Dithiazoles and Related Compounds. Part 3.[1] Preparation of 5*H*-1,4,2-Dithiazoles *via* 1,3-Dipolar Cycloadditions between Nitrile Sulphides and Thiocarbonyl Compounds, and some Conversions into 3,5-Diaryl-1,4,2-dithiazolium Salts[2]

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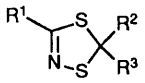
Thermolysis of 1,3,4-oxathiazol-2-ones **3** in the presence of thiocarbonyl compounds gives modest to good yields of the little-known 5*H*-1,4,2-dithiazoles **1**, the reaction being successful with diaryl, aryl alkyl and dialkyl ketones, and thiono esters, but failing with dithio esters and tertiary thioamides. The influence of substituents is discussed. Solvolysis of 5-ethoxy-5*H*-1,4,2-dithiazoles, derived from thiono esters, with perchloric acid in acetic anhydride gives high yields of 3,5-diaryl-1,4,2-dithiazolium salts **9**.

The 5*H*-1,4,2-dithiazoles **1** constitute a little-known ring system. With the exception of examples prepared recently by the reduction of 1,4,2-dithiazolium salts with sodium borohydride,[1,3,4] those postulated as reaction intermediates,[5] and some 1,1-dioxides,[6] only three (spiro) derivatives appear to have



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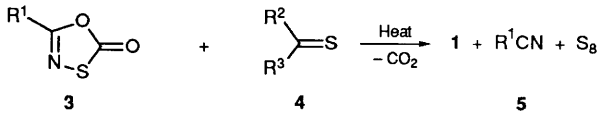
been isolated.[7] A potentially general synthetic route to these compounds, which have an unexplored and possibly rich chemistry, is the 1,3-dipolar cycloaddition of a nitrile sulphide **2**[8] and a thiocarbonyl compound. Although nitrile oxides have been added to carbonyl and to thiocarbonyl groups to give 5*H*-1,4,2-dioxazoles[9] and 5*H*-1,4,2-oxathiazoles[10] respectively, and nitrile sulphides have been added to carbonyl groups to give 2*H*-1,3,4-oxathiazoles,[11] this approach, with one unsuccessful exception,[5] does not appear to have been applied to the preparation of 5*H*-1,4,2-dithiazoles. We report now an investigation into the scope and limitations of this reaction.

Results and Discussion

Preparation of 5H-1,4,2-*Dithiazoles*.—The most convenient method for generating nitrile sulphides[8] **2** is the thermal decomposition of 1,3,4-oxathiazol-2-ones **3** which, in turn, may be prepared[12] bearing a wide variety of substituents R^1. Thermolyses have generally been carried out in the presence of a suitable dipolarophile, which traps the transient nitrile sulphide, with the formation of a five-membered ring heterocycle.[8]

In this work, reactions were carried out by slow dropwise addition during 1–2 h of a xylene solution of an oxathiazolone **3** (Scheme 1) to a boiling solution of the appropriate thiocarbonyl compound **4**, also in xylene under dry N_2. Refluxing was continued until TLC analysis (SiO_2; light petroleum–ether) showed complete consumption of one of the reagents. Equimolar amounts of each reagent were used, yields being little affected in these cases by use of, for example, 2 mol of the thiocarbonyl compound. *o*-Xylene, in which the reactants were more soluble, gave slightly better yields than *p*-xylene; significantly poorer results were obtained in ethylbenzene, chlorobenzene and methoxybenzene. Product 5*H*-1,4,2-dithiazoles **1** (Table 1) were isolated free from by-product nitriles **5** and sulphur by chromatography on silica, and in most cases were purified further by recrystallization. Regioisomeric 1,2,3-dithiazole products were not observed. Inseparable mixtures of diastereoisomers were obtained from reactions with the chiral

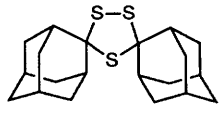


3 **4** **5**

	R^1	R^2	R^3
a	4-$NO_2C_6H_4$	**a** Ph	Ph
b	4-ClC_6H_4	**b** Ph	Bu^t
c	4-FC_6H_4	**c** Ph	Me
d	Ph	**d** Me	Bu^t
e	4-MeC_6H_4	**e**	
f	4-$MeOC_6H_4$	**f**	
g	Bu^t	**g** Ph	OEt
h	Me	**h** 4-ClC_6H_4	OEt
i	2-ClC_6H_4	**i** 3-$MeOC_6H_4$	OEt
		j Ph	OCH_2CF_3

Scheme 1

thioketone **4f**, while adamantanethione **4e** gave as an additional by-product a high yield of the trithiolane **6**.[13] We subsequently found that this same compound **6** could be prepared in similar yield simply by refluxing adamantanethione and sulphur together under N_2 in xylene. No analogous trithiolanes were



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observed in reactions with other thioketones. Cycloadducts were isolated successfully from diaryl, alkyl aryl and dialkyl thioketones, but attempts to prepare trialkyl-1,4,2-dithiazoles from, for example, compounds **3g** and **4e** failed, the nitrile **5** being formed quantitatively. Adducts could also be prepared from the thiono esters **4g–j**, but not from dithio esters or tertiary thioamides. Product 1,4,2-dithiazoles **1** were reasonably stable under the reaction conditions, compound **1e** for example being 55% decomposed into the nitrile **5e**, sulphur and benzophenone, only after 72 h refluxing in xylene.

Yields, analytical results and spectroscopic data for the products **1** are given in Tables 1 and 2, and confirm the proposed structures. Common peaks assignable to the dithiazole ring were not apparent in IR spectra, which are thus

not reported here. Ring carbon atom chemical shifts for the six compounds **1a–f** correlate with Hammett σ_m constants: for δ_{c-3} $r = 0.993$, $\rho = -3.89$ and for δ_{c-5} $r = 0.969$, $\rho = 1.79$. Charge transfer is presumably by σ bond polarisation; interestingly C-3 and C-5 respond in opposite senses (*cf.* the sign of ρ) to the electron demand of the aryl *para*-substituent.

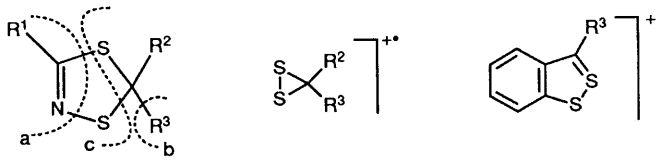
All adducts showed a parent ion in their mass spectra, subsequent fragmentation following one or more of pathways a, b and c (Fig. 1) depending upon substituents. These pathways were all characterized by prominent metastable peaks. For $R^2 = R^3 = Ph$, path a predominated, the fragment **7** losing H to give **8**, or an isomer, as the base peak. For $R^3 = Bu^t$, and for compounds **1q–t**, path b predominated, the resulting dithiazolium cation giving the base peak, and fragmenting further by path a. For compounds **1k–m** all three pathways were followed, the order being b ≫ a > c, while for the alkoxy adducts **1u–w** formation of the fragment **7** was followed by degradation to $R^2C{\equiv}O^+$ as the base peak. In all spectra $R^2C{\equiv}S^+$ was prominent, while $R^1C{\equiv}N^{+\bullet}$ was observed as only a minor ion, being most prominent for electron-releasing R^1. Path c, the reverse of the 1,3-dipolar cycloaddition, if observed, was always a minor process, in contrast with results reported for 2*H*-1,3,4,-oxathiazoles[11] and 5*H*-1,4,2-dioxazoles.[14]

The yields of cycloadducts from the nitrile sulphides **2** have generally been discussed in terms of the stability of the nitrile sulphide *vis-a-vis* the rate of cycloaddition as determined by dipole and dipolarophile frontier orbital energies.[8] In general, for a series of nitrile sulphides **2** yields *increase* with increasingly electron-donating R^1;[11,12,15] however, there are examples where the yields *decrease* in the same order.[16,17]

In the present study, an additional factor is the thermal instability of the thioketone, which will become significant when the rate of fragmentation of the oxathiazolone **3** is slow, as when R^1 is electron withdrawing.[12] It will be seen from Table 1 that for the relatively unstable thioketones **4b–f** yields are little influenced by the nature of R^1. In reactions with the more stable thiobenzophenone **4a**, however, yields are now related to the electronic properties of the dipole substituent R^1, *decreasing* with increasing electron donating power. Since oxathiazolones bearing electron donating R^1 are generally accepted to decompose more rapidly,[12] giving more stable[18] and faster-reacting nitrile sulphides relative to those bearing electron withdrawing R^1, the observed yields from **4a** appear to be in the order opposite to that expected. However, the results may be rationalized if the reaction between the nitrile sulphide and the thiocarbonyl group is slow. For $R^1 = 4\text{-}MeOC_6H_4$, rapid decomposition of the oxathiazolone would lead to a high concentration of nitrile sulphide, which is expected to fragment rapidly to nitrile and sulphur by high order kinetics,[18] leading to a low yield of the cycloadduct **1**. For $R^1 = 4\text{-}NO_2C_6H_4$, decomposition of the oxathiazolone would be slow, generating a low concentration of nitrile sulphide, which should decompose more slowly by something approaching first order kinetics.[18] The higher concentration of dipolarophile is expected to favour adduct formation.[16]

The thiono esters **4g–j** are also thermally stable, but gave only low yields of adducts **1u–x** from the nitrile sulphide **2a**, the other product (*ca.* 85%) being 4-nitrobenzonitrile. Attempts to increase the rate of cycloaddition by making the substituents R^2 or R^3 more electron withdrawing can be seen to have had no significant effect on the yield.

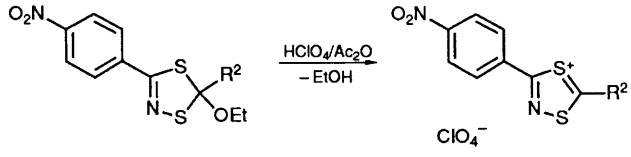
Formation of 3,5-*Diaryl*-1,4,2-*dithiazolium Salts.*—In the early stages of this work,[2] the only known 1,4,2-dithiazolium salts bore a hetero-linked substituent at C-5, which carried much of the positive charge of the cation; examples in which the charge was forced into the heterocyclic ring, thus generating an aromatic cation, were unknown. The observation of a



7 **8**

Fig. 1

prominent dithiazolium cation peak in the mass spectra of most products **4**, through facile loss of R^3, suggested that such aromatic species might be generated synthetically by solvolysis of appropriate substituents R^3. Treatment of the ethoxy adduct **1u** with 70% $HClO_4$ in acetic anhydride for 1 h at 25 °C followed by dilution with anhydrous ether gave the yellow salt **9a** (96%). Similar treatment of the adducts **1v** and **1w**, led to the salts **9b** (86%) and **9c** (91%). The salts were unchanged after storage for 6 months over P_4O_{10}, but rapidly reacted with moisture, or with any solvents more nucleophilic than CF_3CO_2H and CH_3NO_2. ^{13}C NMR chemical shifts for the heterocycle C-3 in the salts **9** (δ_C 182.5) suggested greater positive charge density at this site, and thus greater π delocalisation, than in the analogue **9d** (δ_C 166.42) in which the positive charge lies predominantly on the exocyclic NMe_2 group.[3]



1u R^2 = Ph
1v R^2 = 4-ClC_6H_4
1w R^2 = 3-$MeOC_6H_4$

9a R^2 = Ph
9b R^2 = 4-ClC_6H_4
9c R^2 = 3-$MeOC_6H_4$
9d R^2 = Me_2N

Scheme 2

Although the salts **9** were formed efficiently, the low preparative yields of their precursor ethoxydithiazoles **1u–w** makes this route to 3,5-diaryl-1,4,2-dithiazolium salts less useful than a recently reported alternative.[1]

Experimental

IR spectra were recorded on a Perkin-Elmer 157G instrument with polystyrene being used in calibration. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise stated, on JEOL FX90Q and GSX 270 spectrometers with Me_4Si used as internal reference, and mass spectra on a Hitachi RMS-4 instrument. ^{13}C NMR signals refer to single carbon atoms unless otherwise stated.

The oxathiazolones **3** were prepared from the appropriate amide and chlorocarbonylsulphenyl chloride;[12] **3a** (55%), m.p. 150–151 °C (decomp.) [lit.,[12] (39%), m.p. 168–169 °C (decomp.)] **3b** (40%), m.p. 126–128 °C [lit.,[12] (48%), m.p. 129–131 °C]; **3c** (78%), m.p. 98–99 °C [lit.,[19] (74%), m.p. 99–101 °C]; **3d** (71%), m.p. 71–72 °C [lit.,[12] (83%), m.p. 69–71 °C]; **3e** (50%), m.p. 89–90 °C [lit.,[12] (66%), m.p. 91–92 °C]; **3f** (51%), m.p. 108–109 °C [lit.,[11] (54%), m.p. 111 °C]; **3g** (41%) [lit.,[12] (33%), b.p. 35–36 °C (1.2 mmHg)]; **3h** (44%) [lit.,[12] (56%), b.p. 75–76 °C (30 mmHg)]; and **3i** (84%), m.p. 56–57 °C [lit.,[20] (81%), m.p. 55 °C]. Thiocarbonyl compounds **4** were prepared from the corresponding carbonyl compounds by heating with Lawesson's reagent under N_2 in refluxing toluene or xylene,[21] with the exception of adamantanethione **4e**, which was prepared from adamantanone, and phosphorus pentasulphide in pyridine.[22] The products were purified by column chromatography on silica with ether–light petroleum (b.p. 60–80 °C) (1:5) as the eluent, and were used without further characterisation.

Table 1 Preparative, physical and analytical data for 5*H*-1,4,2-dithiazoles **1**

Compound (formula)	Substituents R¹	R²	R³	Reaction time (h)[a]	Yield (%)	M.p. (°C)	Solvent	Found (%) (Required) C	H	N	M^+
1a $C_{20}H_{14}N_2O_2S_2$	4-$NO_2C_6H_4$	Ph	Ph	24	75	125–126	EtOH	63.35 (63.5)	3.9 (3.7)	7.3 (7.4)	378
1b $C_{20}H_{14}ClNS_2$	4-ClC_6H_4	Ph	Ph	6	40	80–81	EtOH	65.2 (65.3)	4.0 (3.8)	3.8 (3.8)	369/371
1c $C_{20}H_{14}FNS_2$	4-FC_6H_4	Ph	Ph	7	48	56–58	Petroleum	68.6 (68.4)	4.15 (4.0)	3.7 (4.0)	351
1d $C_{20}H_{15}NS_2$	Ph	Ph	Ph	7	35	94–96	EtOH	71.95 (72.05)	4.4 (4.5)	4.25 (4.2)	333
1e $C_{21}H_{17}NS_2$	4-MeC_6H_4	Ph	Ph	7	35	105–107	EtOH–H_2O	72.75 (72.6)	5.05 (4.9)	3.9 (4.05)	347
1f $C_{21}H_{17}NOS_2$	4-$MeOC_6H_4$	Ph	Ph	4	30	150–151	EtOH	69.15 (69.4)	4.85 (4.7)	3.75 (3.85)	363
1g $C_{18}H_{19}NS_2$	Bu^t	Ph	Ph	5	13	55–56	EtOH–H_2O	69.0 (69.0)	6.15 (6.05)	4.35 (4.45)	313
1h $C_{15}H_{13}NS_2$	Me	Ph	Ph	4	10	37.5–38	Petroleum	66.3 (66.4)	4.8 (4.8)	5.15 (5.15)	271
1i $C_{18}H_{18}N_2O_2S_2$	4-$NO_2C_6H_4$	Ph	Bu^t	12	25	118–119	EtOH	60.2 (60.35)	5.1 (5.5)	7.55 (7.8)	358
1j $C_{19}H_{21}NOS_2$	4-$MeOC_6H_4$	Ph	Bu^t	5	15	87–88	EtOH–H_2O	66.15 (66.45)	6.2 (6.1)	3.9 (4.1)	343
1k $C_{15}H_{12}N_2O_2S_2$	4-$NO_2C_6H_4$	Ph	Me	5	20	94–95	$CHCl_3$–Petroleum	57.15 (56.95)	3.95 (3.8)	8.7 (8.85)	316
1l $C_{15}H_{12}ClNS_2$	2-ClC_6H_4	Ph	Me	4	25	Oil		59.05 (58.9)	4.05 (3.95)	4.7 (4.6)	305/307
1m $C_{16}H_{15}NOS_2$	4-$MeOC_6H_4$	Ph	Me	4	19	81–82	EtOH–H_2O	63.85 (63.8)	4.85 (5.0)	4.7 (4.65)	301
1n $C_{13}H_{17}N_2O_2S_2$	4-$NO_2C_6H_4$	Me	Bu^t	5	20	97–98	$CHCl_3$–Petroleum	52.55 (52.7)	5.5 (5.4)	9.25 (9.5)	296
1o $C_{13}H_{16}ClNS_2$	2-ClC_6H_4	Me	Bu^t	5	38	Oil		54.6 (54.65)	5.85 (5.6)	4.75 (4.9)	285/287
1p $C_{14}H_{20}NOS_2$	4-$MeOC_6H_4$	Me	Bu^t	4	21	84–85	EtOH–H_2O	59.9 (59.8)	6.9 (6.75)	5.05 (5.0)	281
1q $C_{17}H_{18}N_2O_2S_2$	4-$NO_2C_6H_4$	C_9H_{14}[c]		6	21	209–210	$CHCl_3$–Petroleum	58.6 (58.95)	5.35 (5.2)	7.95 (8.1)	346
1r $C_{18}H_{21}NOS_2$	4-$MeOC_6H_4$	C_9H_{14}[c]		4	15	118–120	EtOH–$CHCl_3$	65.45 (65.25)	6.0 (6.35)	4.3 (4.2)	331
1s $C_{17}H_{20}N_2O_2S_2$	4-$NO_2C_6H_4$	C_9H_{16}[d]		12	6	130–133	EtOH–H_2O	58.5 (58.6)	5.95 (5.75)	7.75 (8.05)	348
1t $C_{18}H_{23}NOS_2$	4-$MeOC_6H_4$	C_9H_{16}[d]		4	*ca.* 1	Gum			*e*		333
1u $C_{16}H_{14}N_2O_3S_2$	4-$NO_2C_6H_4$	Ph	OEt	24	13	139–141	EtOH	55.75 (55.5)	4.1 (4.05)	7.8 (8.1)	346
1v $C_{16}H_{13}ClN_2O_3S_2$	4-$NO_2C_6H_4$	4-ClC_6H_4	OEt	24	11	112–113	$CHCl_3$–Petroleum	50.4 (50.45)	3.4 (3.4)	7.1 (7.35)	380/382
1w $C_{17}H_{16}N_2O_4S_2$	4-$NO_2C_6H_4$	3-$MeOC_6H_4$	OEt	24	12	139–140	EtOH–H_2O	54.2 (54.25)	4.4 (4.25)	7.4 (7.45)	376
1x $C_{16}H_{11}F_3N_2O_3S_2$	4-$NO_2C_6H_4$	Ph	OCH_2CF_3	24	11	173–174	EtOH	48.05 (48.0)	2.7 (2.75)	6.85 (7.0)	400

[a] In refluxing *p*-xylene; measured from start of addition. [b] Petroleum = light petroleum (b.p. 60–80 °C). [c] Spiroadamantane. [d] Spirobornane. [e] Insufficient product for microanalysis.

Yields: **4a** (90%), m.p. 50–52 °C [lit.,[21] (98%), m.p. 57 °C]; **4b** (34%); **4c** (12%); **4d** (14%); **4e** (67%) [lit.,[22] (90%)]; **4f** (42%); **4g** (87%); **4h** (92%); **4i** (55%) and **4j** (24%).

Preparation of the 5H-1,4,2-*Dithiazoles* **1**.—In general, a solution of the oxathiazolone **3** (0.01 mol) in *p*-xylene (40 ml) was added during 1–2 h to a refluxing solution of the appropriate thiocarbonyl compound **4** (0.01 mol), also in xylene (20 ml) under dry N_2, refluxing being continued for various periods of time until TLC analysis showed the complete consumption of one of the reagents. Total heating times are given in Table 1. The solvent was removed under reduced pressure, and the product was purified by column chromatography [SiO_2; eluent ether–light petroleum (b.p. 60–80 °C)], followed, in the case of solid products, by recrystallisation. By-products were generally the nitrile **5**, sulphur and the carbonyl compound; in the reactions with adamantanethione **4e**, however, the trithiolane **6** was also isolated (60–70%) m.p. 183–185 °C (lit.,[13] m.p. 189–191 °C); δ_H 1.80 (16 H, m, br) and 2.23 (12 H, m, br); δ_C 26.76, 27.08, 36.84, 37.38, 38.08, 39.54 and 90.41; *m/z* 364 (M^+, 10%), 300 (5), 198 (100), 166 (30) and 133 (66). Yields, m.p.s and microanalytical data are given in Table 1, while ^1H and ^{13}C NMR spectroscopic assignments are in Table 2.

Independent Preparation of the 1,2,4-*Trithiolane* **6**.—A mixture of adamantanethione **4e** (0.30 g, 1.8×10^{-3} mol) and sulphur (0.06 g, 2.25×10^{-4} mol) in *p*-xylene (5 ml) was refluxed under N_2 until the red colour disappeared. The solvent was evaporated and the residue was purified by chromatography [SiO_2; eluent ether–light petroleum (b.p. 60–80 °C); 5:1] to give the trithiolane **6** (0.27 g, 82%), m.p. and spectroscopic properties identical with those of the sample described above.

Preparation of the 1,4,2-*Dithiazolium Salts* **9**.—A general

Table 2 ^{1}H and ^{13}C NMR spectroscopic data for selected 5*H*-1,4,2-dithiazoles **1**

	$\delta_H(CDCl_3)$			$\delta_C(CDCl_3)$								
				Dithiazole		R^1						
Compd.	R^1	R^2	R^3	C-3	C-5	Aryl[a]		Alkyl	R^2[a]		R^3	
1a	7.90 (2 H, m)	7.25–7.57 (10 H, m)	*b*	156.57	83.06	138.05i	128.78o		142.53i	127.97o	*b*	
	8.22 (2 H, m)					123.87m	148.44p		128.61m	128.17p		
1b	7.31 (2 H, m)	7.22–7.60 (10 H, m)	*b*	158.07	82.33	131.42i	128.98o		142.90i	128.06o	*b*	
	7.66 (2 H, m)					128.49m[c]	136.62p		128.49m[c]	127.46p		
1c	7.03 (2 H, m)	7.22–7.56 (10 H, m)	*b*	158.08	82.24	129.39i	130.15o		142.96i	127.96o[c]	*b*	
	7.74 (2 H, m)					115.71m	163.96p		128.44m	127.96p[c]		
1d	7.26–7.58 (12H, m)[d]		*b*	159.38	81.80	133.05i	128.10o		142.13i	128.01o	*b*	
	7.76 (2 H, m)					128.55m	130.56p		128.44m	127.79p		
1e	2.35 (3 H, s)	7.24–7.58 (10 H, m)	*b*	159.54	81.69	130.95i	128.12o	21.45	143.23i	128.01o	*b*	
	7.17 (2 H, m)					129.31m	141.01p		128.44m	127.79p		
	7.64 (2 H, m)											
1f	3.81 (3 H, s)	7.24–7.57 (10 H, m)	*b*	159.16	81.69	126.12i	129.85o	55.42	143.18i	128.01o	*b*	
	6.86 (2 H, m)					113.98m	161.54p		128.44m	127.79p		
	7.69 (2 H, m)											
1g	1.24 (9 H, s)	7.22–7.50 (10 H, m)	*b*	172.27	81.37			29.20	143.40i	127.79o	*b*	
								40.14	128.28m	127.58p		
1h	2.20 (3 H, s)	7.23–7.50 (10 H, m)	*b*	150.08	82.72			20.53	143.40i	127.85o	*b*	
									128.39m	127.69p		
1i	7.89 (2 H, m)	7.29 (5 H, s)	1.13 (9 H, s)	158.24	92.20	138.14i	128.99o		141.77i	127.47o[c]		26.60
	8.22 (2 H, m)					123.84m	148.43p		128.50m	127.47p[c]		41.98
1k	7.90 (2 H, m)	7.28–7.40 (3 H, m)	2.32 (3 H, m)	156.40	75.19	138.36i	128.82o		140.90i	127.20o		32.34
	8.24 (2 H, m)	7.52–7.77 (2 H, m)				123.89m	148.49p		128.61m	128.39p		
1n	7.86 (2 H, m)	1.98 (3 H, s)	1.17 (9 H, s)	157.37	85.21	138.47i	128.55o			27.63		27.09
	8.22 (2 H, m)					123.79m	148.27p					40.09
1q[f]	7.88 (2 H, m)	1.62–2.10 (12 H, m)	2.50 (2 H, s, br)	158.02	86.14	138.68i	128.44o		26.06[g]	26.49[g]	35.27[h]	36.78[h]
	8.22 (2 H, m)					123.73m	148.38p		36.95[i]	41.61[j]		
1s[f,k]	7.86 (2 H, m)	0.92–1.04 (9 H, 3s)	1.58–1.84 (5 H, m)	155.31	85.59	138.30i	128.39o		12.73[l]	*13.81*[l]	20.21[l]	*20.53*[l]
	8.22 (2 H, m)	2.16–2.77 (2 H, m)				123.73m	148.27p		20.64[l]	20.75[l]	27.36[h]	33.32[i]
				158.17	*84.40*	*138.56i*			34.94[i]	46.37[g]	46.64[g]	48.59[i]
									49.19[i]	54.66[e]	55.26[e]	55.91[e]
									56.77[e]			
1u	7.96 (2 H, m)	7.29–7.45 (3 H, m)	1.37 (3 H, t)	156.13	115.98	138.36i	128.72o		137.87i	127.90o		14.62
	8.26 (2 H, m)	7.79–7.86 (2 H, m)	3.58 (2 H, q)			124.00m	148.54p		128.07m	128.89p		60.84

[a] i = *ipso*, m = *meta*, o = *ortho*, p = *para*. [b] $R^2 = R^3$. [c] Signals with identical chemical shift not resolved. [d] R^1 and R^2 ^{1}H signals overlap. [e] 1C, s. [f] ^{13}C signals for R^2 and R^3 arranged in order of increasing δ. [g] 1C, d. [h] 2C, t. [i] 1C, t. [j] 2C, d. [k] Mixed diastereoisomers; signals for minor isomer, where identifiable, in italics. [l] 1C, q.

procedure is described. The appropriate 5-ethoxy-5*H*-1,4,2-dithiazole **1** (2.7×10^{-4} mol) was dissolved in acetic anhydride (3 ml) and 70% $HClO_4$ (0.056 g, 3.9×10^{-4} mol) was added at 0 °C. The mixture was stirred at 25 °C for 1 h, anhydrous ether (5 ml) was added dropwise with stirring, and the yellow precipitate was collected by filtration, care being taken to avoid any contact with moisture. The products were purified by dissolution in trifluoroacetic acid, and reprecipitation by dropwise addition of anhydrous ether.

Prepared in this fashion were: 3-(4-*nitrophenyl*)-5-*phenyl*-1,4,2-*dithiazolium perchlorate* **9a** (96%), m.p. > 245 °C (Found: C, 41.85; H, 2.1; N, 6.95. $C_{14}H_9ClN_2O_6S_2$ requires C, 41.95; H, 2.25; N, 7.0%); *m/z* 301 (M^+, 19%); ν_{max}(Nujol)/cm^{-1} 1588, 1525, 1353, 1300 and 1095; $\delta_H(CF_3CO_2H–CD_3NO_2)$ 7.70–8.05 (3 H, m), 8.17 (2 H, m), 8.48 (2 H, m) and 8.56 (2 H, m); $\delta_C(CF_3CO_2H–CD_3NO_2)$ 127.13 (2 C, d), 127.46 (s), 132.20 (2 C, d), 132.40 (2 C, d), 133.31 (2 C, d), 136.36 (s), 142.35 (d), 153.34 (s), 182.53 (s, C-3) and 216.93 (s, C-5); 5-(4-chlorophenyl)-3-(4-nitrophenyl)-1,4,2-dithiazolium perchlorate **9b** (86%), m.p. >245 °C; acceptable microanalysis could not be obtained; ν_{max}(Nujol)/cm^{-1} 1585, 1528, 1349, 1300 and 1089; $\delta_H(CF_3CO_2H–CD_3NO_2)$ 7.81 (2 H, m), 8.20 (2 H, m), 8.49 (2 H, m) and 8.56 (2 H, m); $\delta_C(CF_3CO_2H–CD_3NO_2)$ 125.97 (s), 126.75 (2 C, d), 132.25 (2 C, d), 133.10 (2 C, d), 133.50 (2 C, d), 136.10 (s), 148.38 (s), 153.07 (s), 182.47 (s, C-3) and 214.41 (s, C-5); and 5-(3-*methoxyphenyl*)-3-(4-*nitrophenyl*)-1,4,2-*dithiazolium perchlorate* **9c** (91%), m.p. 217–218 °C (Found: C, 41.55; H, 2.45; N, 6.3. $C_{15}H_{11}ClN_2O_7S_2$ requires C, 41.8; H, 2.55; N, 6.5%); ν_{max}(Nujol)/cm^{-1} 1591, 1523, 1353, 1315, 1293 and 1095; $\delta_H(CF_3CO_2H–CD_3NO_2)$ 4.05 (3 H, s), 7.60–7.90 (4 H, m), 8.49 (2 H, m) and 8.56 (2 H, m); $\delta_C(CF_3CO_2H–CD_3NO_2)$ 57.52 (q), 116.66 (d), 124.98 (d), 126.97 (2 C, d), 128.07 (d), 128.27 (s), 132.36 (2 C, d), 134.41 (d), 136.30 (s), 153.37 (s), 163.32 (s), 182.60 (s, C-3) and 216.41 (s, C-5).

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References

1 Part 2, S. K. Xie, S. Y. Fan, X. Y. Wang and M. P. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2465.
2 Preliminary communication: K. F. Wai and M. P. Sammes, *J. Chem. Soc., Chem. Commun.*, 1988, 852.
3 F. S. Y. Chan, M. P. Sammes and R. L. Harlow, *J. Chem. Soc., Perkin Trans. 1*, 1988, 899.
4 K. F. Wai and M. P. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1990, 808.
5 See *e.g.* D. F. Greig, M. McPherson, R. M. Paton and J. Crosby, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1205.
6 See *e.g.* K. Dickoré, W. Wegler and K. Sasse, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**. 594; G. L'Abbé, G. Vermeulen, S. Toppett, G. S. D. King, J. Aerts and L. Sengier, *J. Heterocycl. Chem.*, 1981, **18**, 1309.

7 D. Noël and J. Vialle, *Bull. Soc. Chim. Fr.*, 1967, 2239.
8 For a review see, R. M. Paton, *Chem. Soc. Rev.*, 1989, **18**, 33.
9 R. Huisgen and W. Mack, *Chem. Ber.*, 1972, **105**, 2805.
10 (*a*) R. Huisgen and W. Mack, *Chem. Ber.*, 1972, **105**, 2815; (*b*) A. Battaglia, A. Dondoni, G. Maccagnani and G. Mazzanti, *J. Chem. Soc. B*, 1971, 2096.
11 A. M. Damas, R. O. Gould, M. M. Harding, R. M. Paton, J. F. Ross and J. Crosby, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2991.
12 R. K. Howe, T. A. Gruner, L. G. Carter, L. L. Black and J. E. Franz, *J. Org. Chem.*, 1978, **43**, 3736.
13 M. M. Campbell and D. M. Evgenios, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2862, 2866.
14 A. Selva, A. Citterio, E. Pella and R. Tonani, *Org. Mass Spectrom.*, 1974, **9**, 1017.
15 R. M. Paton, F. M. Robertson, J. F. Ross and J. Crosby, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1517.
16 R. K. Howe and J. E. Franz, *J. Org. Chem.*, 1974, **39**, 962.
17 D. J. Greig, D. G. Hamilton, M. McPherson, R. M. Paton and J. Crosby, *J. Chem. Soc., Perkin Trans. 1*, 1987, 607.
18 A. Holm, J. J. Christiansen and C. Lohse, *J. Chem. Soc., Perkin Trans. 1*, 1979, 960.
19 A. Senning and J. S. Rasmussen, *Acta Chem. Scand.*, 1973, **27**, 2161.
20 F. Becke and J. Gnad, *Justus Liebigs Ann. Chem.*, 1969, **726**, 110.
21 B. S. Pedersen, S. Scheibye, N. H. Nilsson and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 223; B. S. Pedersen, S. Scheibye, K. Clausen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 293.
22 J. W. Greidanus, *Can. J. Chem.*, 1970, **48**, 3530.

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