Dithiazoles and Related Compounds. Part. 4.[1a] Preparation of 1,4,2-Dithiazolium Salts unsubstituted at C-5 including the Parent Heterocycle,[2] NMR Spectroscopic Evidence for Aromaticity, and some Novel Reactions

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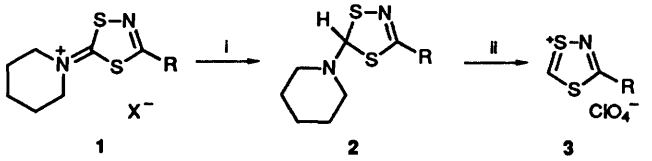
The reaction of 1-(1,4,2-dithiazol-5-ylidene)piperidinium salt **1** and 5-methylthio-1,4,2-dithiazolium salt **5** with sodium borohydride yields 5-piperidino- and 5-methylthio-1,4,2-dithiazoles **2** and **6**, which may be solvolysed with perchloric acid in acetic anhydride to give the title salts, **3**, including the parent unsubstituted compound **3d**. Evidence for aromaticity in these salts is discussed. Similar reduction of the salts **3** yields the first examples of 1,4,2-dithiazoles **10** unsubstituted at C-5. A new synthesis of 1,4,2-dithiazole-5-thiones **4** is reported, and the 3-unsubstituted and 3-methyl derivatives, together with their 5-oxo analogues **9d** and **9e**, are described for the first time. Reaction of the salts **5** with 2,5-dimethylpyrrole gives dithiadiazafulvalenium salts **14**.

We have recently described two different synthetic routes to 5-aryl-1,4,2-dithiazolium salts,[1,3] the second using methodology developed by Shibuya and Yonemoto,[4] which they have also used independently to prepare this same class of compounds.[5] This second approach led recently to the first example of a 1,4,2-dithiazolium salt unsubstituted at C-3.[3] Examples unsubstituted at C-5 were an attractive synthetic goal, (*a*) because their chemistry might be compared with that of the analogous C-2 unsubstituted 1,3-dithiolium salts; (*b*) because the methodology developed might make accessible the parent 1,4,2-dithiazolium cation; and (*c*) because ^{1}H NMR chemical shifts of ring protons might provide a useful probe into the aromaticity of this ring system. We describe here the preparation of the title cations, some of their reactions, and the results of NMR spectroscopic measurements.

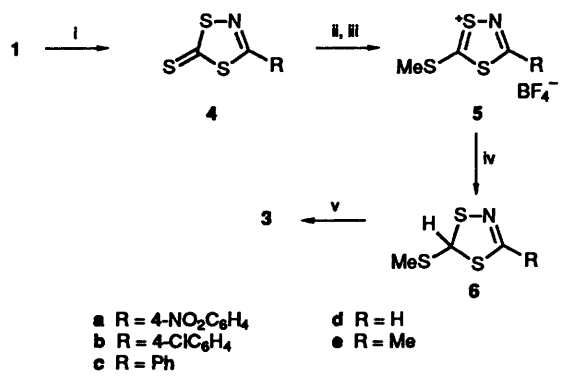
Results and Discussion

1,3-Dithiolium salts, unsubstituted at C-2, have been prepared by reduction of the corresponding 2-amino salts with sodium borohydride, followed by solvolysis in strong acid.[6] An earlier attempt in these laboratories[7] to apply this strategy to the preparation of the title compounds **3** from the salts **1**, led instead to the precipitation of the fluoroborate salt of the dithiazole **2a**, protonated on the piperidine nitrogen atom. We have found subsequently that treatment of the compounds **2** with 60% $HClO_4$ in place of 54% HBF_4, and prolongation of the reaction time to 1 h, resulted in the formation of the salts **3** ($\delta_{5\text{-H}}$ 12.2–12.3) (Scheme 1); however, these could not readily be separated from the co-product piperidinium perchlorate.



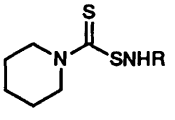
Scheme 1 *Reagents and conditions:* i, $NaBH_4$, H_2O, Et_2O, 0 °C, 30 min; ii, 60% $HClO_4$, Ac_2O, 25 °C, 1 h

An alternative strategy, which seemed likely to eliminate this latter problem, was the solvolysis of the novel 5-methylthiodithiazoles **6** (Scheme 2), an approach which has been used successfully with analogous 1,3-dithiolium salts.[8] The iminiodithiazoles **1a–c** (X = BF_4) were prepared as reported earlier,[7] while the novel salts **1d** and **1e** were prepared from the



Scheme 2 *Reagents and conditions:* i, H_2S, MeOH; ii, Me_2SO, 100 °C; iii, HBF_4, Et_2O; iv, $NaBH_4$, H_2O, Et_2O, 0 °C; v, 70% $HClO_4$, Ac_2O, 0 °C, 1 h

piperidinodithioperformamide **7**, by first acylating with either acetic formic anhydride or acetic anhydride, in chloroform, to give the *N*-acyl derivatives **8d** and **8e** respectively, and then cyclising with perchloric acid and acetic anhydride.[3–5]



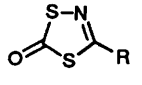
7 R = H
8d R = C(O)H
8e R = C(O)Me

CAUTION: The salt **1e** (X = ClO_4) exploded on isolation; all subsequent work was carried out using the fluoroborate salt. Treatment of solutions of the salts **1** in absolute methanol with hydrogen sulfide led to good (76–78%) yields of the thiones **4** [ν_{max}/cm^{-1} 1070–1090 *vs.* (C=S)]; however, the iminium salt must be very pure for the reaction to be successful. This method complements that using trichloromethanesulfenyl chloride and a thioamide,[9] the latter being unsuitable for preparing examples, *e.g.* compound **1a**, having strongly electron-withdrawing substituents R. The simple thione **4d** is of particular interest because its spectra will be unperturbed by the effect of any substituent R. Since the simple oxo-analogue **9d** was also unknown, both it, and the methyl derivative **9e** for comparison

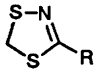
Table 1 ^1H and ^{13}C NMR spectroscopic data for the piperidinium and 1,4,2-dithiazolium salts **1**, **3** and **5**

	δ_H		δ_C			
			Heterocycle		Substituents	
Salt	3-Substituent	5-Substituent	C-3	C-5	3-Substituent[a]	5-Substituent
1a[b,c]	8.10 (2 H), 8.38 (2 H)	1.85 (6 H), 3.77 (2 H) 3.95 (2 H)	165.61	193.67	136.46*i*, 130.45*o* 125.79*m*, 151.47*p*	21.78(t), 25.52(t), 25.79(t) 59.48(t), 62.79(t)
1b[b,c]	7.62 (2 H), 7.98 (2 H)	1.83 (6 H), 3.74 (2 H) 3.91 (2 H)	166.53	193.84	130.34*i*, 130.99*o* 130.67*m*, 140.26*p*	21.83(t), 25.52(t), 25.79(t) 59.27(t), 62.68(t)
1c[d]	7.62–7.76 (3 H) 7.90–8.01 (2 H)	1.94 (6 H), 3.90 (2 H) 4.08 (2 H)	168.45	194.46	132.16*i*, 131.15*o* 129.47*m*, 135.03*p*	22.43(t), 26.14(t), 26.38(t) 59.73(t), 63.14(t)
1d[b]	9.098 (1 H)	1.80 (6 H), 3.73 (2 H) 3.86 (2 H)	158.05[e]	193.91		21.78(t), 25.43(t), 25.62(t) 60.15(t), 62.17(t)
1e[b]	2.705 (3 H)	1.80 (6 H), 3.66 (2 H) 3.81 (2 H)	168.52	195.15	22.55(q)	21.87(t), 25.44(t), 25.73(t) 59.07(t), 62.34(t)
5a[b]	8.24 (2 H), 8.42 (2 H)	3.251 (3 H)	186.53	218.79	135.32*i*, 131.36*o* 126.02*m*, 152.00*p*	26.47(q)
5b[b]	7.66 (2 H), 8.00 (2 H)	3.220 (3 H)	179.93	221.46	129.24*i*, 131.47*o* 131.32*m*, 141.53*p*	26.23(q)
5c[b]	7.65 (3 H), 7.95 (2 H)	3.22 (3 H)				
5d[b]	9.987 (1 H)	3.185 (3 H)	169.89[f]	221.42[g]		26.34(q)
5e[b]	2.990 (3 H)	3.149 (3 H)	182.40	222.10	22.01(q)	25.62(q)
3a[h,i]	8.60 (2 H), 8.80 (2 H)	12.194 (1 H)				
3b[h]	7.72 (2 H), 8.26 (2 H)	12.360 (1 H)	188.26	195.55	129.48*i*, 132.69*o* 132.29*m*, 143.91*o*	
3c[h]	7.72–7.87 (3 H) 8.25–8.36 (2 H)	12.335 (1 H)				
3d[h]	10.803 (1 H)[j]	12.506 (1 H)[j]	175.02[k]	195.70		

[a] *i* = *ipso*, *m* = *meta*, *o* = *ortho*, *p* = *para*. [b] In CD_3CN. [c] Data from ref. 7. [d] In CD_3NO_2. [e] $^1J_{CH}$ 224 ± 1. [f] $^1J_{CH}$ 226.8 ± 0.5. [g] $^3J_{CH}$ 6.8 and 3.6. [h] In CF_3CO_2D–CD_3NO_2. [i] Formed by solvolysis of compound **2a**. [j] $^4J_{HH}$ 0.55 ± 0.11. [k] Assigned in error to a signal at δ 168.7 in ref. 2.

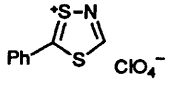


9d R = H
9e R = Me



10b R = 4-ClC$_6$H$_4$
10c R = Ph

purposes, were prepared for similar reasons from the corresponding thiones, using mercury(II) acetate and acetic acid. Full spectroscopic data are recorded in the Experimental section.



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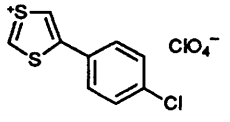

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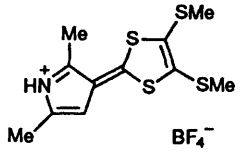
Methylation of the thiones **4**, using Paton and Crosby's method,[10] gave the methylthio salts **5** (50–73%) [δ_H *inter alia ca.* 3.2 (3 H, s)], the simple examples **5d** and **5e**, although fully characterised spectroscopically, proving to be too unstable for obtaining satisfactory microanalyses. Addition of the salts **5** to the stirred two-phase system, aqueous sodium borohydride–diethyl ether, at 0 °C led to smooth reduction in 55–78% yields to the dithiazoles **6** [δ_H *inter alia ca.* 2.15 (3 H, s) and *ca.* 6.5 (1 H, s)]. The 3-methyl compound **6e** was formed in admixture with other products from which it could not satisfactorily be separated. In the mass spectra, the 5-unsubstituted cation was the base peak for compounds **6a–c**, whilst it had an abundance of 25% in the case of the simplest analogue **6d**. Addition of 70% perchloric acid to solutions of the carefully purified dithiazoles **6b–d** in acetic anhydride at 0 °C, followed by stirring for 1 h and dilution with anhydrous diethyl ether, gave precipitates of the highly moisture-sensitive and electrophilic salts **3b–d**, the latter example containing the target parent 1,4,2-dithiazolium cation. Attempts to isolate the nitrophenyl compound **3a** by this method were unsuccessful. All three salts **3b–d** were attacked by solvents more nucleophilic than trifluoroacetic acid (TFA) or nitromethane, and it was not possible to characterise the phenyl derivative **3c** by ^{13}C NMR spectroscopy, since it decomposed too rapidly, even in TFA. The latter salt was, however, reduced successfuly by sodium borohydride in diethyl ether–water to 3-phenyl-1,4,2-dithiazole **10c**, which showed ^1H NMR ring methylene proton signals at δ 4.68. Similar reduction of the 4-chloro analogue **3b** yielded the dithiazole **10b** (δ_H *inter alia* 4.71), although the reaction was unsuccessful with the parent **3d**. These are the first examples of 1,4,2-dithiazoles unsubstituted at C-5.

NMR Spectra of 1,4,2-*Dithiazolium Salts*.—The 1,4,2-dithiazolium cation is formally a 6π-electron system and, therefore, potentially aromatic; evidence for aromaticity may be sought from NMR spectra. The ^1H and ^{13}C NMR data for the salts which were characterised successfully are displayed in Table 1. Comparisons among ^{13}C data for C-5, and among ^1H and ^{13}C data for the C-5 substituent, reveal that these depend little on the nature of the group attached at C-3. In contrast, a change in the substituent at C-5 has a pronounced effect both on δ_{C-3} and on the δ_H values for the group attached at C-3; variations in δ_C values for the C-3 substituent are relatively smaller, but are in the same directions. Specifically, along the series **1**→**5**→**3** for a given C-5 substituent, the signals in question move consistently downfield, suggesting increasing positive charge density at the associated sites. This increase doubtless arises from the parallel decrease in the capacity of the 5-substituent to support positive charge, but at the same time it implies an increase in π delocalisation and thus of aromaticity. The pattern is particularly clear in the 3-unsubstituted salts **1d**, **5d** and **3d**, and accommodates also the NMR data for the salt **11**: δ_{3-H} 9.98 and δ_{C-3} 168.16.[3] The large (*ca.* 1.7 ppm) difference between δ_{3-H} and δ_{5-H} in the parent cation **3d** nevertheless suggests that, in spite of the electronegativity of the ring nitrogen atom, the greater positive charge density lies in

the vicinity of C-5. Data for the salts **3b** and **3d** may usefully be compared with those for the 1,3-dithiolium analogue **12**,[6a] $\delta_{2\text{-H}}$ 11.244, $\delta_{5\text{-H}}$ 9.250, $^4J_{HH}$ 2.2 ± 0.2 Hz, $\delta_{C\text{-}2}$ 178.11, which suggest a lower positive charge density in the latter. ^{13}C NMR spectra for 1,3-dithiolium salts have previously been reported only in the patent literature; full data for the salt **12** are given in the Experimental section.

Reactions at C-5.—In addition to the conversions **1**→**2**, **1**→**4**, **5**→**6** and **3**→**10** described above, one further reaction of 1,4,2-dithiazolium salts was investigated, for comparison with a reaction reported for analogous 1,3-dithiolium salts.

The latter are known to react with pyrroles, and with indole, to yield dithia-azafulvalenium salts *e.g.* **13**,[11a] which may be converted into conducting charge-transfer complexes.[11b] Treatment of an acetonitrile solution of the methylthio salt **5c** with 2,5-dimethylpyrrole at 25 °C, followed by dilution with diethyl ether after 1 h, led to the salt **14c** (68%); the analogues **14a** and **14b** were prepared similarly (*ca.* 80%). The NMR spectra, even



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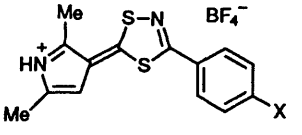

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a X = NO_2
b X = Cl
c X = H

at low temperatures, showed signals corresponding to a single product, indicating that only one geometrical isomer had been formed. This is surprising, since the rotational energy barrier, $\Delta G^{\ddagger}$, about the exocyclic C=C bond is expected to be higher than that (*ca.* 95 kJ mol^{-1}) associated with the exocyclic C=N bond in salts of type **1**,[7] so two geometrical isomers were expected. The pyrrolium ring in the compounds **14** carries greater positive charge than that in compound **13**, as evidenced by the relatively higher field chemical shifts for the ^1H and ^{13}C NMR signals in the latter.[11a] This is further evidence for the dithiazolium cation being more electronegative, and thus more electrophilic, than its 1,3-dithiolium counterpart, due to the presence of the ring nitrogen atom.

Experimental

UV spectra were recorded in 95% ethanol, unless otherwise indicated, on a Shimadzu UV 240 spectrophotometer, FT IR spectra were determined for Nujol mulls, unless otherwise stated, on a Nicolet 20 SXC instrument, and ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise indicated, on JEOL FX 90Q and GSX 270 spectrometers with Me_4Si used as internal reference; ^{13}C NMR signals refer to single carbon atoms unless otherwise indicated. *J* Values are given in Hz. Low and high resolution mass spectra were run on Hitachi RMS-4 and VG 7070S instruments, respectively.

The dithiolium salt **12** was prepared as described by Takamizawa and co-workers;[6a] ν_{max}/cm^{-1} 3050, 1594, 1468, 1406, 1093vs, 1082vs, 1012, 946, 825 and 624; $\delta_H(CF_3CO_2D$–$CD_3NO_2)$ 7.64 (2 H, m), 7.82 (2 H, m), 9.250 (1 H, d, *J* 2.2) and 11.244 (1 H, d, *J* 2.2); $\delta_C(CF_3CO_2D$–$CD_3NO_2)$ 123.03 (s), 131.26 (2 C, d), 132.36 (2 C, d), 138.87 (d), 141.70 (s), 165.50 (s) and 178.11 (d).

Preparation of the Dithiazolylidenepiperidinium Salts **1**.—The salts **1a** (35%) and **1b** (30%) as fluoroborates[7] and **1c** (60%) as the perchlorate[4] were prepared using the method of ref. 7. The piperidinodithioperformamide **7** was prepared using Shibuya's method,[4] 79%, ν_{max}/cm^{-1} 3306, 3225, 1474, 1435, 1239 and 695; δ_H 1.71 (6 H, m), 3.10 (2 H, s) and 3.96 (4 H, s, br); δ_C 24.29 (t), 25.65 (2 C, t), 51.8 (2 C, m, br) and 204.51 (s).

N-*Acylpiperidinodithioperformamides* **8**.—To a stirred solution of dithioperformamide **7** (3.0 g, 0.017 mol) in chloroform (50 cm^3) was added acetic formic anhydride (3.0 g, 0.034 mol), and stirring was continued at 50 °C for 1 h. The solvent was evaporated under reduced pressure, and the residue was recrystallised from ethanol to give N-*formylpiperidinodithioperformamide* **8d** (82%), m.p. 106–107 °C (Found: C, 41.2; H, 5.8; N, 13.5. $C_7H_{12}N_2OS_2$ requires C, 41.2; H, 5.9; N, 13.75%); *m/z* 204 (M^+, 27%), 160 (32) and 128 (100); ν_{max}/cm^{-1} 3165, 1693, 1246, 1220 and 755; δ_H 1.74 (6 H, s), 3.96 (4 H, s, br), 6.96 (1 H, s, br) and 7.99 (1 H, s, br); δ_C 24.11 (t), 25.68 (2 C, t), 51.63 (2 C, m, br), 170.67 (s) and 198.03 (s).

Similarly prepared from the piperidinodithioperformamide **7** and acetic anhydride, with heating at 70 °C for 2 h, was N-*acetylpiperidinodithioperformamide* **8e** (76%), m.p. 109–110 °C (ethanol) (Found: C, 44.25; H, 6.45; N, 12.65. $C_8H_{14}N_2OS_2$ requires C, 44.05; H, 6.4; N, 12.85%); *m/z* 218 (M^+, 6%), 160 (5) and 128 (100); ν_{max}/cm^{-1} 3210, 1716, 1247 and 1227; δ_H 1.72 (6 H, s), 2.29 (3 H, s), 3.97 (4 H, s, br) and 7.09 (1 H, s, br); δ_C 24.12 (2 C, q and t), 25.69 (2 C, t), 52.35 (2 C, m br), 172.39 (s) and 196.29 (s).

Cyclisation. The formyl compound **8d** (1.0 g, 4.9 mmol) was dissolved in acetic anhydride (10 cm^3) and 70% perchloric acid (1.06 g, 7.4 mmol) was added with cooling. The mixture was stirred at 25 °C for 1 h, diethyl ether (10 cm^3) was added slowly, and the precipitate was recrystallised from absolute ethanol to give 1-(1,4,2-*dithiazol-5-ylidene*)*piperidinium perchlorate* **1d** (82%), m.p. 116–118 °C (Found: C, 29.6; H, 3.7; N, 9.45. $C_7H_{11}ClN_2O_4S_2$ requires C, 29.3; H, 3.85; N, 9.75%); ν_{max}/cm^{-1} 3051, 1589, 1564 and 1097.

Similarly prepared from the acetyl compound **8e** using 52% fluoroboric acid in diethyl ether in place of 70% perchloric acid, and heating at 60 °C for 1 h, was 1-(3-*methyl*-1,4,2-*dithiazol*-5-*ylidene*)*piperidinium fluoroborate* **1e** (34%), m.p. 152–153 °C (absolute ethanol) (Found: C, 33.55; H, 4.4; N, 9.65. $C_8H_{13}BF_4N_2S_2$ requires C, 33.35; H, 4.5; N, 9.7%); ν_{max}/cm^{-1} 1595, 1570, 1089 and 1058.

1,4,2-*Dithiazole-5-thiones* **4**.—A general preparation is described. The appropriate iminium salt **1** (2.5 mmol) carefully purified, was dissolved in anhydrous methanol (5 cm^3), and dry hydrogen sulfide was passed into the solution at 25 °C for 1–3 h. Water (30 cm^3) was added and the mixture was extracted with dichloromethane (3 × 30 cm^3); the extracts were washed with water (2 × 30 cm^3), dried ($MgSO_4$), and the solvent was evaporated under reduced pressure.

The following compounds were prepared in this fashion: 3-(4-*nitrophenyl*)-1,4,2-*dithiazole-5-thione* **4a** (77%), m.p. 156–157 °C (acetonitrile–diethyl ether) (Found: C, 37.4; H, 1.7; N, 10.6. $C_8H_4N_2O_2S_3$ requires C, 37.5; H, 1.55; N, 10.95%); *m/z* 256 (M^+, 84%), 180 (81) and 108 (100); ν_{max}/cm^{-1} 1513, 1345, 1072, 952 and 850; δ_H 7.953 (2 H, m) and 8.362 (2 H, m); δ_C 124.61 (2 C, d), 128.57 (2 C, d), 136.43 (s), 149.58 (s), 169.48 (s) and 217.23 (s).

3-(4-Chlorophenyl)-1,4,2-dithiazole-5-thione **4b** (76%), m.p. 114–115 °C (lit.,[9] 108 °C); *m/z* 245, 247 (M^+, 50%), 169, 171 (100), 135, 137 (50) and 108 (55); λ_{max}/nm 258 and 352 (log ε 4.35 and 4.21); ν_{max}/cm^{-1} 1592, 1480, 1089, 942 and 826; δ_H 7.46 (2 H, m) and 7.68 (2 H, m); δ_C 128.85 (2 C, d), 129.73 (2 C, d), 130.32 (s), 138.74 (s), 171.02 (s) and 218.25 (s).

3-Phenyl-1,4,2-dithiazole-5-thione **4c** (77%), m.p. 112–114 °C (lit.,[9] 118 °C); *m/z* 211 (M^+, 57%), 135 (100), 108 (37) and 103 (37); ν_{max}/cm^{-1} 1483, 1445, 1072, 948 and 760; δ_H 7.41–7.57

(3 H, m) and 7.68–7.81 (2 H, m); δ_C 127.68 (2 C, d), 129.37 (2 C, d), 131.84 (s), 132.27 (d), 172.58 (s) and 218.98 (s).

3-*Unsubstituted* 1,4,2-*dithiazole*-5-*thione* **4d** (76%), yellow oil, purified by column chromatography (SiO_2; eluent light petroleum–dichloromethane, 1:1) (Found: M^+, 134.9272. C_2HNS_3 requires *M*, 134.9271); *m/z* 135 (M^+, 100%), 108 (70), 76 (96), 59 (54), 45 (27) and 27 (11); λ_{max}/nm 229, 268 and 339 (log ε 3.86, 3.36 and 4.14); ν_{max}(film)/cm^{-1} 3024, 2943, 1479, 1245, 1075vs, 1028 and 790; δ_H 8.910 (s); δ_C 160.16 (d) and 217.10 (s).

3-*Methyl*-1,4,2-*dithiazole*-5-*thione* **4e** (77%), m.p. 29–30 °C, yellow solid purified by column chromatography (SiO_2; eluent light petroleum–dichloromethane, 3:1) (Found: C, 24.25; H, 1.8; N, 9.45. $C_3H_3NS_3$ requires C, 24.15; H, 2.0; N, 9.4%); *m/z* 149 (M^+, 100%), 108 (84), 76 (99), 73 (91) and 41 (20); λ_{max}/nm 232, 262 and 342 (log ε 4.71, 4.23 and 5.08); ν_{max}(film)/cm^{-1} 2994, 2909, 1557, 1515, 1429, 1370, 1151, 1074, 1033, 767 and 621; δ_H 2.604 (s); δ_C 21.46 (q), 172.06 (s) and 220.41 (s).

1,4,2-*Dithiazol*-5-*ones* **9**.—To a stirred solution of the thione **4d** (0.1 g, 0.74 mmol) in chloroform (1 cm^3) and glacial acetic acid (1 cm^3) was added mercury(II) acetate (0.23 g, 0.74 mmol), and the mixture was heated at 70 °C with stirring for 2 h. The black mixture was cooled, diluted with dichloromethane (10 cm^3) and centrifuged. The supernatant liquid was decanted, the solvent was evaporated, and the residue was purified by column chromatography (SiO_2; eluent light petroleum–dichloromethane, 3:1) to give 1,4,2-dithiazol-5-one **9d** (24%) as an oil, for which the high-resolution MS data could not be obtained, containing a trace of the precursor **4d**; λ_{max}/nm 237 (log ε 3.70); ν_{max}(film)/cm^{-1} 3046, 2950, 1706vs, 1657vs, 1630vs, 1489, 843, 796 and 613; δ_H 8.847 (s); δ_C 153.37 (d) and 196.91 (s).

Similarly was prepared 3-*methyl*-1,4,2-*dithiazol*-5-*one* **9e** (59%) as an oil, purified by column chromatography (SiO_2; eluent light petroleum–dichloromethane, 1:1) (Found: M^+, 132.9650. $C_3H_3NOS_2$ requires *M*, 132.9656); *m/z* 133 (M^+, 39%), 73 (100), 59 (76) and 41 (15); λ_{max}/nm 235 (log ε 3.54); ν_{max}(film)/cm^{-1} 2988, 2896, 1717vs, 1658vs, 1621, 1559, 1515, 1426, 1372, 1156, 857, 784 and 614; δ_H 2.568 (s); δ_C 23.93 (q), 164.00 (s) and 198.95 (s)

5-*Methylthiodithiazolium Salts* **5**.—The method of Paton, Crosby and co-workers was used.[10] In general, the dithiazolethione **4** (3.0 mmol) was stirred with dimethyl sulfate (2 cm^3) at 100 °C (80 °C for compounds **4d** and **4e**) until a homogeneous solution was obtained (*ca.* 20 min). The mixture was cooled, and 52% fluoroboric acid in diethyl ether (0.49 g, 3.0 mmol) was added, followed by dry diethyl ether (10 cm^3). The solid precipitate was separated and recrystallised from acetonitrile–diethyl ether. The following were were thus prepared. 5-*Methylthio*-3-(4-*nitrophenyl*)-1,4,2-*dithiazolium tetrafluoroborate* **5a** (73%), m.p. 133–134 °C (Found: C, 30.25; H, 1.55; N, 7.55. $C_9H_7BF_4N_2O_2S_3$ requires C, 30.2; H, 1.95; N, 7.8%); ν_{max}/cm^{-1} 3098, 1609, 1539, 1348, 1063vs, 1037vs, 1015, 860, 852 and 750.

3-(4-Chlorophenyl-5-methylthio-1,4,2-dithiazolium tetrafluoroborate **5b** (60%), m.p. 134–135 °C (lit.,[10] 139–141 °C); ν_{max}/cm^{-1} 1590, 1477, 1097, 1052vs, 1034vs, 1018, 844, 830 and 661.

5-Methylthio-3-phenyl-1,4,2-dithiazolium tetrafluoroborate **5c** (59%), m.p. 141–142 °C (lit.,[10] 137–138 °C); ν_{max}/cm^{-1} 1508, 1484, 1109, 1050vs, 1036vs, 745 and 727.

3-Unsubstituted 5-methylthio-1,4,2-dithiazolium tetrafluoroborate **5d** (56%), m.p. 111–113 °C (satisfactory microanalysis could not be obtained); ν_{max}/cm^{-1} 3073, 1483, 1430, 1112, 1085vs, 1055vs, 1031vs, 877, 801 and 652.

3-Methyl-5-methylthio-1,4,2-dithiazolium tetrafluoroborate **5e** (50%), m.p. 95 °C (decomp) (satisfactory microanalysis could not be obtained); *m/z* 164 (M^+, 18%), 149 (28), 108 (23), 90 (72), 76 (69) and 49 (100); ν_{max}/cm^{-1} 1510, 1420, 1320, 1285, 1050vs, 958, 942 and 790.

Reduction of Dithiazolium Salts with Sodium Borohydride.—The same general procedure was used to reduce the salts **1**, **3** and **5**. Sodium borohydride (0.38 g, 10 mmol) was dissolved in a vigorously stirred mixture of water (150 cm^3) and diethyl ether (150 cm^3) at 0 °C. The appropriate dithiazolium salt (1.0 mmol) was added in small portions during 5 min, vigorous stirring was continued for 30 min, and the diethyl ether layer was separated and dried ($MgSO_4$). The solvent was evaporated, and the residue was recrystallised, or purified by column chromatography if an oil.

5-*Piperidinodithiazoles* **2**.—Reduction of the salts **1** as above gave (*a*) 3-(4-nitrophenyl)-5-piperidino-1,4,2-dithiazole **2a** (60%), m.p. 108–109 °C (from aqueous methanol) (lit.,[7] 112 °C); (*b*) the 3-(4-chlorophenyl)-5-piperidino-1,4,2-dithiazole **2b** (50%), m.p. 83–84 °C (from aqueous ethanol) (lit.,[7] 82 °C); and (*c*) 3-*phenyl*-5-*piperidino*-1,4,2-*dithiazole* **2c** (58%), m.p. 100 °C (from ethanol) (Found: M^+, 264.0757. $C_{13}H_{16}N_2S_2$ requires *M*, 264.0755); *m/z* 264 (M^+, 14%), 161 (30), 129 (80), 128 (68), 103 (100) and 84 (44); ν_{max}/cm^{-1} 1528, 1489, 1364, 1169, 1089, 990, 937, 759 and 689; δ_H 1.46–1.68 (6 H, m), 2.40–2.52 (4 H, m), 6.630 (1 H, s), 7.35–7.47 (3 H, m) and 7.73–7.90 (2 H, m); δ_C 23.97 (t), 25.35 (2 C, t), 47.70 (2 C, t), 86.68 (d), 128.28 (2 C, d), 128.61 (2 C, d), 130.21 (d), 133.59 (s) and 160.76 (s).

5-*Methylthiodithiazoles* **6**.—Reduction of the salts **5** as above gave (*a*) 5-*methylthio*-3-(4-*nitrophenyl*)-1,4,2-*dithiazole* **6a** (75%), m.p. 96–97 °C (from ethanol) (Found: C, 39.8; H, 2.9; N, 10.0. $C_9H_8N_2O_2S_3$ requires C, 39.7; H, 2.95; N, 10.3%); *m/z* 272 (M^+, 6%), 226 (100), 180 (8), 150 (4) and 76 (44); ν_{max}/cm^{-1} 1604, 1593, 1528, 1514, 1347, 940, 850 and 759; δ_H 2.150 (3 H, s), 6.593 (1 H, s), 7.90 (2 H, m) and 8.25 (2 H, m); δ_C 10.97 (q), 65.82 (d), 123.98 (2 C, d), 128.96 (2 C, d), 137.55 (s), 148.79 (s) and 156.18 (s).

(*b*) 3-(4-*Chlorophenyl*)-5-*methylthio*-1,4,2-*dithiazole* **6b** (55%), m.p. 65–66 °C, purified by column chromatography (SiO_2; eluent light petroleum–diethyl ether, 10:1) (Found: M^+, 260.9511. C_9H_8ClNS requires *M*, 260.9507); *m/z* 161, 263 (M^+, 12%), 214, 216 (100), 169, 171 (11), 137, 139 (21) and 77 (40); ν_{max}(KBr)/cm^{-1} 2907, 1592, 1485, 1398, 1092, 932, 831 and 755; δ_H 2.141 (3 H, s), 6.506 (1 H, s), 7.37 (2 H, m) and 7.68 (2 H, m); δ_C 10.89 (q), 65.12 (d), 129.04 (2 C, d), 129.47 (2 C, d), 131.02 (s), 136.87 (s) and 157.48 (s).

(*c*) 5-*Methylthio*-3-*phenyl*-1,4,2-*dithiazole* **6c** (61%), oil, purified by column chromatography (SiO_2; eluent light petroleum–diethyl ether, 1:1) (Found: M^+, 226.9898. $C_9H_9NS_3$ requires *M*, 226.9897); *m/z* 227 (M^+, 4%), 180 (100), 135 (6), 103 (19), 77 (CHS_2^+, 38) and 77 ($C_6H_5^+$, 15); ν_{max}(film)/cm^{-1} 2901, 1533, 1488, 1446, 1244, 1235, 1075, 933, 756 and 688; δ_H 2.141 (3 H, s), 6.479 (1 H, s), 7.35–7.47 (3 H, m) and 7.70–7.80 (2 H, m); δ_C 10.65 (q), 64.55 (d), 128.20 (2 C, d), 128.69 (2 C, d), 130.61 (d), 132.35 (s) and 158.73 (s).

(*d*) 3-Unsubstituted 5-methylthio-1,4,2-dithiazole **6d** (78%), unstable oil, purified by column chromatography (SiO_2; eluent light petroleum–dichloromethane, 2:1), high-resolution MS data could not be obtained; *m/z* 151 (M^+, 10%), 150 (16), 135 (21), 124 (21), 104 (25), 92 (42), 77 (25), 76 (42), 59 (21) and 45 (100); ν_{max}/cm^{-1} 3012, 2976, 2939, 2912, 1562, 1533, 1511, 1431, 1418, 962, 817, 779vs and 749vs; δ_H 2.097 (3 H, s), 6.445 (1 H, s) and 7.765 (1 H, s); δ_C 10.40 (q), 62.90 (d) and 145.89 (d).

(*e*) 3-Methyl-5-methylthio-1,4,2-dithiazole **6e**, δ_H(60 MHz)

2.11 (3 H, s), 2.23 (3 H, s) and 6.34 (1 H, s), which could not be separated from co-products without decomposition.

5-Unsubstituted Dithiazoles **10**.—Direct reduction of the crude salts **3** as above gave (*a*) 3-(*4-chlorophenyl*)-1,4,2-*dithiazole* **10b** (69%), oil, purified by column chromatography (SiO_2; eluent light petroleum–dichloromethane, 1:1) (Found: C, 44.95; H, 2.85; N, 6.3. $C_8H_6ClNS_2$ requires C, 44.55; H, 2.75; N, 6.5%); ν_{max}/cm^{-1} 1592, 1481, 1400, 1244, 1090, 925, 829 and 778; δ_H 4.708 (2 H, s), 7.350 (2 H, m) and 7.651 (2 H, m); δ_C 39.29 (t), 128.81 (2 C, d), 129.51 (2 C, d), 130.93 (s), 136.65 (2) and 160.79 (s).

(*b*) 3-Phenyl-1,4,2-dithiazole **10c** (73%), oil, purified by column chromatography (SiO_2; eluent light petroleum–dichloromethane, 2:1), too unstable for microanalysis; ν_{max}(film)/cm^{-1} 3058, 3031, 2920, 1554, 1529, 1488, 1445, 1247, 929, 759 and 688; δ_H 4.675 (2 H, s), 7.31–7.45 (3 H, m) and 7.65–7.78 (2 H, m); δ_C 38.98 (t), 128.31 (2 C, d), 128.55 (2 C, d), 130.58 (d), 132.51 (s) and 162.11 (s).

5-Unsubstituted 1,4,2-Dithiazolium Salts **3**.—*From 5-piperidinodithiazoles* **2**. The 3-(4-nitrophenyl) compound **2a** (42 mg, 0.13 mmol) was dissolved in acetic anhydride (1 cm^3) and 60% perchloric acid (44 mg, 0.26 mmol) was added. The mixture was stirred for 1 h at 25 °C, with protection from moisture, dry diethyl ether (5 cm^3) was added, and the precipitated product **3a** was separated and dried *in vacuo*. The ^{1}H NMR spectrum (Table 1) showed the presence of some other products; the compound reacted with the solvent (CF_3CO_2D–CD_3NO_2) before the ^{13}C NMR spectrum could be recorded.

From 5-methylthiodithiazoles **6**. In general, the carefully purified dithiazole **6** (0.5 mmol) was dissolved in acetic anhydride (1 cm^3) and 70% perchloric acid (0.14 g, 1.0 mmol) was added at 25 °C. After stirring for 1 h, diethyl ether (2–3 cm^3) was added, and the precipitated product was separated and dried *in vacuo*; ^{1}H and ^{13}C NMR spectroscopic data are shown in Table 1. (*a*) 3-(4-Chlorophenyl)-1,4,2-dithiazolium perchlorate **3b** was isolated (79%), ν_{max}/cm^{-1} 3083, 3034, 1591, 1458, 1401, 1111, 1093vs, 1015, 956, 844 and 623.

(*b*) 3-Phenyl-1,4,2-dithiazolium perchlorate **3c** was too unstable for successful recording of IR or ^{13}C NMR spectra.

(*c*) 3-Unsubstituted 1,4,2-dithiazolium perchlorate **3d** was isolated (50%), ν_{max}/cm^{-1} 1108 and 1089.

Dithiazol-5-ylidenepyrrolium Salts **14**.—*General procedure*. To a stirred solution of the appropriate methylthio salt **5** (0.6 mmol) in dry acetonitrile (5 cm^3) at 25 °C was added freshly distilled 2,5-dimethylpyrrole (57 mg, 0.6 mmol); the solution turned deep red. Stirring was continued for 2 h, dry diethyl ether was added, and the precipitated product **14** was recrystallised from acetonitrile and diethyl ether. The following compounds were prepared in this fashion. (*a*) 2,5-*Dimethyl*-3-[3-(*4-nitrophenyl*)-1,4,2-*dithiazol*-5-*ylidene*]*pyrrolium tetrafluoroborate* **14a** (82%), m.p. 195–196 °C (decomp.) (Found: C, 41.7; H, 2.75; N, 10.4. $C_{14}H_{12}BF_4N_3O_2S_2$ requires C, 41.5; H, 2.95; N, 10.35%); λ_{max}/nm 259 and 322sh (log ε 4.34 and 4.14); ν_{max}/cm^{-1} 3267, 3209, 3110, 1605, 1531, 1489, 1474vs, 1461vs, 1351, 1084, 992, 919 and 852; δ_H(CD_3CN) 2.261 (3 H, d, *J* 1.2), 2.613 (3 H, s), 6.437 (1 H, q, *J* 1.2), 8.237 (2 H, m), 8.422 (2 H, m) and 10.910 (1 H, s, br); δ_C(CD_3CN) 12.48 (q), 16.30 (q), 109.34 (d), 116.81 (s), 125.94 (2 C, d), 130.99 (2 C, d), 135.95 (s), 137.47 (s), 149.24 (s), 151.61 (s), 172.46 (s) and 191.77 (s).

(*b*) 3-[3-(*4-Chlorophenyl*)-1,4,2-*dithiazol*-5-*ylidene*]-2,5-*dimethylpyrrolium tetrafluoroborate* **14b** (78%), m.p. 194–195 °C (decomp.) (Found: C, 42.7; H, 2.9; N, 7.1. $C_{14}H_{12}BClF_4N_2S_2$ requires C, 42.6; H, 3.05; N, 7.1%); λ_{max}/nm 268, 363 and 419 (log ε 3.31, 3.13 and 3.37); ν_{max}/cm^{-1} 3264, 3210, 3091, 1589, 1525, 1488, 1475vs, 1465vs, 1352, 1086, 993, 923 and 842; δ_H(CD_3CN) 2.251 (3 H, d, *J* 1.2), 2.588 (3 H, s), 6.403 (1 H, q, *J* 1.2), 7.648 (2 H, m), 7.999 (2 H, m) and 10.834 (1 H, s, br); δ_C(CD_3CN) 12.46 (q), 16.22 (q), 109.21 (d), 116.52 (s), 129.76 (s), 131.15 (2 C, d), 131.20 (2 C, d), 137.16 (s), 140.66 (s), 148.56 (s), 173.66 (s) and 192.18 (s).

(*c*) 2,5-*Dimethyl*-3-(3-*phenyl*-1,4,2-*dithiazol*-5-*ylidene*)*pyrrolium tetrafluoroborate* **14c** (68%), m.p. 190–193 °C (decomp.) (Found: C, 46.45; H, 3.6; N, 7.7. $C_{14}H_{13}BF_4N_2S_2$ requires C, 46.65; H, 3.6; N, 7.8%); λ_{max}/nm 257, 361 and 416 (log ε 3.79, 3.69 and 3.92); ν_{max}/cm^{-1} 3269, 3220, 1523, 1496, 1479, 1460vs, 1447vs, 1355, 1073, 992, 921, 814 and 764; δ_H(CD_3CN) 2.256 (3 H, d, *J* 1.2), 2.594 (3 H, s), 6.417 (1 H, q, *J* 1.2), 7.61–7.76 (3 H, m), 8.02–8.07 (2 H, m) and 10.75 (1 H, s, br); δ_C(CD_3CN) 12.45 (q), 16.20 (q), 109.20 (d), 116.37 (s), 129.72 (2 C, d), 131.02 (2 C, d), 134.98 (d), 136.96 (s), 148.19 (s), 175.12 (s) and 192.58 (s).

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