

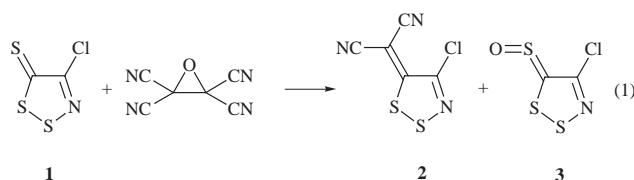
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In the synthesis of dicyanomethylene-1,2,3-dithiazole **2** from dithiazolethione **1** and tetracyanoethylene oxide (TCNEO), formation of the thione-oxide (sulfine) **3** becomes competitive under mild conditions, in the first transfer of oxygen from TCNEO to a thione group. Thione **1** is converted into sulfine **3** in high yield by the usual oxidant, *m*-chloroperbenzoic acid. An isomeric pair of unusual enimino-dithiazoles, **7** and **8**, are minor by-products in the synthesis of the dicyanomethylene compound **2** from TCNEO and 4,5-dichloro-1,2,3-dithiazolium chloride **6**; it is proposed that their formation derives from the ring opened stabilised ylide form of TCNEO acting as a nucleophile through nitrogen **9b**, as well as through carbon **9a**. The reaction of salt **6** and TCNEO in the presence of *N*-chlorosuccinimide yields the oxidised acyliminodithiazole **11** which has been synthesised independently from **6** and dichlorocyanacetamide **12**. Trichloroacetamide reacts with **6** to give the analogous imine **13** which is incorrectly assigned the fused bicyclic structure **14** in the patent literature.

In our first report on the reactions of 4-chloro-1,2,3-dithiazole-5-thione **1** and 4,5-dichloro-1,2,3-dithiazolium chloride **6** with malononitrile, tetracyanoethylene (TCNE) and tetracyanoethylene oxide (TCNEO), we commented on the complexity of the reactions but only described the isolation of the desired dicyanomethylenedithiazole **2**.¹ We now give full details of these reactions which disclose some new transformations and unusual products.

Treatment of the dithiazolethione **1** with TCNEO gave TCNE, sulfur, the dicyanomethylene derivative **2**¹ and 4-chloro-1,2,3-dithiazole-5-thione oxide **3** [reaction (1), Table 1].



We believe that formation of the sulfine **3** is the first reported example of oxygen transfer from TCNEO to a thione. We have proposed a mechanism for the formation of compound **2**.¹

We see from Table 1 that whilst the yield of **2** does not vary greatly with reaction conditions, the yield of sulfine **3** is lower at higher temperatures and falls to zero on long heating. The sulfine is thermally unstable, reverting to thione **1** which could then react with more TCNEO to give the thermally stable dicyanomethylene product **2**. Heating **3** in boiling toluene for

two days gave a moderate recovery of thione **1** (45%); several unidentified minor products were detected by TLC. Two equivalents of TCNEO at the higher temperatures converted all of the thione (and sulfine) into **2**.

Sulfine **3** was obtained as orange needles or orange-red plates which deteriorate on standing at room temperature to give the thione **1**, amongst other minor products, but which are stable at low temperature (-5°C) in the dark. Microanalysis and HRMS gave its formula as C_2ClNOS_3 . Linked scan mass spectrometry (LSMS) showed a strong loss of 48 Da (SO) directly from the parent ion, m/z 185, to give m/z 137; a constant neutral loss scan (CNLS) indicated that the parent ion was the only one to give this direct loss of 48 Da; a search for all the parents of m/z 137 located only the parent ion m/z 185. Thus the mass spectra strongly support the attachment of the oxygen atom to sulfur. Evidence to suggest that the thione sulfur is bonded to oxygen came from LSMS which showed a loss of 83 Da (ClSO) directly from the parent ion; LSMS on the dithiazolethione **1** showed a similar direct loss of 67 Da (ClS).

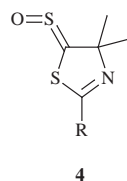
The other spectral data for **3** were consistent with the sulfine structure.² The UV spectrum shows a strong transition at λ_{max} 423 nm ($\log \epsilon$ 3.99) and a weaker transition at 330 nm (3.27), and thione **1** has a similar spectrum [λ_{max} /nm 431 ($\log \epsilon$ 3.83), 337 (3.20) and 302 (3.07)]. The observed blue shift of the first absorption band on going from the thione to the thione oxide is well documented.^{3,4} The IR spectrum shows strong bands at 1041, 1029 and 1013 cm^{-1} in the region for sulfine symmetric and asymmetric stretching.

 Table 1 Reaction of dithiazolethione **1** with TCNEO (1 mmol)

1/mmol	Solvent (ml)	Reaction time/days	$T/^{\circ}\text{C}$	Product yields (%)				
				Sulfur	TCNE	1	2	3
1	PhMe (3)	0.5	110	<i>a</i>	<i>a</i>	19	61	13
1	PhMe (3)	7	20	<i>a</i>	43	18	57	43
0.5	PhMe (3)	5	20	50	45	0	53	44
0.5	PhMe (3)	2	110	<i>a</i>	95	0	72	0
0.5	PhMe (3)	3	110	<i>a</i>	90	0	71	0
0.5	PhH (3)	2.5	80	94	67	0	69	0

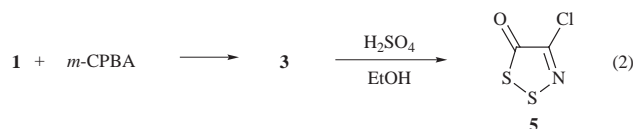
^a Not determined.

Oxidation of sulfur heterocyclic thiones generally occurs on the (more nucleophilic) thione sulfur.⁵ Two configurations (*E* and *Z*) are possible for sulfine **3** but we have seen no evidence for two isomers. Based on a comparison with the thiazole-5-thione oxides **4** which were shown, partly by X-ray crystal-

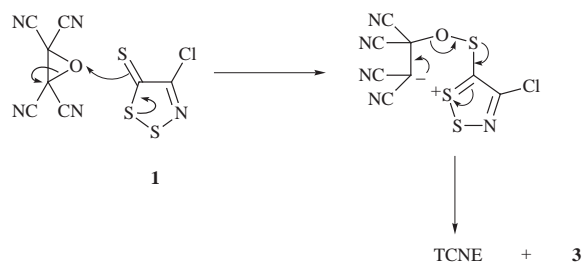


lography, all to be the *Z*-isomers,⁴ we tentatively propose that sulfine **3** is the *Z*-isomer, avoiding the steric and electronic repulsions expected for the *E*-isomer. Strong electron release from the heterocyclic sulfur atoms in **3** will substantially reduce the double bond character of the sulfine C=S bond, thus facilitating rotation about this bond.

Thiones are readily oxidised to sulfines, usually with hydrogen peroxide or peracids,⁵ but this is, we believe, the first such oxidation by TCNEO. Treatment of the thione **1** with *m*-CPBA in cold DCM gave **3** (81%) identical with that formed with TCNEO. Hydrolysis of **3** with sulfuric acid in ethanol (*cf.* refs. 3 and 6) was slow but after 12 h at 50 °C the dithiazolone **5** was obtained in moderate yield (42%) [reaction (2)].



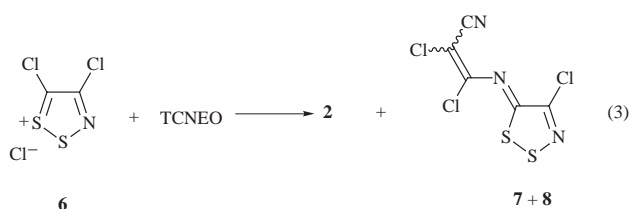
We have postulated that conversion of the thione **1** by TCNEO into the dicyanomethylene product **2** is initiated by nucleophilic opening of the epoxide by attack by the thione sulfur of **1** at carbon.¹ TCNEO could also be attacked by the thione at its highly electrophilic oxygen atom (which is less hindered than the ring carbons) exactly as it is by triphenylphosphine⁷ and nucleophilic alkenes,^{7,8} followed by transfer of the oxygen from carbon to sulfur (Scheme 1). The nucleophilicity of the thione sulfur in **1** will be enhanced by electron release from the ring sulfur atoms.



Scheme 1

Reaction of 4,5-dichloro-1,2,3-dithiazolium chloride **6** with TCNEO

The major product (60%) of this reaction in toluene was the dicyanomethylene compound **2** [reaction (3)].¹ However two



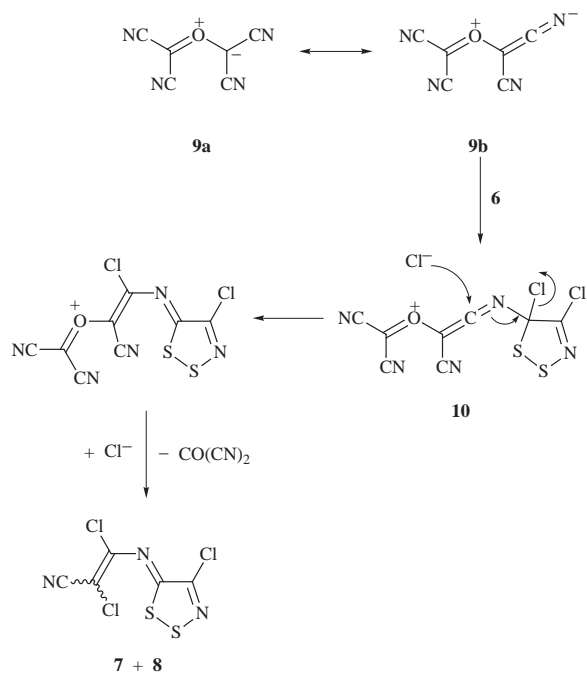
minor isomeric products **7** (3.5%) and **8** (3.5%) were also isolated and are now described. Variation of reaction time (1.5–24 h) and temperature (20–110 °C) had little effect on the yields of all three products.

Compounds **7** and **8** are thermally stable orange (mp 175–177 °C) and orange-red needles (mp 148–154 °C), each with the formula C₅Cl₃N₃S₂ from microanalysis and HRMS, and with very similar spectroscopic properties. Their ¹³C NMR spectra showed five different low field signals; resonances at 114 and 116 ppm suggested the presence of cyano groups and this was supported by strong IR absorptions at 2216 and 2198 cm⁻¹ respectively. The carbon resonances at 150 and 161 ppm for **7** and 150 and 163 ppm for **8** are in the range typical for C-4 and C-5 in 1,2,3-dithiazole imines.⁹ The remaining two carbon signals in each were low field and probably from *sp*² hybridised carbon. Both **7** and **8** show strong UV absorption similar to that of the dithiazoles **1**, **2** and **3**. LSMS was used to investigate the daughter ions of the two highest molecular weight ions *m/z* 271 (M⁺) and 236 (M⁺ – Cl) in **7** and **8**, whose fragmentation patterns were almost identical indicating their close structural similarity. The presence of the 1,2,3-dithiazole ring was supported by the fragment ions *m/z* 137 (C₂CINS₂) for the chlorinated ring, 125 (CCINS₂), 102 (C₂NS₂) the ring itself, 93 (CCINS) the Cl–C=N–S unit, 70 (C₂NS) and 64 (S₂). These assignments were supported by HRMS, which also identified the fragment ions *m/z* 120 (C₃Cl₂N) and 85 (C₃ClN) from the substituent on the dithiazole ring.

On the assumption that the carbon connectivity of the starting materials, salt **6** and TCNEO, has been retained, we assigned the pair of isomeric structures **7** and **8** to these products, but we do not know which is which. Several attempts to produce crystals suitable for X-ray diffraction were unsuccessful.

Mechanism for the formation of **7** and **8**

The major product of the reaction of salt **6** and TCNEO is the dicyanomethylene compound **2**; we proposed¹ that this resulted from initial nucleophilic attack of **6** by TCNEO in its ring-opened stabilised ylide form **9a**, attack being through carbon. The structures of the minor products **7** and **8** suggest that this attack can also occur through nitrogen in the ketenimine resonance form **9b**. This would give the adduct **10** which would then need to undergo rearrangement of chlorine



Scheme 2

Table 2 Reaction of 4,5-dichloro-1,2,3-dithiazolium chloride **6** (1 mmol) with TCNEO (1 mmol) in the presence of NCS (1 mmol)

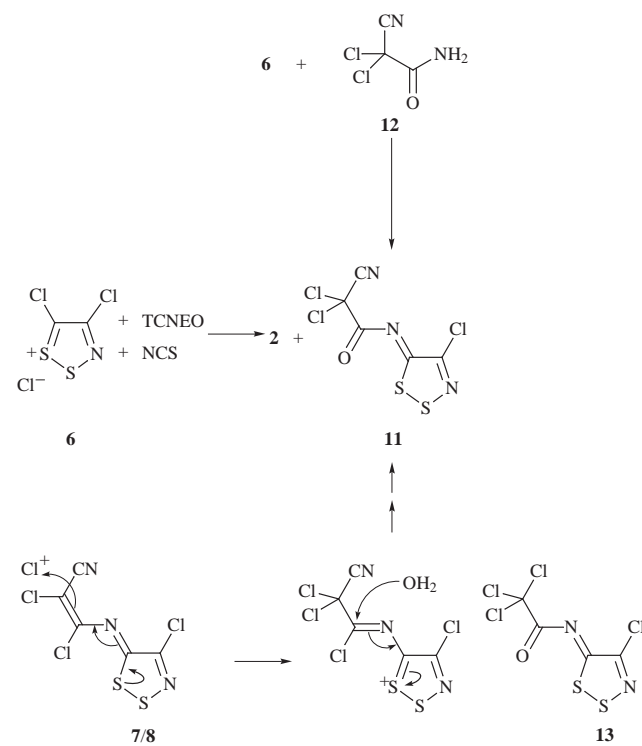
Solvent (ml)	Reaction time/h	<i>T</i> /°C	Product yields (%)		
			7 + 8	2	11
PhMe (3)	1	110 ^a	Trace	55	23
PhMe (3)	48	20 ^b	Trace	58	16

^a Reaction started at 20 °C. ^b Reaction started at -78 °C.

and displacement of carbonyl cyanide by chloride, as shown in Scheme 2 to give the isomers **7** and **8**. The last two steps could possibly occur in the reverse order.

Reaction of dithiazolium salt **6** with TCNEO and NCS

In an early attempt to unravel the formation of the dithiazoles **2**, **7** and **8** from the salt **6** and TCNEO, we introduced a source, NCS, of electrophilic chlorine, with the results shown in Table 2. With one equivalent each of **6**, TCNEO and NCS in toluene the major product was again the dicyanomethylene compound **2**, in much the same yield as before. Only traces of the iminodithiazoles **7** and **8** were now formed but these were replaced in somewhat higher yield by a new product, the dichlorocynoacetamidodithiazole **11** (Scheme 3). Compound **11** was recognised (TLC, LRMS) as one of the trace products in the reactions of the salt **6** and TCNEO in the absence of NCS.

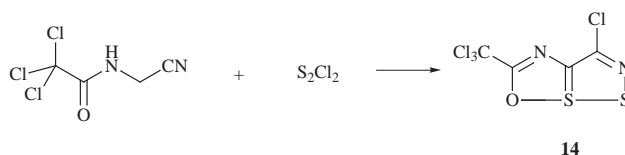


Scheme 3

Compound **11** was obtained as cream coloured needles, mp 91 °C, shown to be C₅Cl₃N₃OS₂ by microanalysis and HRMS. Its mass spectrum showed a strong loss of 108 Da (C₂Cl₂N) to give *m/z* 179 (C₃ClN₂OS₂), both formulae being supported by HRMS. This fragmentation occurred so readily that a strong parent ion, *m/z* 287, could only be obtained by FAB spectrometry. The ¹³C NMR spectrum showed five different carbon environments, a nitrile group resonance at 113 ppm being supported by the IR spectrum (2255 cm⁻¹). A high field carbon resonance at 66 ppm was presumably from a saturated carbon; two of the remaining three resonances at 175 and 171 ppm suggested a carbonyl group which was supported by an IR signal at 1627 cm⁻¹ indicative of an amide.

Further fragmentation of the ion *m/z* 179 was shown by LSMS to give NS, S₂ and ClCNS typical of 4-chloro-1,2,3-dithiazoles, and the UV absorption at 400 nm (log ε 4.19) was similar to that of dithiazoles **1** and **3**. All this evidence suggested the unexpected dichlorocynoacetamidodithiazole structure **11**, and this was confirmed by independent synthesis, albeit in low yield (18%), from the salt **6** and 2,2-dichloro-2-cyanoacetamide **12**,¹⁰ the product being identical with that above. Another product of this last reaction was the dithiazolethione **1** (31%) which is often formed, as a relatively minor product, in reactions of salt **6** with nucleophiles. For comparison with the dichloroacetamide **12** reaction, **6** was treated with commercially available trichloroacetamide under the same conditions. The thione **1** was again formed in similar yield (30%) together with the trichloroacetamidoimine **13**, mp 99–102 °C.

An isomer of **13** with the interesting bicyclic structure **14** has been reported in the patent literature.¹¹ It was prepared from trichloroacetylaminocetonitrile by treatment with SCl₂ or S₂Cl₂ (Scheme 4), and had mp 99–100 °C. The only other data



Scheme 4

given were a sulfur and chlorine analysis. Since the melting point of this compound is close to that for **13** (99–102 °C) it seems very likely that **13** and **14** are the same compound. Since compounds **11** and **13** have very similar spectroscopic properties, **13** presumably has the same monocyclic ring structure as **11**, which has been proved by X-ray crystallography.¹² This shows that in **11** the separation of the carbonyl oxygen and the dithiazole S-1 atoms (2.50 Å) is much longer than a covalent oxygen-sulfur bond (1.58 Å), though less than the sum of their van der Waals radii (3.25 Å). Furthermore compounds **11** and **13** are analogous to *α*-(3*H*-1,2-dithiol-3-ylidene) ketones which show 'no bond' resonance between the oxygen and sulfur atoms making the carbonyl stretching frequency difficult to observe.¹³ We suggest therefore that the bicyclic structure **14** proposed¹¹ for the trichloromethyl compound is incorrect, and some or all of the 30 or so analogous 2-substituted 3-oxa-3aλ⁴,4-dithia-6-chloro-1,5-diazapentalene structures may need similar revision.

In considering a possible mechanism for the formation of **11** from salt **6**, TCNEO and NCS, we see that **11** could arise from **7** and **8** by the addition of the elements of hypochlorous acid to the C-C double bond, followed by elimination of hydrogen chloride. This can readily be envisaged in the NCS reaction if moisture were present in the reaction mixture or during the work up procedure, as shown in Scheme 3. Alternatively it is possible that it is a precursor of **7** and **8** (see Scheme 2) which is intercepted by oxidation and hydrolysis to give the isolated product **11**.

Experimental

Light petroleum refers to the fraction, bp 60–80 °C. Solvents and reactions were carried out under dry nitrogen. Anhydrous magnesium sulfate was used for drying organic extracts, and volatiles were removed under reduced pressure. Reactions and column eluents were monitored by TLC using aluminium backed thin layer chromatography plates (Merck Kieselgel 60 F₂₅₄) viewed under UV light at 254 and 350 nm. Dry flash chromatography on Sorbsil C60 M40 silica was used for separations. UV and IR spectra were measured on Perkin-Elmer Lambda II and Perkin-Elmer 1710FT spectrometers respectively. ¹³C NMR spectra were measured on JEOL GSX 270 (at 68 MHz), Bruker AM300WB (at 76 MHz), Bruker

RX-400 (at 100 MHz) and Bruker AM500 (at 125 MHz) machines. Mass spectra were recorded on VG micromass 7070E or Autospec 'Q' machines. Microanalyses were carried out on a Perkin-Elmer 2400 CHN analyser.

Reaction of 4-chloro-5H-1,2,3-dithiazole-5-thione 1 with tetra-cyanoethylene oxide (see Table 1)

To a stirred solution of the thione **1**¹⁴ (84.5 mg, 0.5 mmol) in toluene (3 ml) at ca. 20 °C, TCNEO (144 mg, 1 mmol) was added in one portion. After 5 days no dithiazole thione remained (TLC). Chromatography (light petroleum) gave sulfur (8 mg, 50%) and further elution (light petroleum–DCM, 4:1) gave 3-chloro-5H-1,2,3-dithiazole-5-thione oxide **3** (41 mg, 44%) as orange needles, mp 60 °C decomp. (from 1,2-dichloroethane–pentane) (Found: C, 13.2; N, 7.5. C₂ClNOS₃ requires C, 13.0; N, 7.6%); λ_{max}(DCM)/nm 330 (log ε 3.27), 423 (3.99); ν_{max}(Nujol)/cm⁻¹ 1555w, 1298w, 1229s, 1209s, 1118m, 1041s, 1029s and 1013s (C=S=O), 951w, 893s, 794s, 787s, 781s, 722w, 607s; δ_C(68 MHz; CDCl₃) 188.58 (C-5), 138.69 (C-4); *m/z* (CI) 203 (M⁺+NH₄⁺, 100%), 186 (MH⁺, 57), 169 (M⁺ – O, 4), 138 (MH⁺ – OS, 3), 102 (C₂NS₂⁺, 9), 70 (C₂NS⁺, 3), 64 (S₂⁺, 3), 52 (16) (Found: MH⁺, 185.8891. C₂ClNOS₃ requires MH, 185.8909); LSMS: (EI, *B/E* of *m/z* 185) 169 (M⁺ – O, 5%), 153 (M⁺ – S, 10), 137 (M⁺ – OS, 72), 121 (100), 109 (15), 102 (M⁺ – ClOS, 36), 96 (22), 93 (20), 79 (11), 76 (15), 70 (21), 64 (10); (EI, *B²/E* of *m/z* 137) 185 (M⁺, 20%); CNLS: [EI, *B/E*(1 – *E*²)^{1/2} of 48 Da] 185 (M⁺, 100%). Further elution (light petroleum–DCM, 3:2) gave TCNE (58 mg, 45%), mp 197–199 °C, identical with an authentic specimen. A final elution (DCM) gave 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)propanedinitrile **2** (53 mg, 53%) as an orange solid, identical with that reported.¹

Independent synthesis of 3-chloro-5H-1,2,3-dithiazole-5-thione oxide 3

To a stirred solution of 4-chloro-5H-1,2,3-dithiazole-5-thione **1** (17 mg, 0.10 mmol) at 0 °C a solution of *m*-CPBA (23 mg, 0.13 mmol) in DCM (2 ml) was added slowly. The mixture was allowed to warm to ca. 20 °C after which time TLC indicated an orange product and no starting material. The mixture was washed with water (3 × 10 ml), with aqueous sodium hydrogen carbonate (0.05 M, 1 × 5 ml), and again with water (1 × 5 ml). The organic layer was dried, filtered and the volatiles were removed. Crystallisation of the residue at 0 °C gave the title compound **3** (15 mg, 81%) as orange needles, mp 60 °C decomp. (from 1,2-dichloroethane–pentane), identical with that described above.

4-Chloro-5H-1,2,3-dithiazol-5-one 5

To a stirred solution of 3-chloro-5H-1,2,3-dithiazole-5-thione oxide **3** (20 mg, 0.11 mmol) in EtOH (2 ml) at ca. 20 °C, concentrated sulfuric acid (0.2 ml) was added. The mixture was warmed (50 °C) for 12 h and then diluted with DCM (20 ml) and washed with water (3 × 10 ml). The organic layer was dried, filtered and the volatiles were removed; chromatography (DCM) gave the title compound **5** (7 mg, 42%) as a yellow solid, mp 37–38 °C, δ_C(76 MHz; CDCl₃) 182.81 (C-5), 146.72 (C-4); *m/z* (EI) 153 (M⁺, 39%), 125 (M⁺ – CO, 20), 93 (CCINS⁺, 23), 64 (S₂⁺, 100), identical with an authentic specimen.¹⁴

Reaction of 4,5-dichloro-1,2,3-dithiazolium chloride 6 with tetra-cyanoethylene oxide

To a stirred suspension of 4,5-dichloro-1,2,3-dithiazolium chloride **6**¹⁴ (207 mg, 1 mmol) in toluene (3 ml) at ca. 20 °C, TCNEO (144 mg, 1 mmol) was added in one portion. The mixture was heated under reflux for 24 h and then allowed to cool to ca. 20 °C. Chromatography (light petroleum–DCM, 1:1) gave a mixture of two isomers that could be separated by preparative layer chromatography (light petroleum–ether, 5:1)

to give 1-[N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)amino]-1,2-dichloroethene-2-carbonitrile **7** and **8**. Isomer **7**, (less polar on TLC) (9.5 mg, 3.5%) as orange needles, mp 175–177 °C (from cyclohexane) (Found: C, 22.3; N, 15.3. C₅Cl₃N₃S₂ requires C, 22.1; N, 15.5%); λ_{max}(DCM)/nm 270 (log ε 3.86), 353 inf (3.43), 411 inf (4.16), 427 (4.21), 447 inf (4.10), 478 inf (3.66); ν_{max}(Nujol)/cm⁻¹ 2216s (CN), 1639w, 1556s (C=N), 1531m, 1488s, 1297w, 1242w, 1215s, 1158m, 1091s, 892s, 850w, 811m, 721w, 682s; δ_C(100 MHz; [D₂H₂]⁺DCM) 160.69 (C-5), 150.25 (N=C=C), 147.91 (C-4), 114.12 (CN), 100.26 [(NC)C=C]; *m/z* (EI) 271 (M⁺, 23%), 236 (M⁺ – Cl, 24), 210 (M⁺ – CCIN, 7), 179 (2), 162 (1), 151 (M⁺ – C₃Cl₂N, 1), 143 (4), 137 (3), 125 (15), 120 (5), 102 (C₂NS₂⁺, 7), 93 (CCINS⁺, 12), 85 (9), 70 (C₂NS⁺, 19), 64 (S₂⁺, 100) (Found: M⁺, 270.8563. C₅Cl₃N₃S₂ requires M, 270.8599); LSMS: (EI, *B/E* of *m/z* 271) 236 (M⁺ – Cl, 100%), 210 (M⁺ – CCIN, 9), 193 (3), 175 (6), 146 (7), 137 (5), 125 (6), 120 (4), 110 (3), 102 (6), 93 (4), 85 (3), 79 (5), 64 (4); (EI, *B/E* of *m/z* 236) 210 (26%), 201 (100), 175 (51), 169 (67), 140 (30), 137 (23), 131 (23), 120 (16), 117 (58), 108 (20), 102 (36), 96 (20), 93 (32), 85 (11), 82 (38), 79 (21), 70 (29), 67 (25), 64 (10). Isomer **8** (more polar on TLC) (9.5 mg, 3.5%) as red–orange needles, mp 148–154 °C (from cyclohexane) (Found: C, 22.4; N, 15.3. C₅Cl₃N₃S₂ requires C, 22.1; N, 15.5%); λ_{max}(DCM)/nm 269 (log ε 3.91), 364 inf (3.55), 425 inf (4.18), 439 (4.19), 460 inf (4.05), 494 inf (3.59); ν_{max}(Nujol)/cm⁻¹ 2275w, 2230w, 2216w and 2198m (CN), 1637w, 1556s, 1545s, 1515m, 1307w, 1231w, 1205m, 1141m, 1109m, 877s, 812m, 703m, 677w; δ_C(125 MHz; [D₂H₂]⁺DCM) 162.73 (C-5), 150.47 (N=C=C), 142.80 (C-4), 115.51 (CN), 95.89 [(NC)C=C]; *m/z* (EI) 271 (M⁺, 35%), 236 (M⁺ – Cl, 35), 210 (M⁺ – CCIN, 11), 179 (6), 162 (5), 151 (M⁺ – C₃Cl₂N, 4), 143 (4), 137 (3), 125 (18), 120 (6), 102 (C₂NS₂⁺, 7), 93 (CCINS⁺, 14), 70 (C₂NS⁺, 15), 64 (S₂⁺, 100) (Found: M⁺, 270.8590. C₅Cl₃N₃S₂ requires M, 270.8599); LSMS: (EI, *B/E* of *m/z* 271) 236 (M⁺ – Cl, 100%), 210 (M⁺ – CCIN, 12), 178 (4), 143 (4), 137 (4), 125 (6), 120 (7), 102 (6), 93 (5), 85 (2), 64 (7); (EI, *B/E* of *m/z* 236) 210 (22%), 201 (100), 175 (50), 169 (48), 140 (11), 137 (34), 131 (25), 120 (14), 117 (49), 108 (16), 105 (14), 102 (37), 93 (32), 82 (26), 79 (16), 70 (31), 67 (12), 64 (8). Further elution (DCM) gave 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)propanedinitrile **2** (123 mg, 61%), identical with that reported.¹

Reaction of 4,5-dichloro-1,2,3-dithiazolium chloride 6 with tetra-cyanoethylene oxide in the presence of *N*-chlorosuccinimide (see Table 2)

To a stirred solution of 4,5-dichloro-1,2,3-dithiazolium chloride **6** (207 mg, 1 mmol) in toluene (3 ml) at ca. 20 °C, *N*-chlorosuccinimide (133 mg, 1 mmol) was added followed by TCNEO (144 mg, 1 mmol). The mixture was heated under reflux for 1 h and then allowed to cool to ca. 20 °C. Chromatography (light petroleum–DCM, 1:1) gave N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-2,2-dichloro-2-cyanoacetamide **11** (66 mg, 23%) as cream coloured needles, mp 91 °C (from heptane) (Found: C, 20.9; N, 14.3. C₅Cl₃N₃OS₂ requires C, 20.9; N, 14.6%); λ_{max}(DCM)/nm 232 (log ε 3.56), 260 (3.46), 394 inf (4.19), 400 (4.19); ν_{max}(Nujol)/cm⁻¹ 2255w (CN), 1627s (C=N), 1466s, 1397s, 1266s, 1196m, 1187m, 1065w, 965w, 896s, 831s, 784s, 704s, 693s, 671m; δ_C(68 MHz; [D₂H₂]⁺DCM) 175.39 (C=O), 171.25 (C-5), 151.48 (C-4), 113.54 (CN), 65.74 (CCl₂); *m/z* (EI) 287 (M⁺, 2%), 253 (MH⁺ – Cl, 2), 224 (M⁺ – CClO, 3), 179 (M⁺ – C₂Cl₂N, 100), 162 (3), 151 (M⁺ – C₃Cl₂NO, 6), 118 (4), 108 (7), 93 (CCINS⁺, 6), 86 (14), 74 (6), 64 (S₂⁺, 20) (Found: M⁺, 286.8559. C₅Cl₃N₃OS₂ requires M, 286.8548); LSMS: (EI, *B/E* of *m/z* 287) 252 (2%), 233 (2), 224 (2), 179 (100), 151 (1), 141 (1), 110 (2), 108 (4), 102 (1), 86 (1); (EI, *B/E* of *m/z* 179) 163 (25%), 151 (100), 143 (80), 137 (16), 128 (30), 118 (54), 113 (18), 105 (27), 93 (CCINS⁺, 25), 86 (57), 79 (34), 70 (32), 64 (S₂⁺, 39), 58 (CNS⁺, 20), 46 (NS⁺, 5). Further elution (DCM) gave 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)propanedinitrile **2** (111 mg, 55%), identical with that reported.¹

Independent synthesis of *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dichloro-2-cyanoacetamide **11**

To a stirred suspension of 4,5-dichloro-1,2,3-dithiazolium chloride **6** (414 mg, 2 mmol) in DCM (10 ml) at ca. 20 °C, 2,2-dichloro-2-cyanoacetamide **12**¹⁰ (304 mg, 2 mmol) was added. After stirring for 2 h Hünig's base (695 µl, 4 mmol) was slowly introduced. The mixture became black and copious white fumes of hydrogen chloride were evolved. After 5 h the mixture was filtered and all volatiles were removed. Chromatography (light petroleum–DCM, 8:1) of the residue gave 4-chloro-5*H*-1,2,3-dithiazole-5-thione **1** (52 mg, 31%), identical with an authentic specimen. Further elution (DCM) gave the title compound **11** (103 mg, 18%) as cream coloured needles, mp 91 °C (from heptane), identical with that described above.

N-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2,2-trichloroacetamide **13**

To a stirred suspension of 4,5-dichloro-1,2,3-dithiazolium chloride **6** (828 mg, 4 mmol) in DCM (20 ml) at ca. 20 °C, 2,2,2-trichloroacetamide (644 mg, 4 mmol) was added followed by the slow addition of Hünig's base (1390 µl, 8 mmol). After 4 h the mixture was filtered and all volatiles were removed. Chromatography (light petroleum–DCM, 8:1) of the residue gave 4-chloro-5*H*-1,2,3-dithiazole-5-thione **1** (93 mg, 30%) identical with an authentic specimen. Elution with DCM gave the title compound **13** (426 mg, 36%) as cream coloured needles, mp 99–102 °C (from heptane) (Found: C, 16.4; N, 9.3. C₄Cl₄N₂OS₂ requires C, 16.2; N, 9.5%); λ_{max}(DCM)/nm 230 (log ε 3.72), 257 (3.54), 394 (4.11); ν_{max}(Nujol)/cm⁻¹ 1611s (C=N), 1487s, 1417s, 1397s, 1268s, 1189m, 1173w, 978w, 895m, 850s, 829m, 766m, 698m, 686s, 670w; δ_c(68 MHz; [²H₂]DCM) 175.21 (C=O), 173.74 (C-5), 151.03 (C-4), 93.60 (CCl₃); *m/z* (EI) 296 (M⁺, 3%), 233 (M⁺ – CClO, 34), 179 (M⁺ – CCl₃, 100), 162 (2), 151 (M⁺ – C₂Cl₃O, 3), 117 (19), 110 (7), 93 (CCINS⁺, 4), 86 (18), 64 (S₂⁺, 11) (Found: M⁺, 295.8234. C₄Cl₄N₂OS₂ requires *M*, 295.8206).

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