

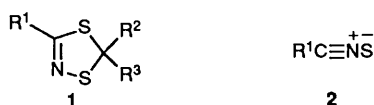
## Dithiazoles and Related Compounds. Part 3.<sup>1</sup> Preparation of 5*H*-1,4,2-Dithiazoles via 1,3-Dipolar Cycloadditions between Nitrile Sulphides and Thiocarbonyl Compounds, and some Conversions into 3,5-Diaryl-1,4,2-dithiazolium Salts<sup>2</sup>

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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,<sup>1,3,4</sup> those postulated as reaction intermediates,<sup>5</sup> and some 1,1-dioxides,<sup>6</sup> only three (spiro) derivatives appear to have

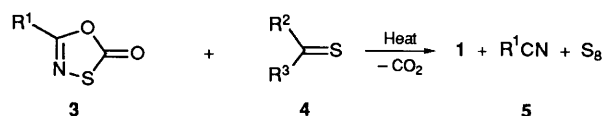




been isolated.<sup>7</sup> A potentially general synthetic route to these compounds, which have an unexplored and possibly rich chemistry, is the 1,3-dipolar cycloaddition of a nitrile sulphide **2**<sup>8</sup> and a thiocarbonyl compound. Although nitrile oxides have been added to carbonyl and to thiocarbonyl groups to give 5*H*-1,4,2-dioxazoles<sup>9</sup> and 5*H*-1,4,2-oxathiazoles<sup>10</sup> respectively, and nitrile sulphides have been added to carbonyl groups to give 2*H*-1,3,4-oxathiazoles,<sup>11</sup> this approach, with one unsuccessful exception,<sup>5</sup> 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 5*H*-1,4,2-Dithiazoles.**—The most convenient method for generating nitrile sulphides<sup>8</sup> **2** is the thermal decomposition of 1,3,4-oxathiazol-2-ones **3** which, in turn, may be prepared<sup>12</sup> bearing a wide variety of substituents R<sup>1</sup>. 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.<sup>8</sup>

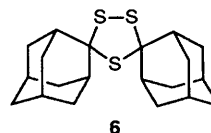
In this work, reactions were carried out by slow dropwise addition during 1–2 h of a xylene solution of an oxathiazolone **3** (Scheme 1) to a boiling solution of the appropriate thiocarbonyl compound **4**, also in xylene under dry N<sub>2</sub>. Refluxing was continued until TLC analysis (SiO<sub>2</sub>; 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



R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
a 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	a Ph	Ph
b 4-ClC <sub>6</sub> H <sub>4</sub>	b Ph	Bu <sup>t</sup>
c 4-FC <sub>6</sub> H <sub>4</sub>	c Ph	Me
d Ph	d Me	Bu <sup>t</sup>
e 4-MeC <sub>6</sub> H <sub>4</sub>	e 	
f 4-MeOC <sub>6</sub> H <sub>4</sub>	f 	
g Bu <sup>t</sup>	g Ph	OEt
h Me	h 4-ClC <sub>6</sub> H <sub>4</sub>	OEt
i 2-ClC <sub>6</sub> H <sub>4</sub>	i 3-MeOC <sub>6</sub> H <sub>4</sub>	OEt
	j Ph	OCH <sub>2</sub> CF <sub>3</sub>

Scheme 1

thioketone **4f**, while adamantanethione **4e** gave as an additional by-product a high yield of the trithiolane **6**.<sup>13</sup> We subsequently found that this same compound **6** could be prepared in similar yield simply by refluxing adamantanethione and sulphur together under N<sub>2</sub> in xylene. No analogous trithiolanes were



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  $\sigma_m$  constants: for  $\delta_{C-3}$   $r = 0.993$ ,  $\rho = -3.89$  and for  $\delta_{C-5}$   $r = 0.969$ ,  $\rho = 1.79$ . Charge transfer is presumably by  $\sigma$  bond polarisation; interestingly C-3 and C-5 respond in opposite senses (*cf.* the sign of  $\rho$ ) 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  $R^2 = R^3 = \text{Ph}$ , path a predominated, the fragment **7** losing H to give **8**, or an isomer, as the base peak. For  $R^3 = \text{Bu}^t$ , 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  $b \gg a > c$ , while for the alkoxy adducts **1u–w** formation of the fragment **7** was followed by degradation to  $R^2C=O^+$  as the base peak. In all spectra  $R^2C=O^+$  was prominent, while  $R^1C=N^{++}$  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<sup>11</sup> and 5*H*-1,4,2-dioxazoles.<sup>14</sup>

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.<sup>8</sup> In general, for a series of nitrile sulphides **2** yields increase with increasingly electron-donating  $R^1$ ;<sup>11,12,15</sup> however, there are examples where the yields decrease in the same order.<sup>16,17</sup>

In the present study, an additional factor is the thermal instability of the thioetone, which will become significant when the rate of fragmentation of the oxathiazolone **3** is slow, as when  $R^1$  is electron withdrawing.<sup>12</sup> It will be seen from Table 1 that for the relatively unstable thioetones **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,<sup>12</sup> giving more stable<sup>18</sup> 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  $R^1 = 4\text{-MeOC}_6\text{H}_4$ , 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,<sup>18</sup> leading to a low yield of the cycloadduct **1**. For  $R^1 = 4\text{-NO}_2\text{C}_6\text{H}_4$ , 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.<sup>18</sup> The higher concentration of dipolarophile is expected to favour adduct formation.<sup>16</sup>

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-nitrobenzothionitrile. 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,<sup>2</sup> 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

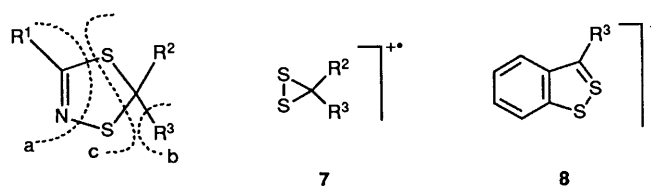
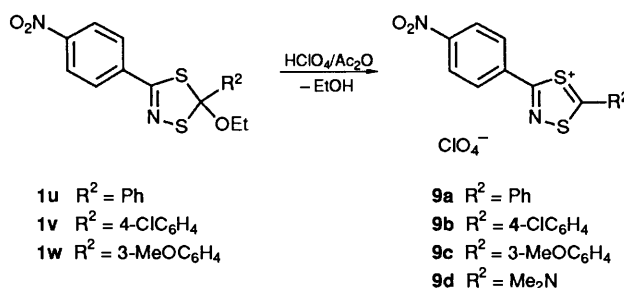


Fig. 1

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%  $\text{HClO}_4$  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  $\text{P}_4\text{O}_{10}$ , but rapidly reacted with moisture, or with any solvents more nucleophilic than  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{CH}_3\text{NO}_2$ .  $^{13}\text{C}$  NMR chemical shifts for the heterocycle C-3 in the salts **9** ( $\delta_{\text{C}}$  182.5) suggested greater positive charge density at this site, and thus greater  $\pi$  delocalisation, than in the analogue **9d** ( $\delta_{\text{C}}$  166.42) in which the positive charge lies predominantly on the exocyclic  $\text{NMe}_2$  group.<sup>3</sup>



Scheme 2

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

## Experimental

IR spectra were recorded on a Perkin-Elmer 157G instrument with polystyrene being used in calibration.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$ , unless otherwise stated, on JEOL FX90Q and GSX 270 spectrometers with  $\text{Me}_4\text{Si}$  used as internal reference, and mass spectra on a Hitachi RMS-4 instrument.  $^{13}\text{C}$  NMR signals refer to single carbon atoms unless otherwise stated.

The oxathiazolones **3** were prepared from the appropriate amide and chlorocarbonylsulphenyl chloride;<sup>12</sup> **3a** (55%), m.p. 150–151 °C (decomp.) [lit.,<sup>12</sup> (39%), m.p. 168–169 °C (decomp.)]; **3b** (40%), m.p. 126–128 °C [lit.,<sup>12</sup> (48%), m.p. 129–131 °C]; **3c** (78%), m.p. 98–99 °C [lit.,<sup>19</sup> (74%), m.p. 99–101 °C]; **3d** (71%), m.p. 71–72 °C [lit.,<sup>12</sup> (83%), m.p. 69–71 °C]; **3e** (50%), m.p. 89–90 °C [lit.,<sup>12</sup> (66%), m.p. 91–92 °C]; **3f** (51%), m.p. 108–109 °C [lit.,<sup>11</sup> (54%), m.p. 111 °C]; **3g** (41%) [lit.,<sup>12</sup> (33%), b.p. 35–36 °C (1.2 mmHg)]; **3h** (44%) [lit.,<sup>12</sup> (56%), b.p. 75–76 °C (30 mmHg)]; and **3i** (84%), m.p. 56–57 °C [lit.,<sup>20</sup> (81%), m.p. 55 °C]. Thiocarbonyl compounds **4** were prepared from the corresponding carbonyl compounds by heating with Lawesson's reagent under  $\text{N}_2$  in refluxing toluene or xylene,<sup>21</sup> with the exception of adamantanthione **4e**, which was prepared from adamantanone, and phosphorus pentasulphide in pyridine.<sup>22</sup> 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			Reaction time (h) <sup>a</sup>	Yield (%)	M.p. (°C)	Solvent	Found (%) (Required)			
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>					C	H	N	M <sup>+</sup>
<b>1a</b> C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	Ph	24	75	125–126	EtOH	63.35 (63.5)	3.9 (3.7)	7.3 (7.4)	378
<b>1b</b> C <sub>20</sub> H <sub>14</sub> ClNS <sub>2</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	Ph	Ph	6	40	80–81	EtOH	65.2 (65.3)	4.0 (3.8)	3.8 (3.8)	369/371
<b>1c</b> C <sub>20</sub> H <sub>14</sub> FNS <sub>2</sub>	4-FC <sub>6</sub> H <sub>4</sub>	Ph	Ph	7	48	56–58	Petroleum	68.6 (68.4)	4.15 (4.0)	3.7 (4.0)	351
<b>1d</b> C <sub>20</sub> H <sub>15</sub> NS <sub>2</sub>	Ph	Ph	Ph	7	35	94–96	EtOH	71.95 (72.05)	4.4 (4.5)	4.25 (4.2)	333
<b>1e</b> C <sub>21</sub> H <sub>17</sub> NS <sub>2</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	Ph	Ph	7	35	105–107	EtOH–H <sub>2</sub> O	72.75 (72.6)	5.05 (4.9)	3.9 (4.05)	347
<b>1f</b> C <sub>21</sub> H <sub>17</sub> NOS <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	Ph	4	30	150–151	EtOH	69.15 (69.4)	4.85 (4.7)	3.75 (3.85)	363
<b>1g</b> C <sub>18</sub> H <sub>19</sub> NS <sub>2</sub>	Bu <sup>†</sup>	Ph	Ph	5	13	55–56	EtOH–H <sub>2</sub> O	69.0 (69.0)	6.15 (6.05)	4.35 (4.45)	313
<b>1h</b> C <sub>15</sub> H <sub>13</sub> NS <sub>2</sub>	Me	Ph	Ph	4	10	37.5–38	Petroleum	66.3 (66.4)	4.8 (4.8)	5.15 (5.15)	271
<b>1i</b> C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	Bu <sup>†</sup>	12	25	118–119	EtOH	60.2 (60.35)	5.1 (5.5)	7.55 (7.8)	358
<b>1j</b> C <sub>19</sub> H <sub>21</sub> NOS <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	Bu <sup>†</sup>	5	15	87–88	EtOH–H <sub>2</sub> O	66.15 (66.45)	6.2 (6.1)	3.9 (4.1)	343
<b>1k</b> C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	Me	5	20	94–95	CHCl <sub>3</sub> –Petroleum	57.15 (56.95)	3.95 (3.8)	8.7 (8.85)	316
<b>1l</b> C <sub>15</sub> H <sub>12</sub> ClNS <sub>2</sub>	2-ClC <sub>6</sub> H <sub>4</sub>	Ph	Me	4	25	Oil	59.05 (58.9)	4.05 (3.95)	4.7 (4.6)	305/307	
<b>1m</b> C <sub>16</sub> H <sub>15</sub> NOS <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	Me	4	19	81–82	EtOH–H <sub>2</sub> O	63.85 (63.8)	4.85 (5.0)	4.7 (4.65)	301
<b>1n</b> C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Me	Bu <sup>†</sup>	5	20	97–98	CHCl <sub>3</sub> –Petroleum	52.55 (52.7)	5.5 (5.4)	9.25 (9.5)	296
<b>1o</b> C <sub>13</sub> H <sub>16</sub> ClNS <sub>2</sub>	2-ClC <sub>6</sub> H <sub>4</sub>	Me	Bu <sup>†</sup>	5	38	Oil	54.6 (54.65)	5.85 (5.6)	4.75 (4.9)	285/287	
<b>1p</b> C <sub>14</sub> H <sub>20</sub> NOS <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	Me	Bu <sup>†</sup>	4	21	84–85	EtOH–H <sub>2</sub> O	59.9 (59.8)	6.9 (6.75)	5.05 (5.0)	281
<b>1q</b> C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>9</sub> H <sub>14</sub> <sup>c</sup>		6	21	209–210	CHCl <sub>3</sub> –Petroleum	58.6 (58.95)	5.35 (5.2)	7.95 (8.1)	346
<b>1r</b> C <sub>18</sub> H <sub>21</sub> NOS <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	C <sub>9</sub> H <sub>14</sub> <sup>c</sup>		4	15	118–120	EtOH–CHCl <sub>3</sub>	65.45 (65.25)	6.0 (6.35)	4.3 (4.2)	331
<b>1s</b> C <sub>17</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>9</sub> H <sub>16</sub> <sup>d</sup>		12	6	130–133	EtOH–H <sub>2</sub> O	58.5 (58.6)	5.95 (5.75)	7.75 (8.05)	348
<b>1t</b> C <sub>18</sub> H <sub>23</sub> NOS <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	C <sub>9</sub> H <sub>16</sub> <sup>d</sup>		4	ca. 1	Gum				<sup>e</sup>	333
<b>1u</b> C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	OEt	24	13	139–141	EtOH	55.75 (55.5)	4.1 (4.05)	7.8 (8.1)	346
<b>1v</b> C <sub>16</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	OEt	24	11	112–113	CHCl <sub>3</sub> –Petroleum	50.4 (50.45)	3.4 (3.4)	7.1 (7.35)	380/382
<b>1w</b> C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	3-MeOC <sub>6</sub> H <sub>4</sub>	OEt	24	12	139–140	EtOH–H <sub>2</sub> O	54.2 (54.25)	4.4 (4.25)	7.4 (7.45)	376
<b>1x</b> C <sub>16</sub> H <sub>11</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	OCH <sub>2</sub> CF <sub>3</sub>	24	11	173–174	EtOH	48.05 (48.0)	2.7 (2.75)	6.85 (7.0)	400

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

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

**Preparation of the 5*H*-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<sub>2</sub>, 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<sub>2</sub>; 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.,<sup>13</sup> m.p. 189–191 °C); δ<sub>H</sub> 1.80 (16 H, m, br) and 2.23 (12 H, m, br); δ<sub>C</sub> 26.76, 27.08, 36.84, 37.38, 38.08, 39.54 and 90.41; *m/z* 364 (*M*<sup>+</sup>, 10%), 300 (5), 198 (100), 166 (30) and 133 (66). Yields, m.p.s and microanalytical data are given in Table 1, while <sup>1</sup>H and <sup>13</sup>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<sup>-3</sup> mol) and sulphur (0.06 g, 2.25 × 10<sup>-4</sup> mol) in *p*-xylene (5 ml) was refluxed under N<sub>2</sub> until the red colour disappeared. The solvent was evaporated and the residue was purified by chromatography [SiO<sub>2</sub>; 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**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data for selected 5*H*-1,4,2-dithiazoles **1**

Compd.	$\delta_{\text{H}}(\text{CDCl}_3)$			$\delta_{\text{C}}(\text{CDCl}_3)$									
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Dithiazole		R <sup>1</sup>			Alkyl	R <sup>2a</sup>	R <sup>3</sup>		
				C-3	C-5	Aryl <sup>a</sup>							
<b>1a</b>	7.90 (2 H, m) 8.22 (2 H, m)	7.25–7.57 (10 H, m)	<i>b</i>	156.57	83.06	138.05i 123.87m	128.78o 148.44p			142.53i 128.61m	127.97o 128.17p	<i>b</i>	
<b>1b</b>	7.31 (2 H, m) 7.66 (2 H, m)	7.22–7.60 (10 H, m)	<i>b</i>	158.07	82.33	131.42i 128.49m <sup>c</sup>	128.98o 136.62p			142.90i 128.49m <sup>c</sup>	128.06o 127.46p	<i>b</i>	
<b>1c</b>	7.03 (2 H, m) 7.74 (2 H, m)	7.22–7.56 (10 H, m)	<i>b</i>	158.08	82.24	129.39i 115.71m	130.15o 163.96p			142.96i 128.44m	127.96o <sup>c</sup> 127.96p <sup>c</sup>	<i>b</i>	
<b>1d</b>	7.26–7.58 (12H, m) <sup>d</sup> 7.76 (2 H, m)		<i>b</i>	159.38	81.80	133.05i 128.55m	128.10o 130.56p			142.13i 128.44m	128.01o 127.79p	<i>b</i>	
<b>1e</b>	2.35 (3 H, s) 7.17 (2 H, m) 7.64 (2 H, m)	7.24–7.58 (10 H, m)	<i>b</i>	159.54	81.69	130.95i 129.31m	128.12o 141.01p	21.45		143.23i 128.44m	128.01o 127.79p	<i>b</i>	
<b>1f</b>	3.81 (3 H, s) 6.86 (2 H, m) 7.69 (2 H, m)	7.24–7.57 (10 H, m)	<i>b</i>	159.16	81.69	126.12i 113.98m	129.85o 161.54p	55.42		143.18i 128.44m	128.01o 127.79p	<i>b</i>	
<b>1g</b>	1.24 (9 H, s)	7.22–7.50 (10 H, m)	<i>b</i>	172.27	81.37			29.20 40.14		143.40i 128.28m	127.79o 127.58p	<i>b</i>	
<b>1h</b>	2.20 (3 H, s)	7.23–7.50 (10 H, m)	<i>b</i>	150.08	82.72			20.53		143.40i 128.39m	127.85o 127.69p	<i>b</i>	
<b>1i</b>	7.89 (2 H, m) 8.22 (2 H, m)	7.29 (5 H, s)	1.13 (9 H, s)	158.24	92.20	138.14i 123.84m	128.99o 148.43p			141.77i 128.50m	127.47o <sup>c</sup> 127.47p <sup>c</sup>	26.60 41.98	
<b>1k</b>	7.90 (2 H, m) 8.24 (2 H, m)	7.28–7.40 (3 H, m)	2.32 (3 H, m)	156.40	75.19	138.36i 123.89m	128.82o 148.49p			140.90i 128.61m	127.20o 128.39p	32.34	
<b>1n</b>	7.86 (2 H, m) 8.22 (2 H, m)	1.98 (3 H, s)	1.17 (9 H, s)	157.37	85.21	138.47i 123.79m	128.55o 148.27p			27.63		27.09 40.09	
<b>1q<sup>f</sup></b>	7.88 (2 H, m) 8.22 (2 H, m)	1.62–2.10 (12 H, m)	2.50 (2 H, s, br)	158.02	86.14	138.68i 123.73m	128.44o 148.38p			26.06 <sup>g</sup> 36.95 <sup>i</sup>	26.49 <sup>g</sup> 41.61 <sup>j</sup>	35.27 <sup>h</sup> 20.21 <sup>l</sup>	36.78 <sup>h</sup> 20.53 <sup>l</sup>
<b>1s<sup>f,k</sup></b>	7.86 (2 H, m) 8.22 (2 H, m)	0.92–1.04 (9 H, 3s)	1.58–1.84 (5 H, m)	155.31	85.59	138.30i 123.73m	128.39o 148.27p			12.73 <sup>l</sup> 20.64 <sup>l</sup> 34.94 <sup>i</sup> 49.19 <sup>i</sup> 56.77 <sup>e</sup>	13.81 <sup>l</sup> 20.75 <sup>l</sup> 46.37 <sup>g</sup> 54.66 <sup>e</sup>	20.21 <sup>l</sup> 27.36 <sup>h</sup> 46.64 <sup>g</sup> 55.26 <sup>e</sup>	20.53 <sup>l</sup> 33.32 <sup>i</sup> 48.59 <sup>i</sup> 55.91 <sup>e</sup>
<b>1u</b>	7.96 (2 H, m) 8.26 (2 H, m)	7.29–7.45 (3 H, m) 7.79–7.86 (2 H, m)	1.37 (3 H, t) 3.58 (2 H, q)	156.13	115.98	138.36i 124.00m	128.72o 148.54p			137.87i 128.07m	127.90o 128.89p	14.62 60.84	

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

procedure is described. The appropriate 5-ethoxy-5*H*-1,4,2-dithiazole **1** ( $2.7 \times 10^{-4}$  mol) was dissolved in acetic anhydride (3 ml) and 70% HClO<sub>4</sub> (0.056 g,  $3.9 \times 10^{-4}$  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<sub>14</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>6</sub>S<sub>2</sub> requires C, 41.95; H, 2.25; N, 7.0%; *m/z* 301 (*M*<sup>+</sup>, 19%);  $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$  1588, 1525, 1353, 1300 and 1095;  $\delta_{\text{H}}(\text{CF}_3\text{CO}_2\text{H}-\text{CD}_3\text{NO}_2)$  7.70–8.05 (3 H, m), 8.17 (2 H, m), 8.48 (2 H, m) and 8.56 (2 H, m);  $\delta_{\text{C}}(\text{CF}_3\text{CO}_2\text{H}-\text{CD}_3\text{NO}_2)$  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;  $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$  1585, 1528, 1349, 1300 and 1089;  $\delta_{\text{H}}(\text{CF}_3\text{CO}_2\text{H}-\text{CD}_3\text{NO}_2)$  7.81 (2 H, m), 8.20 (2 H, m), 8.49 (2 H, m) and 8.56 (2 H, m);  $\delta_{\text{C}}(\text{CF}_3\text{CO}_2\text{H}-\text{CD}_3\text{NO}_2)$  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<sub>15</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>7</sub>S<sub>2</sub> requires C, 41.8; H, 2.55; N, 6.5%);  $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$  1591, 1523, 1353, 1315, 1293 and 1095;  $\delta_{\text{H}}(\text{CF}_3\text{CO}_2\text{H}-\text{CD}_3\text{NO}_2)$  4.05 (3 H, s), 7.60–7.90 (4 H, m), 8.49 (2 H, m) and 8.56 (2 H, m);  $\delta_{\text{C}}(\text{CF}_3\text{CO}_2\text{H}-\text{CD}_3\text{NO}_2)$  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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