzene. The benzene extracts were washed with water (× 3), dried, and evaporated. Chromatography (alumina; 12 × 2·5 cm) of the residue with benzene and evaporation of the red eluates gave the [^{2}H]*thioaldehyde* (212 mg), red needles (from cyclohexane), m.p. 102—104° (Found: C, 52·4; H + D, 3·9; N, 7·5. $C_8H_6DNS_2$ requires C, 52·7; H + D, 4·4; N, 7·7%). Rechromatography of the mother liquors gave a further 63 mg of product (total yield 275 mg, 78%).

2,3,6-*Trimethylpyrrolo*[2,1-b]*thiazole*-5-[^{2}H]*thiocarbaldehyde* (24).—2,3,6-Trimethylpyrrolo[2,1-*b*]thiazole (6) (330

† The weak $n \longrightarrow \pi^*$ bands could not be measured owing to the low solubility of the thioaldehyde.

mg, 2 mmol) was treated as in the preceding experiment. The crude product was chromatographed (alumina; 12 × 1·9 cm) with benzene. Recrystallisation from cyclohexane–benzene (3 : 1) gave the [^{2}H]*thioaldehyde* as red needles, m.p. 168—170° (Found: C, 57·2; H + D, 5·4; N, 6·8. $C_{10}H_{10}DNS_2$ requires C, 57·1; H + D, 5·8; N, 6·8%). A further 40 mg of product obtained by rechromatography of the residue from the mother liquors brought the total yield to 340 mg (83%).

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