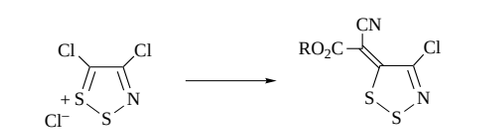
New routes to benzothiophenes, isothiazoles and 1,2,3-dithiazoles

Kumaraswamy Emayan, Russell F. English, Panayiotis A. Koutentis and Charles W. Rees

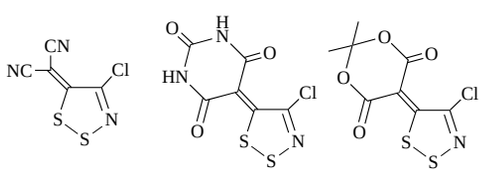
Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY

4,5-Dichloro-1,2,3-dithiazolium chloride 1 condenses with active methylene compounds, such as malononitrile, barbituric acid and Meldrum's acid, to give the dithiazol-5-ylidene derivatives, such as 3, 4 and 5, in modest yields. Better yields are obtained from 4-chloro-1,2,3-dithiazole-5-thione 6. Thus the thione 6 condenses with diphenyldiazomethane in a very mild version of the Barton double extrusion synthesis of hindered alkenes; this requires neither heat to extrude nitrogen nor a phosphine to abstract sulfur, to give the alkene 7 (83%) (Scheme 1). This alkene rearranges at room temperature, with loss of hydrogen chloride and sulfur, to give the benzothiophene 13 (89%) in a new thiophene ring-forming reaction (Scheme 2). The thione 6 also condenses with tetracyanoethylene oxide to give a better yield of the dicyanomethylene compound 3 (70%) (Scheme 4). Compound 3, in turn, reacts with morpholine and with chloride ions (Scheme 5) to give 3-morpholino- 19 (60%) and 3-chloro- 20 (100%) isothiazole-4,5-dicarbonitrile, in a new isothiazole ring synthesis. Mechanisms are proposed for all of these reactions.

In their original description of the preparation of 4,5-dichloro-1,2,3-dithiazolium chloride **1** and its reactions with water, hydrogen sulfide and primary amines, Appel *et al*. also reported that methyl and ethyl cyanoacetate condensed with **1** to give the 1,2,3-dithiazole-5-ylidene products **2** in good yield.[1] We have extended the reaction of **1** with several binucleophilic aromatic amines since subsequent cyclisation of the products have furnished simple routes to a variety of cyanoheterocyclic compounds.[2] We were therefore encouraged to explore the condensation of the salt **1** with other active methylene compounds to



1 **2**



3 **4** **5**

form a carbon–carbon double bond functionalised by the electrophilic dithiazole ring which might undergo similarly useful cyclisations.

The reactions were conducted as usual[2] in stirred dichloromethane at room temperature, followed by addition of pyridine before work-up. The reactions were usually slow and only low yields of products were isolated with compounds such as diethyl malonate, dibenzoylmethane, dimedone and barbituric acid. Yields were somewhat improved by stirring the reaction mixture for 12–48 h at room temperature before the addition of pyridine. Thus, malononitrile, barbituric acid and Meldrum's acid gave **3** (40%), **4** (35%) and **5** (26%), respectively.

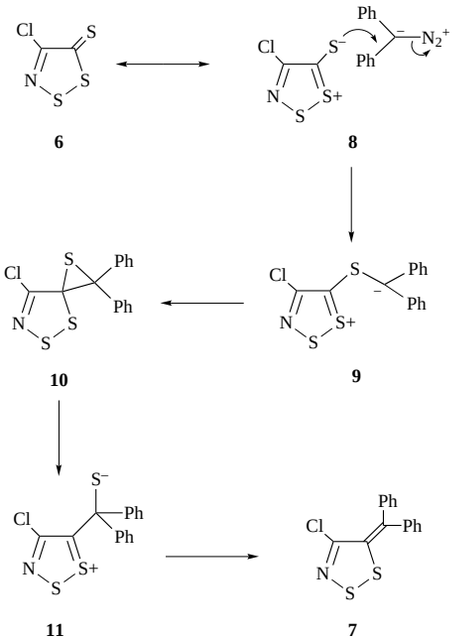
4-Chloro-5*H*-1,2,3-dithiazole-5-thione 6

Diphenylmethane failed to react with the salt **1** to give the analogous product **7**, under a variety of conditions, and use of preformed lithium or sodium derivatives of diphenylmethane led only to decomposition of the heterocyclic ring and formation of 4-chloro-5*H*-1,2,3-dithiazole-5-thione **6**. The thione **6**, which can be prepared in high yield (95%) by treatment of **1** with hydrogen sulfide in acetonitrile,[1] is a maroon solid which gives an intensely yellow solution in all but the most polar organic solvents. There is little solvent effect on the position of the C=S vibration in the IR spectrum which is close to 1180 cm^{-1} in light petroleum, tetrachloromethane, diethyl ether and chloroform, and as a Nujol mull. The thione **6** is a common by-product in reactions of the salt **1** with nucleophiles, indicative of some opening of the dithiazole ring.

The ready availability of the thione **6** suggested a possible synthesis of the hindered alkene **7** from **6** and diphenyldiazomethane, based upon the Barton two-fold extrusion process for the formation of highly hindered carbon–carbon double bonds.[3] In this, a diazoalkane adds to a thiocarbonyl group to give a 1,3,4-thiadiazoline from which dinitrogen is extruded thermally and then sulfur is removed from the thiirane, usually with triphenylphosphine.[4] When we added diphenyldiazomethane to a solution of the dithiazolethione **6** in benzene or dichloromethane at room temperature there was a spontaneous evolution of gas followed by the precipitation of sulfur. After evaporation of the reaction mixture, chromatography of the residue gave an orange oil identified by spectroscopy and mass spectrometry as (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)diphenylmethane **7** (83%). The ^{1}H NMR spectrum of this, although not well resolved, appeared to show that each peak is doubled, indicating that the two phenyl groups of **7** are in different environments.

Thus, the diazoalkane–thione reaction had proceeded to the final alkene, without the need for heat to extrude nitrogen or of triphenylphosphine to abstract sulfur. This indicates the possibility of a modified mechanism, not involving cycloaddition to a thiadiazoline, but driven by the enhanced nucleophilicity of the thione sulfur in **6** arising from its 6π-aromatic structure **8** (Scheme 1). The zwitterion **9** so formed could collapse rapidly to the thiirane **10** from which the thiirane sulfur is readily lost, possibly *via* the new zwitterion **11** with its highly nucleophilic exocyclic sulfur being transferred in a series of bimolecular reactions[5] leading ultimately to **7** and S_8.

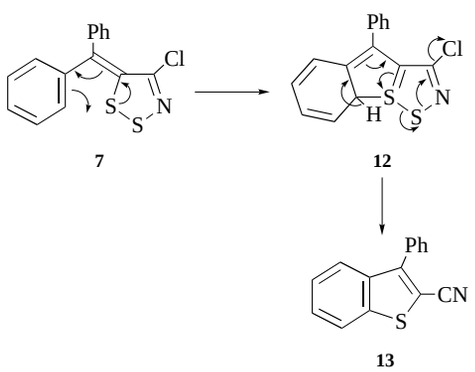
When stored overnight, the dithiazole **7** decomposed to sulfur and a colourless compound whose mass spectrum indicated the loss of one atom each of hydrogen, sulfur and chlorine, and the IR spectrum of which showed the presence of a nitrile



Scheme 1

group. This suggested that the product could be 3-phenylbenzo-[*b*]thiophene-2-carbonitrile **13** and this was confirmed by an independent synthesis. Benzophenone was condensed with acetonitrile to form 3,3-diphenylacrylonitrile[6] which, with disulfur dichloride in the presence of pyridine,[7] gave a product **13**, identical with that already described. Hydrolysis of **13** gave the 2-carboxylic acid with spectroscopic properties in agreement with those in the literature.[8]

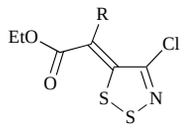
The clean conversion of the dithiazole **7** into the benzothiophene **13** (89%) under such mild conditions (or indeed the one-pot conversion of the thione **6** and diphenyldiazomethane into **13**) is quite striking and represents a new way of constructing the thiophene ring. The overall process is similar to the conversion of the *N*-phenyl imine **6** (=NPh for =S), derived from the salt **1** and aniline, into benzothiazole-2-carbonitrile;[2] this latter conversion requires strong heat presumably because of the greater stability of the imine **8** (PhN^- for S^-) compared with the alkene **7**. A possible mechanism is shown in Scheme 2. Ring



Scheme 2

closure between the phenyl and heterocyclic rings could be an electrocyclic process (arrows in **7**) to give **12**. Elimination of hydrogen chloride and extrusion of sulfur (possibly *via* the nitrile sulfide) would be greatly facilitated by the stability of the benzothiophene system and the cyano group of **13**.

We looked briefly at the reaction of two other diazo compounds with the thione **6**. Ethyl diazoacetate was less reactive than diphenyldiazomethane and required refluxing in benzene; a single geometrical isomer was obtained in 63% yield. This is probably **14**, (R=H), where the carbonyl oxygen can interact

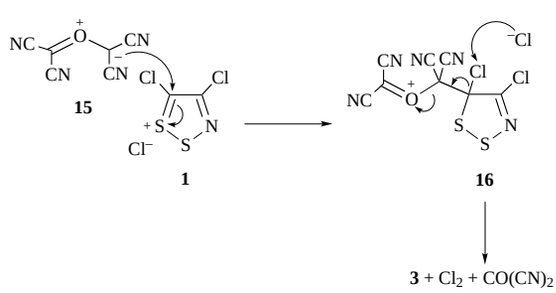


with S-1 of the dithiazole ring; the IR carbonyl stretching frequency is found at 1662 cm^{-1}, *ca.* 60 cm^{-1} lower than expected for an ordinary acrylic ester. Diethyl diazomalonate is less reactive still and condensed with the thione **6** only at reflux in xylene to give the analogous product **14**, (R=CO_2Et), in 37% yield. In spite of the modest yield, this is a better preparation of **14**, (R=CO_2Et), than treatment of 4,5-dichloro-1,2,5-dithiazolium chloride **1** with diethyl malonate. The IR spectrum of **14**, (R=CO_2Et), has two carbonyl absorptions at 1737 and 1662 cm^{-1}, and the ^{1}H NMR spectrum shows that the two ethyl groups are in different environments.

(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)propanedinitrile 3

The malononitrile derivative **3** seemed a good initial substrate to test the possibility of side-chain cyclisation onto the thiadiazole ring. Appropriate nucleophiles could be generated by addition to a nitrile triple bond, and the presence of two nitriles meant that cyclisation could occur either at S-1, with opening of the heterocyclic ring, or at C-4, with displacement of chlorine. Although compound **3** was formed in relatively good yield (40%) from malononitrile and the salt **1** under the earlier conditions, it was tedious to purify and we needed a better source. Replacement of pyridine by Hünig's base in this preparation led to a lower yield of **3** (25%) together with a substantial amount of the thione **6** (70%).

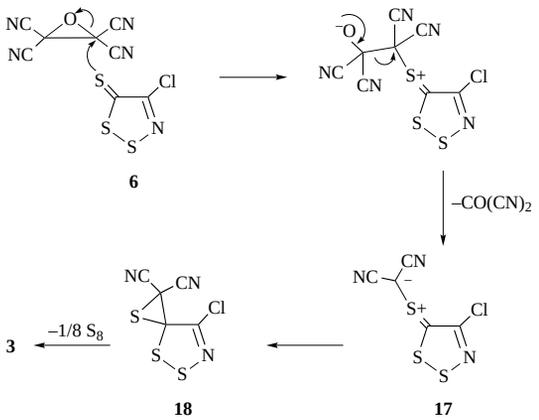
We therefore turned to the reactions of the salt **1** and the thione **6** with two other sources of the dicyanomethylene group, tetracyanoethylene (TCNE)[9] and tetracyanoethylene oxide (TCNEO).[10] These reactions were successful though rather complex and full details of all the products and reaction mechanisms will be reported later.[11] Treatment of the salt **1** with TCNEO (1 equiv.) in toluene at room temperature for 24 h or at reflux for 1.5 h gave the desired dicyanomethylene compound **3** in improved yield (*ca.* 60%). A possible explanation is that TCNEO reacts as a nucleophile through its ring-opened stabilised ylide form **15**[12] to give the adduct **16** which collapses to give **3**, carbonyl cyanide and chlorine (Scheme 3).



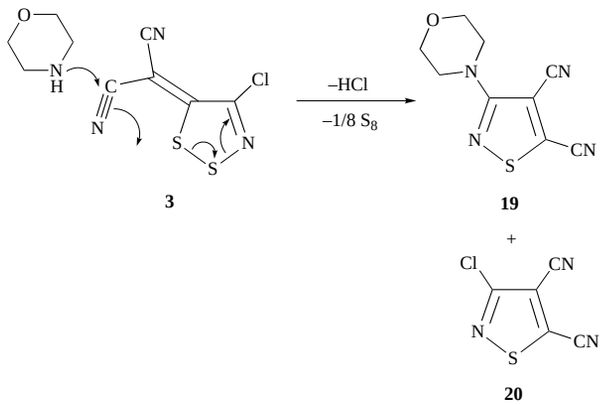
Scheme 3

TCNE reacts with thiones to give dicyanomethylene compounds in high yield *via* 2 + 2 cycloadducts and elimination of thiocarbonyl cyanide.[13] However TCNE did not react with the dithiazolethione **6** in refluxing toluene or even xylene. This may be a further indication of the significance of the dipolar contribution **8** to the 'thione' structure.

TCNEO also reacts with thiones to give dicyanomethylene compounds. The reaction is thought to occur by nucleophilic attack on the epoxide ring by the thione sulfur followed by fragmentation to give carbonyl cyanide and a thiocarbonyl ylide[9] (*cf.* Scheme 4). These ylides can be isolated when strongly electron-releasing groups are present to stabilise the positive



Scheme 4



Scheme 5

charge, but otherwise they collapse to the thiirane which loses sulfur to give the observed dicyanomethylene product. Treatment of the thione **6** with TCNEO (1 or 2 equiv.) in benzene or toluene from room temperature to 110 °C for up to 7 days did give the desired product **3** in yields in the range 53–72%, together with other products,[11] the best yield being obtained with TCNEO (2 equiv.) in toluene at 110 °C for 2 days. A reasonable mechanism, in line with earlier proposals,[9] is shown in Scheme 4. As was reported for the reaction in Scheme 1, no intermediates in the conversion of the thione **6** into the dicyanomethylene derivative **3** were observed. The same structural features favour the direct formation of the stabilised products **7** and **3**, the thiocarbonyl ylide **17** and the thiirane **18** (Scheme 4) being closely analogous to **9** and **10** (Scheme 1), respectively.

A new synthesis of isothiazoles

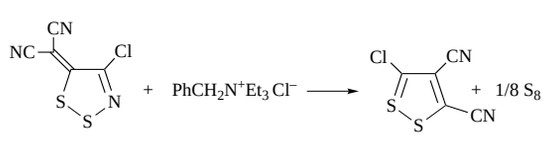
With a good route to the dicyanomethylenedithiazole **3** available, we were able to investigate the possible cyclisation of nucleophilic side-chains on the dithiazole ring, such as we have observed with many imino-dithiazole derivatives.[2] Compound **3** itself is stable and does not undergo spontaneous cyclisation. However, the addition of an amine to a nitrile group in **3** should generate a suitable nucleophile, and the addition of amines to unactivated nitriles is known to be catalysed by cuprous chloride.[14] We therefore treated compound **3** with morpholine in boiling benzene in the presence of cuprous chloride and this gave 4,5-dicyano-3-morpholinoisothiazole **19** in modest yield (40%) together with a trace of 3-chloro-4,5-dicyanoisothiazole **20** (see below). The structure of compound **19** was assigned from its spectroscopic data and confirmed by X-ray structure determination.[15] We assume that **19** is formed by addition of morpholine to a cyano group (possibly a pre-equilibrium addition to either cyano group) and cyclisation onto S-1 with formation of the aromatic isothiazole ring and a new cyano group (Scheme 5). The trace of 3-chloroisothiazole **20** isolated suggested that chloride ion could compete with morpholine in the initial addition. Furthermore, the chlorine in **20** was shown to be readily displaced by morpholine to give the major product **19** in high yield.

In view of the formation of any 3-chloro-4,5-dicyanoisothiazole **20** in the morpholine reaction (Scheme 5), we treated the dicyanomethylenedithiazole **3** with a catalytic (10%) source of chloride, anhydrous benzyltriethylammonium chloride, in refluxing benzene or toluene to give the isothiazole **20** and sulfur almost quantitatively (see Table 1). Yields were slightly lower when a full equivalent of the tetraalkylammonium chloride was used. The reaction was very slow in refluxing dichloromethane. The short and high yielding sequence from the salt **1** to the isothiazole **20** *via* the thione **6** and the dicyano compound **3**, provided a ready source of this fully functionalised isothiazole, a new and synthetically versatile intermediate with two adjacent cyano groups and a readily displaced chlorine atom.

In view of the high reactivity of the dicyano compound **3** towards chloride ions in an uncatalysed reaction, we repeated its reaction with morpholine (Scheme 5) but without the cuprous chloride catalyst. The morpholinoisothiazole **19** was again formed and could be isolated in yields comparable to the 'catalysed' reaction. Presumably, the small equilibrium amount of morpholine-cyano group adduct is efficiently intercepted by intramolecular attack on S-1 of the dithiazole ring (Scheme 5).

In conclusion, we have described the condensation of the dithiazolium salt **1** with active methylene compounds to form, for example, the dicyanomethylene derivative **3**, an improved synthesis of **3** from TCNEO and the thione **6**, and a remarkably mild (room temperature, no phosphine) example of the Barton two-fold extrusion process for the formation of hindered alkenes in the reaction of the thione **6** with diphenyldiazomethane. We have also described a new route to the benzothiophene **13** and to the highly functionalised isothiazoles **19** and **20** in the ready rearrangement of **3** with morpholine and chloride ions. These simple reactions, of potentially wide scope, are worthy of further investigation.

Table 1 Conversion of the dithiazole **3** into the isothiazole **20** with benzyl(triethyl)ammonium chloride



3 (mmol)	Solvent (3 ml)	Temp. (°C)	Reaction time (h)	$PhCH_2N^+Et_3\ Cl^-$ (%)	**20** (%)	S_8 (%)
0.32	C_6H_6	80	48	10	100	98
0.84	PhMe	110	48	10	95	94
0.31	C_6H_6	80	48	100	86	90

Experimental

For general experimental details and the preparation of the reagent **1**, see our related papers.[2] Tetracyanoethylene[16] and tetracyanoethylene oxide[10] were prepared by literature methods.

Reaction of 4,5-dichloro-1,2,3-dithiazolium chloride 1 with active methylene compounds

2-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-5,5-dimethylcyclohexane-1,3-dione. To a suspension of dimedone (280 mg, 2.0 mmol) in DCM (10 ml) was added the salt **1** (417 mg, 2.0 mmol). The mixture was stirred at ambient temperature for 0.5 h, after which pyridine (0.32 ml, 4.0 mmol) was added to it. The mixture was filtered and then purified by dry flash chromatography to give 4-chloro-5*H*-1,2,3-dithiazole-5-thione **6** (60 mg) and the *title compound* (147 mg, 27%) as orange crystals, mp 135–137 °C (Found: C, 43.3; H, 3.5; N, 4.9. $C_{10}H_{10}ClNO_2S_2$ requires C, 43.55; H, 3.65; N, 5.1%); λ_{max}(EtOH)/nm 265 (log ε 3.90) and 465 (4.05); ν_{max}(CCl_4)/cm^{-1} 2962, 1727, 1673s, 1578s, 1452s, 1329s, 1304, 1245, 1174, 1105 and 862; δ_H(270 MHz, $CDCl_3$) 2.71 (2H, s), 2.67 (2H, s) and 1.14 (6H, s); *m*/*z* (EI) 275 (M^+, 18%), 240 ($M^+ - Cl$, 100), 225 ($M^+ - CH_3$, −Cl, 26), 184 (21), 177 (12) and 83 (12).

Reaction with diethyl malonate. A mixture of diethyl malonate (160 mg, 1.0 mmol) and the salt **1** (209 mg, 1.0 mmol) in DCM (5 ml) was stirred at ambient temperature for 0.5 h, after which pyridine (0.16 ml, 2.0 mmol) was added to it and stirring continued for a further 16 h. The mixture was then filtered and purified by dry flash chromatography (20 g silica gel, 2.5% gradient from light petroleum to DCM, 20 ml fractions). Elution with 17.5–20% DCM gave compound **6** (37 mg) and with 53–68% DCM an oil shown by NMR spectroscopy and mass spectrometry to consist of diethyl malonate (55%) and diethyl (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)malonate **14** (R = CO_2Et; 45%). This compound was prepared in pure form from diethyl diazomalonate (see below).

(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,3-diphenylpropane-1,3-dione. A mixture of dibenzoylmethane (449 mg, 2.0 mmol) and the salt **1** (417 mg, 2.0 mmol) in DCM (10 ml) was stirred at ambient temperature for 16 h. The salt **1** (315 g, 76% recovery) was then filtered off and the filtrate was purified by dry flash chromatography to give dibenzoylmethane (153 mg, 34% recovery) and the *title compound* (91 mg, 13%) as orange crystals, mp 149–153 °C (Found: C, 56.5; H, 2.7; N, 3.85. $C_{17}H_{10}ClNO_2S_2$ requires C, 56.7; H, 2.8; N, 3.9%); λ_{max}(EtOH)/nm 253 (log ε 4.24), 442 (4.19) and 463 (4.16); ν_{max}(CCl_4)/cm^{-1} 3064w, 1672, 1552, 1448, 1299s, 1287s, 1261, 1194, 1174, 1130, 1019, 836, 691 and 646; δ_H(270 MHz, $CDCl_3$) 7.18–7.39 (6H, m), 7.45–7.53 (2H, m) and 7.75–7.80 (2H, m); *m*/*z* (EI) 359 (M^+, 24%), 324 ($M^+ - Cl$, 13), 296 ($M^+ - Cl$, −CO, 12), 224 (81) and 105 ($PhCO^+$, 100).

(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)propanedinitrile 3. *Method 1.*—To a suspension of the salt **1** (830 mg, 4 mmol) in dichloromethane (30 ml) was added propanedinitrile (260 mg, 4 mmol). The mixture was stirred at room temperature for 12 h after which pyridine (0.65 ml, 8 mmol) was added to it and stirring continued for a further 2 h. Flash chromatography on silica gel (twice) eluting with dichloromethane–light petroleum (1 : 1) gave the *title compound* **3** (320 mg, 40%) as orange crystals from dichloromethane–light petroleum, mp 181–182 °C (Found: C, 29.8; N, 20.7. $C_5ClN_3S_2$ requires C, 29.8; N, 20.8%); λ_{max}(DCM)/nm 260 (log ε 3.56), 295 (3.10), 425 (4.13); ν_{max}(Nujol)/cm^{-1} 2219s (CN) and 2189w (CN), 1457s, 1249w, 1142m, 941w, 891m, 810m, 722w; δ_C(68 MHz, $CDCl_3$) 167.31 (C-5), 143.25 (C-4), 115.63 (CN), 110.44 (CN) and 67.32 [$C(CN)_2$]; *m*/*z* (EI) 201 (M^+, 100%), 140 ($M^+ - CClN$, 26), 108 ($M^+ - CClNS$, 15), 105 (11), 93 ($CClNS^+$, 93), 81 (14), 76 (14), 70 (27) and 64 (S_2^+, 52).

Method 2.—To a stirred suspension of the salt **1** (830 mg, 4 mmol) in DCM (30 ml) at *ca.* 20 °C, propanedinitrile (264 mg, 4 mmol) was added in one portion. The mixture was stirred for 2 h after which Hünig's base (1.39 ml, 8 mmol) was added to it slowly. The mixture became black and copious fumes of hydrogen chloride were evolved. TLC indicated the presence of two products. After 12 h the volatile components were removed from the mixture and chromatography (light petroleum–DCM, 1 : 1) of the residue gave 4-chloro-5*H*-1,2,3-dithiazole-5-thione **6** (237 mg, 70%) as a red solid, identical with an authentic sample.[1] Further elution (DCM) gave the title compound **3** (201 mg, 25%) as an orange solid identical with that described above.

Method 3.—To a stirred solution of the thione **6** (84.5 mg, 0.5 mmol) in toluene (3 ml) at *ca.* 20 °C, was added tetracyanoethylene oxide (144 mg, 1 mmol) in one portion. After 5 days no dithiazolethione remained (TLC). Work-up and chromatography with light petroleum followed by DCM gave, in the final fractions, compound **3** (53 mg, 53%) identical with that descibed above. A similar reaction in toluene under reflux for 2 days gave **3** (72%) yield.

5-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)hexahydropyrimidine-2,4,6-trione 4. To a suspension of the salt **1** (830 mg, 4 mmol) in dichloromethane (30 ml) was added barbituric acid (510 mg, 4 mmol). The mixture was stirred at room temperature for 48 h after which pyridine (0.65 ml, 8 mmol) was added to it and stirring continued for a further 2 h. The product was separated by flash chromatography on silica gel eluting with dichloromethane to give the *title compound* **4** (360 mg, 35%) as a red solid from dichloromethane–light petroleum, mp 265–266 °C (Found: C, 27.4; H, 1.1; N, 15.9. $C_6H_2ClN_3O_3S_2$ requires C, 27.3; H, 0.8; N, 15.9%); (Found: M^+, 262.9247. $C_6H_2ClN_3O_3S_2$ requires *M*, 262.9226); ν_{max}(Nujol)/cm^{-1} 3400s (NH) and 1680–1780 3 bands (C=O); δ_H(270 MHz, DMSO) 6.7 (br); *m*/*z* (EI) 263 (M^+, 10%), 228 ($M^+ - Cl$, 100), 185 (85) and 64 (S_2^+, 64).

5-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione 5. To a suspension of the salt **1** (830 mg, 4 mmol) in dichloromethane (30 ml) was added Meldrum's acid (580 mg, 4 mmol). The mixture was stirred at room temperature for 48 h after which pyridine (0.65 ml, 8 mmol) was added to it and stirring continued for a further 2 h. The product was separated by flash chromatography on silica gel eluting with dichloromethane to give the *title compound* **5** (290 mg, 26%) as red crystals from dichloromethane–light petroleum, mp 200–201 °C (Found: C, 34.4; H, 1.9; N, 5.0. $C_8H_6ClNO_4S_2$ requires C, 34.4; H, 2.2; N, 5.0%); ν_{max}(Nujol)/cm^{-1} 1700, 1690s (C=O), 1470s, 1420s, 1390, 1380m and 1300s; δ_H(270 MHz, $CDCl_3$) 1.9 (s); *m*/*z* (EI) 279 (M^+, 3%), 179 (16), 177 (37), 64 (S_2^+, 64), 44 (CO_2, 100).

Reactions of 4-chloro-5*H*-1,2,3-dithiazole-5-thione 6

(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)diphenylmethane 7. Diphenyldiazomethane (56 mg, 0.29 mmol) was added to a solution of the thione **6** (50 mg, 0.29 mmol) in DCM (2 ml). The mixture was stirred at ambient temperature for 1 h and then filtered. The mixture was separated by dry flash chromatography (10 g silica gel, 10 ml fractions, 2% gradient from light petroleum to DCM). Elution with 18–22% DCM gave the *title compound* **7** (73 mg, 83%) as an orange coloured oil; ν_{max}(CCl_4)/cm^{-1} 3061w, 1127, 699s and 622; δ_H(270 MHz, $CDCl_3$) 7.0–7.2 (m); *m*/*z* (EI) 303 (M^+, 73%), 268 ($M^+ - Cl$, 44), 237 ($MH^+ - ClS$, 73), 236 ($M^+ - ClS$, 66), 235 ($M^+ - HClS$, 82), 210 ($M^+ - ClSCN$, 90), 204 ($M^+ - ClS_2$, 19), 203 ($M^+ - HClS_2$, 21), 178 ($M^+ - ClCNS_2$, 14), 165 ($M^+ - HClCCNS_2$, 44) and 77 (Ph^+, 24). When compound **7** was stored at ambient temperature for 16 h, its orange colour faded and the resulting mixture was separated by dry flash chromatography (10 g silica gel, 2% gradient light petroleum to DCM, 10 ml fractions). Elution with 16–18% DCM gave 3-*phenylbenzo*[b]*thiophene*-2-*carbonitrile* **13** (61 mg, 89%) as a crystalline solid, mp 78–81 °C (Found: C, 76.6; H, 3.8; N, 5.9. $C_{15}H_9NS$ requires C, 76.6; H, 3.9; N, 5.95%); ν_{max}(CCl_4)/cm^{-1} 3066, 1665s, 1601, 1448, 1318, 1278s, 941, 919, 701s and 639;

δ_H(270 MHz, $CDCl_3$) 7.78–7.85 (3H, m) and 7.44–7.63 (6H, m); *m/z* (EI) 235 (M^+, 100%), 208 ($M^+ - HCN$, 6), 190 ($M^+ -$ CHS, 7) and 104 (12).

3-*Phenylbenzo*[b]*thiophene*-2-*carbonitrile* **13** *from* 3,3-*diphenylacrylonitrile*.—A mixture of 3,3-diphenylacrylonitrile[6] (2.05 g, 10.0 mmol), pyridine (0.16 ml, 2.0 mmol), and disulfur dichloride (2.4 ml, 30 mmol) was heated at 140 °C for 5 h and then poured into ice-water (100 ml). The precipitate was filtered off and extracted with ethanol (100 ml). The extract was evaporated to give the title compound **13** (2.09 g, 89%), identical with that described above.

Ethyl (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)acetate 14 (R=H). A mixture of ethyl diazoacetate (228 mg, 2.0 mmol) and the thione **6** (170 mg, 1.0 mmol) in benzene (10 ml) was heated at reflux for 16 h. The mixture was evaporated *in vacuo* and the residue was purified by dry flash chromatography (10 g silica gel, 3.33% gradient from light petroleum to DCM, 15 ml fractions). Elution with 3.33–10% DCM gave sulfur (26 mg, 80%), and 33–43% DCM gave the *title compound* (141 mg, 63%) as yellow needles, mp 97–98 °C (Found: C, 32.2; H, 2.7; N, 6.3. $C_6H_6ClNO_2S_2$ requires C, 32.2; H, 2.7; N, 6.3%); λ_{max}(EtOH)/nm 252 (log ε 3.71) and 400 (3.94); ν_{max}(CCl_4)/cm^{-1} 2984w, 1662, 1542, 1315s, 1201s, 1155s, 1040 and 515; δ_H(270 MHz, $CDCl_3$) 6.69 (1H, s), 4.31 (2H, q, *J* 7.1 Hz) and 1.35 (3H, *J* 7.1 Hz); δ_C(69 MHz, $CDCl_3$) 168.8 (C=O), 155.0 (C-5), 145.2 (C-4), 107.4, 61.6 and 14.4 (CH_3); *m/z* (EI) 223 (M^+, 70%), 195 ($M^+ - C_2H_4$, 5), 188 (M^+ − Cl, 44), 178 (M^+ − OEt, 86), 160 ($M^+ - C_2H_4$, −Cl, 100), 151 (M^+ − EtOH, −CN, 99), 99 (ClS_2^+, 10) and 64 (S_2^+, 28).

Diethyl (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)malonate 14 (R=CO_2Et). A mixture of diethyl diazomalonate (372 mg, 2.0 mmol) and the thione **6** (170 mg, 1.0 mmol) in xylene (5 ml) was heated at reflux for 6 h. After this, the mixture was concentrated by solvent removal *in vacuo* and the residue was purified by dry flash chromatography (20 g silica gel, 5% gradient from light petroleum to DCM, 20 ml fractions). Elution with 5–15% DCM gave sulfur (45 mg, 1.4 mmol), with 30% DCM the thione **6** (2 mg), and with 75–90% DCM the *title compound* (111 mg, 37%) as an orange oil (Found: M^+, 294.9747. $C_9H_{10}ClNO_4S_2$ requires *M*, 294.9740); λ_{max}(EtOH)/nm 355 (log ε 3.55) and 390sh (3.09); ν_{max}(CCl_4)/cm^{-1} 2984, 2940, 1737 (C=O), 1662 (C=O), 1286, 1250 and 1176; δ_H(270 MHz, $CDCl_3$) 4.36 (2H, q, *J* 7.08), 4.33 (2H, q, *J* 7.08), 1.37 (3H, t, *J* 7.08) and 1.34 (3H, t, *J* 7.08); *m/z* (EI) 295 (M^+, 32%), 260 (M^+ − Cl, 35), 250 (M^+ − OEt, 36), 232 ($M^+ - C_2H_4$, −Cl, 31), 222 (13), 204 (5), 186 (100), 178 (16), 151 (10), 145 (18) and 105 (31).

3-Morpholinoisothiazole-4,5-dicarbonitrile 19

Method 1. To a solution of (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)propanedinitrile **3** (200 mg, 1 mmol) and morpholine (0.17 ml, 1 mmol) in benzene (10 ml) was added solid cuprous chloride (1 equiv.) at room temperature. The mixture was heated under reflux for 12 h after which the solvent was removed under reduced presssure. The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1:4) to give the *title compound* **19** (132 mg, 60%) as yellow crystals from dichloromethane–light petroleum, mp 185–187 °C (Found: M^+, 220.0437. $C_9H_8N_4OS$ requires *M*, 220.0419); λ_{max}(DCM)/nm 375 (log ε 3.50); ν_{max}(Nujol)/cm^{-1} 2224 (CN), 1520s, 1515s, 1464s, 1445s, 1375m, 1348w, 1326w, 1303m, 1279s, 1263s, 1235m, 1219m, 1175w, 1120s, 1069w, 1038m, 1022w, 1003w, 955m, 936m, 898w, 874m, 863m, 842w, 801w, 727w and 651m; δ_H(270 MHz, $CDCl_3$) 3.83 (4H, t, CH_2O) and 3.67 (4H, t, CH_2N); δ_C(68 MHz, $CDCl_3$) 165.43 (C-3), 142.74 (C-5), 111.39 (CN), 108.27 (CN), 102.92 (C-4), 66.09 (CH_2O) and 48.0 (CH_2N); *m/z* (EI) 220 (M^+, 50%), 177 ($M^+ - C_2H_3O$, 26), 162 ($M^+ - C_3H_6O$, 100), 135 (52), 107 (24).

Method 2. To a stirred solution of 3-chloroisothiazole-4,5-dicarbonitrile **20** (47 mg, 0.28 mmol) in toluene (2 ml) at 80 °C (bath temperature), under nitrogen, was added morpholine (195 μl, 2.24 mmol). After 8 h no starting material remained (TLC) and the mixture was allowed to cool to *ca.* 20 °C. Chromatography (DCM) gave the title compound **19** (49 mg, 80%) as yellow prisms, mp 185–187 °C identical with that described above.

3-Chloroisothiazole-4,5-dicarbonitrile 20 (see Table 1)

To a stirred solution of (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-propanedinitrile **3** (64 mg, 0.32 mmol) in benzene (3 ml) at 80 °C, was added benzyl(triethyl)ammonium chloride (7 mg, 10 mol%) in one portion. After 2 days no starting material **3** remained (TLC). The mixture was allowed to cool to *ca.* 20 °C when chromatography (light petroleum) gave sulfur (10 mg, 98%); further elution light petroleum–DCM gave the *title compound* **20** (54 mg, 100%) as colourless needles, mp 98 °C (cyclohexane–pentane) (Found: C, 35.8; N, 24.6. C_5ClN_3S requires C, 35.5; N, 24.85%); λ_{max}(DCM)/nm 245 (log ε 3.76), 253 infl (3.69), 291 (3.83) and 295infl (3.82); ν_{max}(Nujol)/cm^{-1} 2248 (CN), 2239m (CN), 1643w (C=N), 1510s (C=C), 1366m, 1356s, 1196m, 1175s, 1147w, 1020m, 980w, 858m, 829m, 697w and 632m; δ_C(68 MHz, $CDCl_3$) 152.5 (C-3), 143.29 (C-5), 116.65 (C-4), 109.26 (CN) and 107.75 (CN); *m/z* (EI) 169 (M^+, 100%), 123 (M^+ − NS, 1), 108 ($C_4N_2S^+$, 26), 93 ($CClNS^+$, 46), 82 (C_3NS^+, 6), 76 ($C_4N_2^+$, 4) and 70 (C_2NS^+, 18) (Found: M^+, 168.9490. C_5ClN_3S requires *M*, 168.9501).

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