Synthesis and Reactions of 1,4,2-Dithiazines, Bis(1,4,2-dithiazines) and 1,2,3-Dithiazines by Ring Expansion of 1,3- or 1,2-Dithiolium Cations

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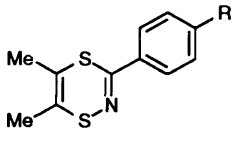
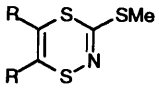
5,6-Dimethyl-3-(2-thienyl)-1,4,2-dithiazine **6**, and 3,3'-(*meta*- and *para*-phenylene)bis(5,6-dimethyl-1,4,2-dithiazines) **10** and **12** have been synthesised, by reaction of the corresponding 1,3-dithiolium or bis(1,3-dithiolium) salts, **5**, **9** and **11**, with a mixture of iodine and aqueous ammonia. A range of the 1,4,2-dithiazine derivatives have been desulfurised to yield isothiazoles upon thermolysis in refluxing toluene. Photolysis of the 1,4,2-dithiazines in the presence of dimethyl acetylenedicarboxylate, tetracyanoethylene and norbornene gives Diels–Alder adducts of the intermediate 1,2-dithiones, and nitrile fragments. Grignard reagents react at S-1 of the 1,4,2-dithiazines, fragmenting the ring to afford nitrile and 1,2-dithioethene moieties. The 1,2,3-dithiazine derivatives **28** and **31** have been isolated from the reaction of the 1,2-dithiolium salts with a mixture of iodine and ammonia; desulfurisation of the 1,2,3-dithiazines occurs readily at room temperature to yield isothiazoles.

Heterocyclothiazines that contain three or more heteroatoms continue to attract keen attention, because the extensive π-electron delocalisation and multiple bonding that occurs in these heterocycles gives rise to a fascinating range of chemical, physical and structural properties.[1,2] Heteroaromatic 6- and 10-π-electron systems have been widely studied; however, 8 π-electron analogues are generally far less accessible, and, consequently, their chemistry is not well explored. Initial studies on the 8 π-electron 1,4,2-dithiazine heterocycle were reported by Fanghänel *et al.*[3] and Nakayama *et al.*[4] We have recently developed an interest in this system and have established an efficient synthetic route to a new range of functionalised derivatives, exemplified by the monocyclic compounds **1a–e** and **2a**, and the bicyclic system **2b**.[5] Solution electrochemical



1 **a** R = OMe
b R = Me
c R = H
d R = Br
e R = NO_2

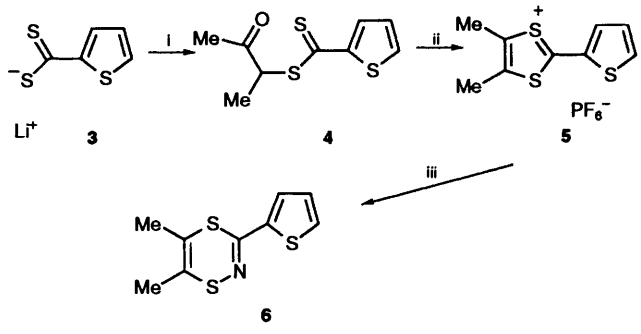


2 **a** R = H
b R–R = S-$[CH_2]_2$-S

and X-ray crystallographic studies on 1,4,2-dithiazines were reported for the first time.[5] The present paper is concerned primarily with reactions of the 1,4,2-dithiazine ring, and with the preparation of derivatives of the rare, isomeric 1,2,3-dithiazine heterocycle.

Results and Discussion

Synthesis of New 1,4,2-*Dithiazine and Bis*(1,4,2-*Dithiazine*) *Derivatives*.—The present study involves the 1,4,2-dithiazine systems **1a–d**, **2a**, **2b**, **6**, **10** and **12**. The syntheses of **1a–d**, **2a** and **b** have been described elsewhere,[5] whereas compounds **6**, **10** and **12** have not been reported previously. Their preparation, discussed briefly below, is based upon ring-expansion of the appropriate 1,3-dithiolium salt **5**, or bis(1,3-dithiolium) salts **9** and **11**, using a mixture of iodine and ammonia at room temperature, as we have detailed previously for compounds **1**



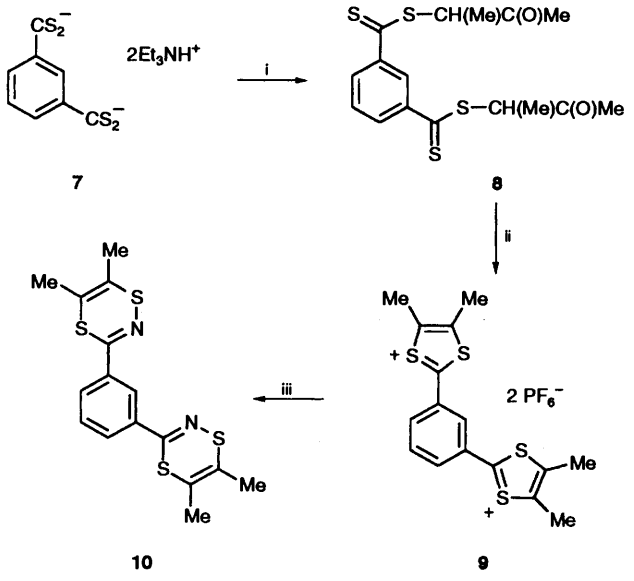
Scheme 1 *Reagents and conditions:* i, 3-chlorobutan-2-one, CH_2Cl_2, 20 °C; ii, H_2SO_4 (conc.) CH_2Cl_2, −20 °C, followed by water, HPF_6, 20 °C; iii, iodine, ammonia (aq.) CH_3CN, 20 °C

and **2**,[5b] using a modification of the procedure of Yonemoto and Shibuya.[6]

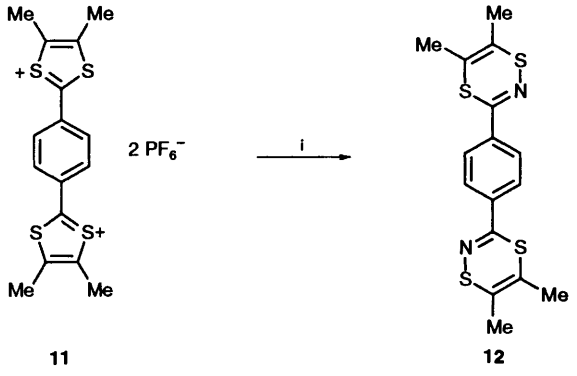
The 3-(2-thienyl) derivative **6**, which is the first 1,4,2-dithiazine derivative to bear a pendant heterocyclic substituent, was prepared in three steps (49% overall yield) from the known thiophene-2-carbodithioate salt **3**[7] (Scheme 1). Alkylation of the salt **3** with 3-chlorobutan-2-one gave the dithioester **4** (91% yield) which cyclised upon treatment with sulfuric acid at −20 °C to give the dithiolium cation which was isolated as the hexafluorophosphate salt **5** (62%). The conversion of the salt **5** into the 1,4,2-dithiazine derivative **6** was accomplished cleanly (86% yield) by treatment of **5** with 3 mol equiv. of iodine and an excess of aqueous ammonia at room temperature.

3,3'-*meta*-phenylenebis(1,4,2-dithiazine) **10** was synthesised analogously, from the bis(carbodithioate) salt **7**, *via* compounds **8** and **9** (Scheme 2). The dication salt **9** decomposed rapidly upon isolation; immediate reaction of an impure sample of **9** with iodine–ammonia was needed to obtain bis(1,4,2-dithiazine) **10**. The overall yield of compound **10** from the bis(dithioester) **8** was only 2%, so further reactions of **10** were not explored. The stable 2,2'-*para*-phenylenebis(dithiolium) dication salt **11** was prepared according to the literature procedure,[8] and subsequent ring expansion afforded the 3,3'-*para*-phenylenebis(1,4,2-dithiazine) derivative **12** in 44% yield (Scheme 3).

Reactions of 1,4,2-*Dithiazine and Bis*(1,4,2-*dithiazine*) *Derivatives*.—There are a few reports on 1,4,2-dithiazine reactivity,



Scheme 2 *Reagents and conditions:* same as Scheme 1



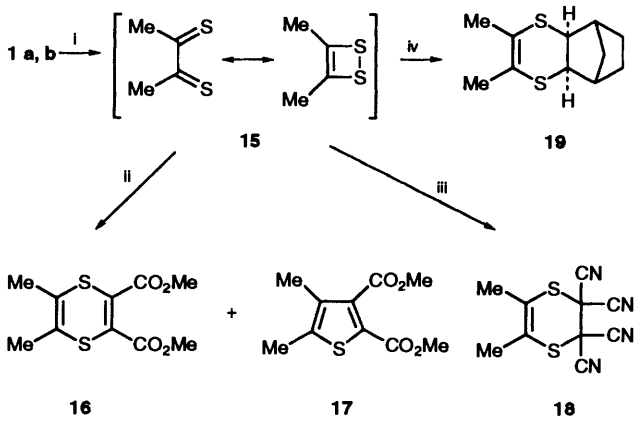
Scheme 3 *Reagents and conditions:* i, iodine, ammonia (aqueous), MeCN–DMF, 20 °C

notably by Fanghänel and coworkers,[3b,d] the most widely documented reaction being the thermal extrusion of sulfur to yield isothiazoles. We now describe a range of reactions of the hitherto unexplored 1,4,2-dithiazine derivatives **1**, **2**, **6** and **12**.

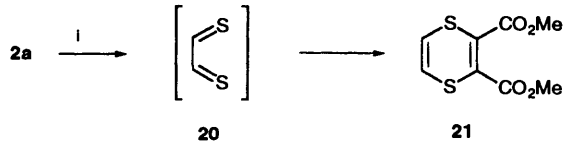
Thermal extrusion of sulfur proceeded readily from the 1,4,2-dithiazine derivatives **1a–c**, to produce the new isothiazoles **13a–c** in 55–100% yields; optimum conditions were 24 h reflux

13 a R = 4-$MeOC_6H_4$
b R = 4-MeC_6H_4
c R = Ph
d R = 4-NCC_6H_4
e R = 2-Thienyl

in toluene. Assignment of the product structure as isothiazoles **13**, rather than the corresponding thiazole isomers, has literature precedent[3a,d] (although in many cases the data given do not distinguish unambigously between the two isomers) and is consistent with the results of CNDO/2 calculations.[3d] Conclusive proof of isothiazole structure came from comparison of the ^1H and ^{13}C NMR spectra of the product obtained from thermolysis of **1c** with an authentic sample of the thiazole isomer **14** (prepared from thiobenzamide and 3-chlorobutan-2-one); the spectra of the two compounds were decisively different



Scheme 4 *Reagents and conditions:* i, photolysis, toluene; ii, DMAD; iii, tetracyanoethene; iv, norbornene



Scheme 5 *Reagents and conditions:* i, photolysis, DMAD

(see Experimental section). Thermolysis of the bis(1,4,2-dithiazine) derivative **12** (refluxing toluene, 5 h) was anomalous, leading not to the corresponding bis(isothiazole) derivative, but to the isothiazole derivative **13d** (69% yield) instead, resulting from fragmentation of one of the 1,4,2-dithiazine rings to yield a nitrile group. At higher temperature (refluxing 1,2-dichlorobenzene, *i.e.* 180 °C) the 1,4,2-dithiazine derivative **1a** behaved similarly, yielding 4-methoxybenzonitrile (38% yield) along with a trace of the isothiazole **13a**.

Under photolytic conditions, 3-aryl-1,4,2-dithiazines fragmented cleanly into the corresponding aryl nitrile derivative. For example, photolysis of compound **1b** in toluene for 23 h gave a quantitative yield of 4-cyanotoluene, while decreasing the reaction time to 2 h gave a 15% yield of 4-cyanotoluene and a 60% recovery of the dithiazine **1b**. Despite careful monitoring of the reactions by TLC and NMR, the isothiazole **13b** was not detected in these experiments. The isothiazole **13b** (obtained by thermolysis of **1b**) was recovered unchanged after photolysis in toluene for 24 h (as expected from literature precedent)[9] demonstrating that the formation of nitrile products in the above reactions does not proceed *via* isothiazole intermediates. The intermediacy of α-dithione compound **15** (which may possess a tautomeric 1,2-dithiete structure)[10] was, therefore, clearly implied in this retro-Diels–Alder mode of fragmentation of the 1,4,2-dithiazine system. Attempts were made to trap intermediate **15** by reaction with dienophiles. Similar trapping of thermally-generated 1,2-dithiocarbonyl compounds has been reported previously.[11]

Irradiation of toluene solutions of the dithiazines **1a** and **b** in the presence of dimethyl acetylenedicarboxylate (DMAD) resulted in the isolation of the 1,4-dithiine and thiophene derivatives **16** and **17** in low yields (Scheme 4). The thiophene **17** is presumably formed by desulfurisation of the dithiine **16**.[12] Analogous products were not obtained by irradiating the dithiazine **2a** and DMAD under the same conditions, although the dithiine **21** was isolated in 4% yield by irradiating **2a** in neat DMAD, thereby providing evidence for the intermediacy of dithioglyoxal **20** (Scheme 5). The major component in all cases was brown polymeric material which could not be characterised. Irradiation of a toluene solution of **1a** in the presence of tetracyanoethylene afforded the 1,4-dithiine derivative **18** (6% yield), whilst using a large excess of norbornene as trap gave

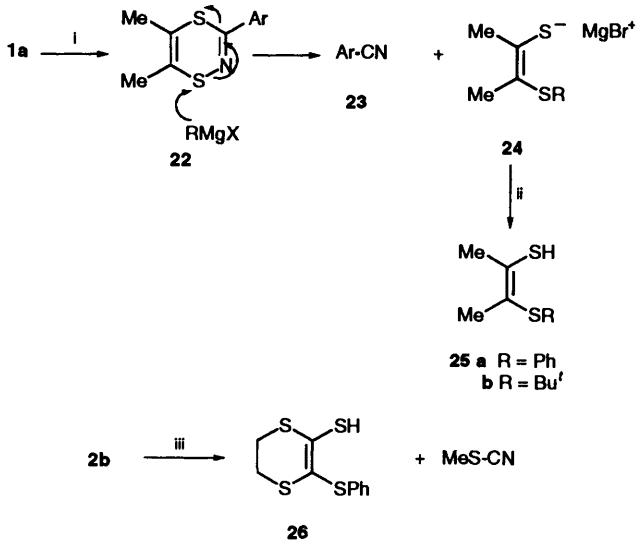
product **19** (HRMS evidence) in a yield of 30%. Thermolysis of **1a** in the presence of DMAD, tetracyanoethylene or benzyne (generated from benzenediazonium-2-carboxylate) gave predominantly unchanged starting material and/or isothiazole, with no isolation of pure products resulting from reaction of the dienophile. As more efficient routes to α-dithione intermediates are known,[11] these trapping reactions were not explored further.

Reactions of 1,4,2-dithiazines with strong electrophiles, *e.g.* acetyl chloride and mineral acids, are known to result in ring contraction.[3b] Attempts to methylate the dithiazine **1a** with iodomethane at room temperature, or at reflux in acetone, or with dimethyl sulfate at 20 °C or 90 °C were unsuccessful; starting material was recovered unchanged. Reaction of **1a** with a large excess of dimethyl sulfate in toluene at reflux resulted in a complex mixture of methylated products (NMR evidence) which could not be purified. The reaction of 2-thienyl derivative **6** under Friedel–Crafts acylation conditions is notable because, although no acylated product was isolated, the novel isothiazole **13e** was obtained, albeit in only 8% yield. This product was formed at 20 °C, *i.e.* well below the temperature required for thermal desulfurisation of 1,4,2-dithiazines. Unchanged starting material was also present at room temperature, and at *ca.* 60 °C, intractable polymeric material predominated. This suggests that Lewis acids may promote the desulfurisation of 1,4,2-dithiazines, although compound **6** was recovered unchanged from stirring with a large excess of phosphorus oxychloride in dichloromethane at room temperature.

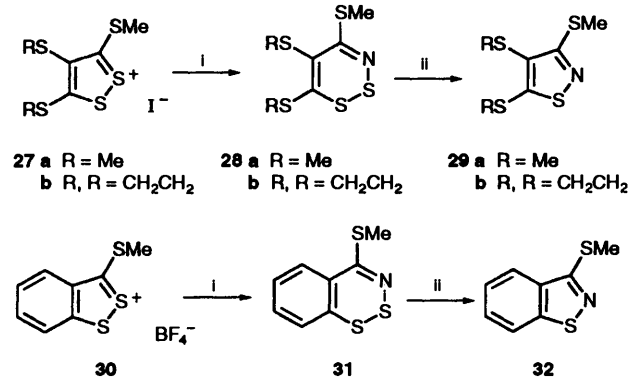
Reactions of the 1,4,2-dithiazine ring system with nucleophiles are virtually unexplored. We have studied the reactions with hydride and Grignard reagents. Reaction of **1a** with lithium aluminium hydride (2 mol) in diethyl ether destroyed the ring system: 4-methoxybenzylamine was the only isolated product. Sodium borohydride was allowed to react with **1a** and **d** in diethyl ether to yield 4-methoxybenzonitrile and 4-bromobenzonitrile, respectively, in *ca.* 70% yields: no sulfur-containing products were isolated from these reactions. The reactions of 1,4,2-dithiazines with Grignard reagents proved to be more fruitful (Scheme 6). The dithiazine **1a** was treated with 5 equiv. of phenylmagnesium bromide in diethyl ether at room temperature to yield, after acidic work-up, the phenyl vinyl sulfide derivative **25a** (85% yield) and 4-methoxybenzonitrile. In a similar reaction, *tert*-butylmagnesium chloride and compound **1a** gave product **25b** (23% yield) although this reaction was far less efficient than the previous example, requiring a much longer reaction time. The bicyclic 1,4,2-dithiazine derivative **2b** was treated with phenylmagnesium bromide to afford the 2,3-dihydro-1,4-dithiine derivative **26** (75% yield). The proposed mechanism for these reactions is shown in Scheme 6, with initial attack of the nucleophile occurring at S-1 of the dithiazine ring of **22**. Subsequent fragmentation yields nitrile and thiolate moieties **23** and **24**, the latter being protonated during work-up to give the isolated products **25a**, **b** and **26**. Analogous attack of hydride at S-1 of **1a** and **d** would explain the products isolated from those reactions reported above. One example of a fragmentation of a 1,4,2-dithiazine derivative bearing a methylsulfanyl group at C-3 upon reaction with methylmagnesium bromide had been reported previously by Fanghänel, who postulated a different mechanism for ring opening.[3b] The products which we obtained from the 3-aryl derivatives **1a** and **d** cannot be explained by this previous mechanism,[3b] demonstrating that the course of these reactions is dependent upon the substituent at C-3. Nucleophilic attack at S-1, as shown in Scheme 6, is consistent with the results of CNDO/2 data, which predict that for the parent unsubstituted 1,4,2-dithiazine system S-1 is more electrophilic than S-4.[3d]

Synthesis of the 1,2,3-*Dithiazine Derivatives by Ring Expansion of the* 1,2-*Dithiolium Cations.*—We wished to explore the scope of the iodine–ammonia reaction in the preparation of other heterocyclothiazines, and we now report that this methodology can be used to convert 1,2-dithiolium cations into 1,2,3-dithiazine derivatives. The salts **27a**, **b** and **30** were treated with a mixture of iodine and ammonia using a range of stoichiometries of reagents to find the optimum conditions for 1,2,3-dithiazine formation. The 1,2,3-dithiazine derivatives **28a**, **b** and **31** were isolated from reactions of **27a**, **b** and **30**, respectively, in yields of 14–39%. The corresponding isothiazoles **29a** and **b** were isolated from the product mixtures (*ca.* 10% yield) and their formation could not be prevented, even when the reaction was performed at −20 °C; lowering the reaction temperature reduced the overall yields of dithiazine plus isothiazole products. Ring expansion of **30** at 20 °C afforded **31** (25% yield) with no isothiazole **32** being detected. We had shown previously that ring expansion of the salt **33** yielded the isothiazole **34** (84% yield) and had postulated that this reaction proceeded *via* a 1,2,3-dithiazine intermediate[13] which we were unable to isolate. It would appear, therefore, that the presence of the methylsulfanyl substituent at C-4 of the 1,2,3-dithiazine ring, stabilises the heterocycle against desulfurisation. Chloroform solutions of the 1,2,3-dithiazine derivatives **28a**, **b** and **31** extruded sulfur during storage for 7 days at room temperature to yield the isothiazole derivatives **29a**, **b** and **32** in quantitative yields (Scheme 7).

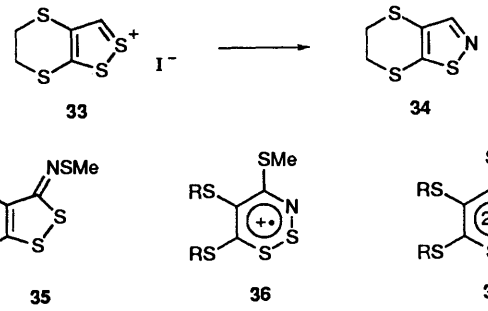
NMR and mass spectra were entirely consistent with the 1,2,3-dithiazine structures **28** and **31**, although these data did not discount possible isomeric structures, *e.g.* 3-imino-1,2-dithiole



Scheme 6 *Reagents and conditions:* i, RMgX, diethyl ether, 20 °C; ii, HCl, H_2O; iii, PhMgBr, diethyl ether, 20 °C, then HCl, H_2O



Scheme 7 *Reagents and conditions:* i, iodine, ammonia (aqueous), MeCN, 20 °C; ii, $CHCl_3$, 20 °C



33 **34** **35** **36** **37**

Table 1 Cyclic voltammetric data

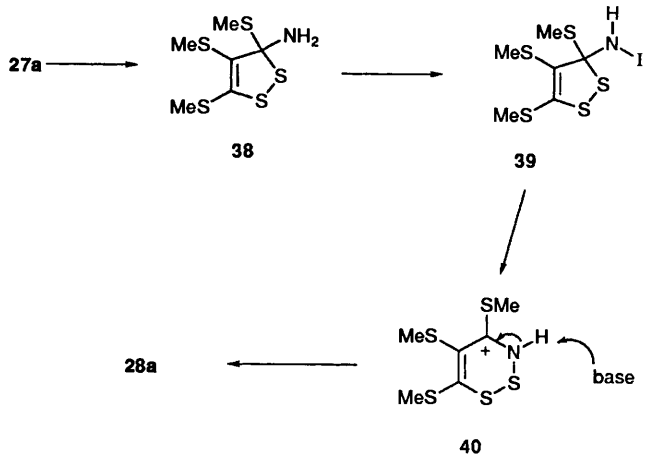
Compd.[a]	E_1^{ox}/V	E_1^{red}/V	$E_1^{1/2}$/V	E_1^{ox}/V	ΔE/V[b]
28a	1.27	1.21	1.24	1.64	0.40
28b	1.28	1.19	1.24	1.58	0.34
31	1.37	1.31	1.34	1.68	0.34
2b[c]	1.20	1.13	1.17	1.58	0.41

[a] Compound (*ca.* 10^{-3} mol dm^{-3}) in anhydrous dichloromethane, electrolyte $Bu_4N^+PF_6^-$ (*ca.* 10^{-2} mol dm^{-3}), Pt electrode *vs.* Ag/AgCl, 20 °C. [b] $\Delta E = E_2^{ox} - E_1^{1/2}$. [c] Data from ref. 5*b*.

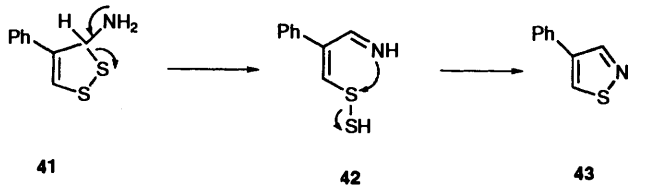
derivatives, such as **35**, or isothiazolethione derivatives. Solution electrochemical data, obtained by cyclic voltammetry, provided compelling evidence for the 1,2,3-dithiazine structures **28a**, **b** and **31**. The data (Table 1) are strikingly similar to those of the 1,4,2-dithiazine derivatives, *e.g.* compound **2b**, that we reported previously[5] and are inconsistent with isomeric 1,2-dithiole or isothiazole structures.[13] (The facile desulfurisation reactions of **28** and **31**, reported above, are also inconsistent with these alternative structures.) Single-electron oxidations, E_1^{ox}, of compounds **28** and **31** occurred at potentials of between 1.27 and 1.37 V (*vs.* Ag/AgCl), corresponding to oxidation of the neutral 8 π-electron 1,2,3-dithiazine system to the 7 π-electron cation radical species **36**. This is an irreversible process for all derivatives studied; the corresponding cathodic reduction peaks, E_1^{red}, were observed as weak shoulders. A second irreversible oxidation, E_2^{ox}, was observed at *ca.* 1.6 V for all derivatives **28a**, **b** and **31** to form 6 π-electron 1,2,3-dithiazinium dications **37**. Data for the 1,2,3-benzodithiazine **31** show that this compound is slightly harder to oxidise than derivatives **28a** and **b**; this may be due to the ability of **28a** and **b** to distribute positive charge on additional exocyclic sulfur atoms, thereby stabilising the oxidised redox states.

There are very few literature reports of compounds containing the 1,2,3-dithiazine heterocycle,[1b,14] and, hitherto, the only known 8 π-electron derivatives were obtained electrochemically.[14b,c] The mechanism we propose for the formation of the 1,2,3-dithiazines **28** and **31** from precursor 1,2-dithiolium salts, shown in Scheme 8 for derivative **27a**, is analogous to that proposed for the conversion of 1,3-dithiolium cations into 1,4,2-dithiazines under similar conditions.[5] Nucleophilic attack by ammonia at C-3 of cation **27a**, gives the intermediate amine adduct **38**, which undergoes oxidative iodination to afford the halogeno amine **39**, which loses iodide ion with concomitant S–N bond formation to afford cation **40**, which is then deprotonated to yield the product **28a**.

Other workers have established that the reaction of 1,2-dithiolium cation salts with anhydrous ammonia leads to the formation of isothiazole derivatives, although 1,2,3-dithiazines were not postulated to be intermediates in these processes.[15] A brief consideration of this previous work in the light of our observations is, therefore, needed. The reactions reported by Olofson and coworkers were conducted at reflux in ethanol, and/or products were isolated by vacuum distillation at 98–135 °C, and an addition–elimination pathway was suggested to



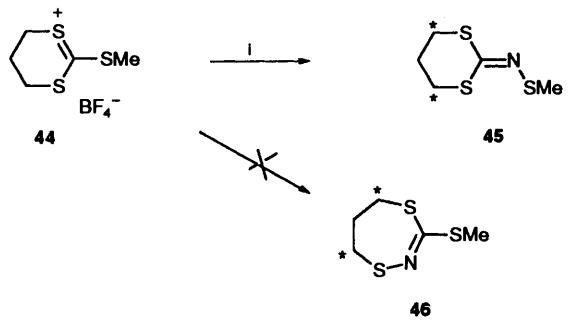
Scheme 8



Scheme 9

explain the formation of isothiazoles (Scheme 9).[15b] Nucleophilic attack by ammonia at C-3 of the 4-phenyl-1,2-dithiolium cation gives the amine adduct **41**, which is analogous to the intermediate **38**. Compound **41** was considered to ring-open to the imine **42**, which undergoes ring-closure, as shown, to form the isothiazole **43** (although the detection of hydrogen sulfide was not reported). Whilst this mechanism could account for our observation that the 1,2-dithiolium cation **33** yields isothiazole **34**, without the corresponding 1,2,3-dithiazine being detected,[13] it is clearly not the mechanism that yields the 1,2,3-dithiazines **28** and **31**, and subsequently the isothiazoles **29** and **32**, respectively. The spectroscopic data (NMR, IR and MS: see Experimental section) and cyclic voltammetric data (Table 1) for the 1,2,3-dithiazines **28** and **31** do not fit analogues of either of Olofson's proposed intermediates **41** (*i.e.* **38**) or **42**. Olofson's reactions were conducted under anhydrous conditions, whereas our experiments involve aqueous ammonia solution in the presence of iodine and it seems clear that different mechanisms operate under these two sets of conditions. Formation of a 1,2,3-dithiazine would not be expected to occur in the absence of iodine, as this would require hydride loss from the intermediate **38** or **41** (*cf.* iodide loss from **39**).

We have also explored, for the first time, the reaction of a six-membered cationic sulfur heterocycle with a mixture of iodine and ammonia. 2-Methylsulfanyl-1,3-dithianylium salt **44**, which was prepared by methylation of the corresponding thione using dimethyl sulfide, was treated with iodine–ammonia (2.5 equiv. iodine) to yield a product identified from NMR spectra, MS data and C, H, N combustion analysis as either the imine **45** or the isomeric dithiazepine **46** (5% yield, which could not be improved by varying the stoichiometry of iodine) arising from exocyclic or endocyclic insertion of nitrogen into a C–S bond, respectively (Scheme 10). The product has been assigned the imine structure **45** based upon variable-temperature ^{1}H NMR data. At 22 °C in deuteriobenzene the protons of the asterisked methylene groups of **45** or **46** are two distinct triplets with a chemical shift difference of 0.083 ppm. The triplets begin to coalesce when the spectrum is obtained at 50 °C, and coalescence is complete at *ca.* 70 °C; notably, the other proton signals of the molecule remained sharp at this temperature. This



Scheme 10 *Reagents and conditions:* i, iodine, ammonia (aqueous), acetonitrile, 20 °C

observation is entirely consistent with faster inversion of the imine nitrogen of structure **45** at higher temperatures, while raising the temperature would be expected to have little effect on the NMR spectrum of isomer **46**. The formation of product **45** provides the first example from our work with 1,3-dithiolium cations[5] and 1,2-dithiolium cations of the iodine–ammonia reaction leading to imine formation with retention of the C-2 substituent of the salt, although Yonemoto and Shibuya have reported isolation of a five-membered ring imine analogous to **45** under similar conditions.[6a]

Conclusions

Studies on the synthesis and reactions of derivatives of the 1,4,2-dithiazine heterocycle have been extended: thermolytic sulfur extrusion from the ring system yields new isothiazole derivatives in high yield, while photolysis generates 1,2-dithiones, which have been intercepted in low yields by Diels–Alder reactions with dienophiles. Grignard reagents react at S-1 of the 1,4,2-dithiazine ring leading to fragmentation to nitrile and 1,2-dithioethene moieties. The first chemical synthesis of the unsaturated 1,2,3-dithiazine ring system has been achieved by reactions of 1,2-dithiolium cations with a mixture of iodine and aqueous ammonia at room temperature. 1,2,3-Dithiazines are desulfurised at room temperature to yield isothiazoles in high yield.

Experimental

General Procedures.—Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer model 547, 577 and 1600-FTIR spectrometers; samples were either Nujol mulls, embedded in KBr discs, or thin films between KBr plates, as indicated. Solution-state UV spectra were recorded on a Kontron Uvikon 930 instrument, with solvents as indicated. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 500 (500.139 and 125.770 MHz), Bruker AC 250 (250.134 and 62.896 MHz) and Varian Gemini 200 (199.975 and 50.284 MHz) instruments, operating at the frequencies quoted in parentheses, for hydrogen and carbon nuclei, respectively. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS) as internal reference. All coupling constants, *J*, are quoted in Hz. Mass spectra were obtained on a VG 7070E instrument, operating at 70 eV, with ionisation modes as indicated; ammonia was used as the impingent gas for chemical ionisation mode. Elemental analyses were performed on a Carlo-Erba Strumentazione. TLC analyses were performed using Merck pre-coated silica (0.2 mm) aluminium backed sheets. Column chromatography was carried out using Merck silica gel (70–230 mesh) or alumina (70–230 mesh), the latter neutralised by pre-soaking in ethyl acetate for 24 h; eluent solvents are as indicated. Nitrogen was dried by passing it through a column of P_2O_5; reactions were routinely carried out under nitrogen, unless otherwise stated. Solvents were dried over, and distilled from the following reagents, under a dry nitrogen atmosphere: diethyl ether (sodium metal); toluene ($LiAlH_4$); chlorocarbons (P_2O_5); acetonitrile (CaH_2). All other reagents were reagent grade and used as supplied, unless otherwise stated. Cyclic voltammetry (CV) experiments were performed in a one-compartment cell with platinum working and counter electrodes and a silver–silver chloride reference electrode. Measurements were made with a BAS 100 Electrochemical Analyser and were compensated for internal resistance. The cell contained a solution of the test compound (*ca.* 10^{-3} mol dm^{-3}), with oven-dried (120 °C) tetrabutylammonium hexafluorophosphate (*ca.* 10^{-2} mol dm^{-3}) as supporting electrolyte, in anhydrous dichloromethane. Photolysis reactions were carried out in 1 cm diameter quartz tubes, in either dry toluene or neat dienophile, as stated, with substrate concentration of *ca.* 0.3 mol dm^{-3}. The sealed tube was placed 30 cm from a Variac 270 (1 kW, 4 A) UV lamp. The tube contents were not externally cooled and solution temperatures of 35–40 °C were recorded during irradiation.

3-Oxobutan-2-yl Thiophene-2-carbodithioate **4**.—A solution of 3-chlorobutan-2-one (19.5 g, 183 mmol) in dry dichloromethane was added dropwise over 0.8 h to a stirred solution of the salt **3**[7] (15.9 g, 61 mmol) in dry dichloromethane (200 cm^3) at 20 °C. Stirring was continued at 20 °C for 72 h after which solvent was removed under reduced pressure and the residue was chromatographed on a silica column, eluting with dichloromethane, to afford *compound* **4** (12.8 g, 91%) as a red crystalline solid, m.p. 37–38 °C (Found: C, 47.3; H, 4.5. $C_9H_{10}OS_3$ requires C, 46.9; H, 4.4%); *m/z* (CI) 231 ($M^+ + 1$); ν_{max}(thin film)/cm^{-1} 3100, 2980, 1720, 1505, 1405, 1350, 1250 and 1045; δ_H(250 MHz; $CDCl_3$) 7.82 (1 H, d, *J* 5), 7.66 (1 H, d, *J* 5), 7.11 (1 H, t, *J* 5), 4.88 (1 H, q, *J* 7), 2.30 (3 H, s) and 1.54 (3 H, d, *J* 7).

4,5-Dimethyl-2-(2-thienyl)-1,3-dithiol-1-ium Hexafluorophosphate **5**.—A solution of the dithioester **4** (2.0 g, 8.6 mmol) in dry dichloromethane (20 cm^3) was added dropwise with stirring over 0.2 h to sulfuric acid (30 cm^3; conc.) at −20 °C and the mixture stirred for a further 1 h at between −20 and −10 °C, before the temperature was raised to 20 °C. Dropwise addition of the mixture to water (500 cm^3) followed by addition of hexafluorophosphoric acid (60%; 7.4 cm^3, 50 mmol) gave a precipitate which was extracted into dichloromethane (6 × 80 cm^3) and the combined organic layers were washed with water, dried ($MgSO_4$) and partially evaporated under reduced pressure to a volume of *ca.* 100 cm^3. This solution was then added to diethyl ether (500 cm^3) with stirring, to produce a precipitate which was filtered off and dried *in vacuo* to afford the *salt* **5** (1.92 g, 62%) as an ochre powder, m.p. 135–136 °C (decomp.) (Found: C, 30.0; H, 2.5. $C_9H_9F_6PS_3$ requires C, 30.2; H, 2.5%); *m/z* (FAB; MeCN) 213 (M^+); ν_{max}(KBr)/cm^{-1} 3130, 1535, 1415, 1370, 1030, 835, 745 and 550; δ_H(250 MHz; CD_3CN) 8.12 (1 H, br s), 8.02 (1 H, br s), 7.36 (1 H, br s) and 2.62 (6 H, s).

5,6-Dimethyl-3-(2-thienyl)-1,4,2-dithiazine **6**.—To a stirred solution of the 1,3-dithiolium salt **5** (4.3 g, 12 mmol) and iodine (4.5 g, 36 mmol) in acetonitrile (200 ml) at 20 °C was added dropwise ammonia solution (33%; 6.8 cm^3, 120 mmol). The resultant mixture was stirred for 17 h at 20 °C and then added to water (300 cm^3). The aqueous solution was extracted with dichloromethane (3 × 60 cm^3) and the combined extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product which was chromatographed on a silica column, eluent dichloromethane–hexane (1:3 v/v), to afford *compound* **6** (2.34 g, 86%) as an orange oil

(Found: C, 47.9; H, 4.0; N, 6.2. $C_9H_9NS_3$ requires C, 47.5; H, 4.0; N, 6.2%); *m/z* (EI) 227 (M^+); (CI) 228 ($M^+ + 1$); ν_{max}(thin film)/cm^{-1} 3090, 2920, 1615, 1540, 1420, 1230, 1050 and 830; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 396 and 293; δ_H(250 MHz; $CDCl_3$) 7.62 (1 H, d, *J* 5), 7.43 (1 H, d, *J* 6), 7.03 (1 H, t, *J* 4), 2.09 (3 H, s) and 2.06 (3 H, s); δ_C(500 MHz; $CDCl_3$) 156.5, 140.4, 131.8, 130.8, 129.8, 127.3, 121.5, 20.6 and 18.8.

Bis(3-*oxobutan*-2-*yl*) m-*Phenylenebis*(*carbodithioate*) **8**.—Following the procedure described for compound **4**, a solution of the salt **7**[16] (2.73 g, 6.3 mmol) and 3-chlorobutan-2-one (2.69 g, 25.2 mmol) in dry dichloromethane (150 cm^3) was stirred for 5 h at reflux, followed by 68 h at 20 °C, to afford *compound* **8** (1.70 g, 73%) as a viscous red oil [Found: C, 51.1; H, 4.9%; *m/z* (EI) 369.9941. $C_{16}H_{18}O_2S_4$ requires C, 51.9; H, 4.9%; *m/z* 370.0189]; ν_{max}(thin film)/cm^{-1} 2930, 1710, 1585, 1445, 1355, 1045, 855 and 795; δ_H(250 MHz; $CDCl_3$) 8.57 (1 H, s), 8.17 (2 H, d, *J* 8), 7.44 (1 H, t, *J* 8), 4.89 (2 H, q, *J* 6), 2.35 (6 H, s) and 1.60 (6 H, d, *J* 6).

2,2′-(m-*Phenylene*)*bis*(4,5-*dimethyl*-1,3-*dithiol*-1-*ium*) *Bis*(*hexafluorophosphate*) **9**.—Following the procedure described for the salt **5** a solution of the bis(dithioester) **8** (740 mg, 2 mmol) in dry dichloromethane (10 cm^3) was added to sulfuric acid (20 cm^3; conc.) over 0.3 h at −20 °C and stirred for a further 1 h at between −20 and −10 °C. Addition of the mixture to water (300 cm^3) followed by addition of hexafluorophosphoric acid (60%; 2.0 cm^3, 14 mmol) afforded a pale buff precipitate of the salt **9** which began to darken immediately. The precipitate was filtered off rapidly and washed with water (2 × 50 cm^3). This material was used immediately in the next step without further purification or characterisation.

3,3′-(m-*Phenylene*)*bis*(5,6-*dimethyl*-1,4,2-*dithiazine*) **10**.—Following the procedure described for compound **6**, ammonia solution (33%; 1.2 cm^3, 20 mmol) was added to a solution of the bis(1,3-dithiolium) salt **9** (from the above preparation, quantity unknown) and iodine (0.76 g, 6 mmol) in acetonitrile (150 cm^3). The resultant mixture was stirred for 18 h at 20 °C to afford *compound* **10** [15 mg, 2.1%; for two steps from the bis(dithioester) **8**] as a yellow solid, m.p. 65–68 °C (Found: C, 53.1; H, 4.5; N, 8.1. $C_{16}H_{16}N_2S_4$ requires C, 52.7; H, 4.4; N, 7.7%); *m/z* (EI) 364 (M^+); (CI) 365 ($M^+ + 1$); ν_{max}(KBr)/cm^{-1} 2915, 1530, 1145, 895, 805, 775 and 680; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 397, 269 and 231; δ_H(250 MHz; $CDCl_3$) 8.60 (1 H, s), 8.08 (2 H, d, *J* 8), 7.43 (1 H, t, *J* 8), 2.12 (6 H, s) and 2.06 (6 H, s); δ_C(500 MHz; $CDCl_3$) 162.7, 136.2, 130.7, 130.6, 128.7, 128.0, 121.2, 20.8 and 18.7.

3,3′-(p-*Phenylene*)*bis*(5,6-*dimethyl*-1,4,2-*dithiazine*) **12**.—Following the procedure for compound **6**, ammonia solution (33%; 0.3 cm^3, 4.9 mmol) was added to a solution of the bis(1,3-dithiolium) salt **11**[17] (154 mg, 0.25 mmol) and iodine (130 mg, 1 mmol) in acetonitrile–*N*,*N*-dimethylformamide (75 cm^3; 4:1 v/v). The resultant mixture was stirred for 2 h at 20 °C to afford *compound* **12** (40 mg, 44%) as an orange solid, m.p. 142–145 °C (Found: C, 53.2; H, 4.3; N, 7.6. $C_{16}H_{16}N_2S_4$ requires C, 52.7; H, 4.4; N, 7.7%); *m/z* (DEI; toluene) 364 (M^+); (DCI) 365 ($M^+ + 1$); ν_{max}(KBr)/cm^{-1} 2910, 1490, 1405, 1230, 1120, 915, 860 and 840; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 417, 294 and 252sh; δ_H(250 MHz; $CDCl_3$) 8.02 (4 H, s), 2.10 (6 H, s) and 2.05 (6 H, s); δ_C(500 MHz; $CDCl_3$) 162.5, 138.0, 130.8, 128.4, 121.3, 21.0 and 18.8.

3-(4-*Methoxyphenyl*)-4,5-*dimethylisothiazole* **13a**.—A solution of 1,4,2-dithiazine **1a**[5b] (251 mg, 1 mmol) in dry toluene (5 cm^3) was refluxed for 18 h. The solvent was removed under reduced pressure and the residue chromatographed on a silica column, eluting with dichloromethane, to afford *compound* **13a** (160 mg, 73%) as a pale yellow oil [Found: C, 65.3; H, 5.6; N, 6.2%; *m/z* (CI) 237.1109 ($M^+ + 18$). $C_{12}H_{13}NOS$ requires C, 65.7; H, 6.0; N, 6.4%; *m/z* 237.1062]; ν_{max}(thin film)/cm^{-1} 2960, 1615, 1520, 1400, 1295, 1250, 1175 and 1035; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 298 and 265; δ_H(250 MHz; $CDCl_3$) 7.56 (2 H, d, *J* 9), 6.95 (2 H, d, *J* 9), 3.81 (3 H, s), 2.42 (3 H, s) and 2.19 (3 H, s); δ_C(500 MHz; $CDCl_3$) 168.1, 159.8, 158.0, 129.9, 129.6, 129.4, 114.0, 55.3, 12.5 and 12.1.

4,5-*Dimethyl*-3-(p-*tolyl*)*isothiazole* **13b**.—Following the procedure described for compound **13a**, a solution of 1,4,2-dithiazine **1b**[5b] (235 mg, 1 mmol) in dry toluene (5 cm^3) was refluxed for 22 h to afford *compound* **13b** (203 mg, 100%) as a pale yellow crystalline solid, m.p. 33–34 °C (Found: C, 70.6; H, 6.5; N, 6.5. $C_{12}H_{13}NS$ requires C, 70.9; H, 6.5; N, 6.9%); *m/z* (EI) 203 (M^+); (CI) 204 ($M^+ + 1$); ν_{max}(thin film)/cm^{-1} 2920, 1450, 1360, 1230, 1180, 1010, 815 and 730; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 295 and 260; δ_H(250 MHz; $CDCl_3$) 7.51 (2 H, d, *J* 8), 7.24 (2 H, d, *J* 8), 2.43 (3 H, s), 2.38 (3 H, s) and 2.20 (3 H, s); δ_C(500 MHz; $CDCl_3$) 168.4, 158.1, 138.3, 133.8, 129.2, 129.1, 128.8, 21.1, 12.6 and 12.0.

4,5-*Dimethyl*-3-*phenylisothiazole* **13c**.—Thermolysis of 1,4,2-dithiazine **1c**[5b] (221 mg, 1.0 mmol) in dry toluene (20 cm^3) for 17 h at 111 °C, following the procedure for compound **13a**, gave *compound* **13c** as a pale yellow oil (104 mg, 55%); ν_{max}(thin film)/cm^{-1} 3057, 2921, 1540, 1448, 1360, 1008, 769 and 699; δ_H(250 MHz; $CDCl_3$) 7.61 (2 H, d, *J* 7), 7.42 (3 H, m), 2.43 (3 H, s) and 2.19 (3 H, s); δ_C(500 MHz; $CDCl_3$) 168.3, 158.2, 136.6, 129.2, 128.3, 12.4 and 12.0 (lit.,[9] spectroscopic data not recorded). †

3-(4-*Cyanophenyl*)-4,5-*dimethylisothiazole* **13d**.—Following the procedure for compound **13a**, a solution of the bis(1,4,2-dithiazine) **12** (100 mg, 0.27 mmol) in dry toluene (15 cm^3) was refluxed for 5 h to afford *compound* **13d** (40 mg, 69%) as a white crystalline solid, m.p. 111–114 °C; [*m/z* (EI) 214.0463. $C_{12}H_{10}N_2S$ requires *m/z* 214.0565]; ν_{max}(KBr)/cm^{-1} 2920, 2230, 1180, 1145, 1015, 860, 830 and 555; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 291, 270 and 234; δ_H(250 MHz; $CDCl_3$) 7.75 (4 H, s), 2.50 (3 H, s) and 2.24 (3 H, s); δ_C(500 MHz; $CDCl_3$) 166.0, 159.6, 140.6, 132.2, 129.4, 129.0, 118.7, 112.1, 12.4 and 12.1.

Photolysis of the 1,4,2-*Dithiazine* **1a** *in the Presence of a Trap.—Representative procedure.* A solution of the 1,4,2-dithiazine **1b**[5b] (100 mg, 0.42 mmol) and DMAD (0.52 cm^3, 4.2 mmol) in dry toluene (3 cm^3) was irradiated for 24 h. Solvent and unchanged DMAD were removed under reduced pressure and the residue was chromatographed on a silica column eluting with dichloromethane to afford *dimethyl* 5,6-*dimethyl*-1,4-*dithiine*-2,3-*dicarboxylate* **16** (8 mg, 6%) as a yellow oil; [*m/z* (EI) 260.0075. $C_{10}H_{12}O_4S_2$ requires 260.0177]; ν_{max}(thin film)/cm^{-1} 2952, 1725, 1571, 1434, 1250, 1075, 1015 and 760; δ_H(250 MHz; $CDCl_3$) 3.83 (6 H, s) and 2.05 (6 H, s). Continued elution gave *dimethyl* 4,5-*dimethylthiophene*-2,3-*dicarboxylate* **17** (6 mg, 4%) as a yellow oil; [*m/z* (EI) 228.0270. $C_{10}H_{12}O_4S$ requires 228.0456]; ν_{max}(thin film)/cm^{-1} 2952, 1732, 1471, 1436, 1286, 1243, 1091 and 1034; δ_H(250 MHz; $CDCl_3$) 3.93 (3 H, s), 3.83 (3 H, s), 2.37 (3 H, s) and 2.09 (3 H, s).

Similarly, photolysis of the 1,4,2-dithiazine **1a** (251 mg, 1

† These data were decisively different from those of 4,5-dimethyl-2-phenylthiazole **14**, prepared from thiobenzamide and 3-chlorobutan-2-one (56% yield).[18] Selected spectroscopic data found: ν_{max}(thin film)/cm^{-1} 3061, 2919, 1546, 1461, 1243, 1001, 761 and 689; δ_H(250 MHz; $CDCl_3$) 7.84 (2 H, d, *J* 7), 7.31 (3 H, m), 2.32 (3 H, s) and 2.24 (3 H, s); δ_C(500 MHz; $CDCl_3$) 162.5, 148.6, 133.4, 128.6, 128.1, 125.8, 125.4, 14.2 and 10.6 (lit.,[18] spectroscopic data not recorded).

mmol) and DMAD (1.24 cm^3, 10 mmol) in dry toluene (3 cm^3) for 20 h gave compounds **16** (7 mg, 6%) and **17** (51 mg, 22%).

2,2,3,3-*Tetracyano*-5,6-*dimethyl*-1,4-*dithiine* **18**.—Following the procedure for compound **16**, a solution of the 1,4,2-dithiazine **1a** (251 mg, 1 mmol) and tetracyanoethane (1.92 g, 15 mmol) in dry toluene (2 cm^3) was irradiated for 25 h to afford *compound* **18** (*ca.* 16 mg, 6%) as an orange oily solid; [*m/z* (EI) 246.0002. $C_{10}H_6N_4S_2$ requires 246.0034]; δ_H(250 MHz; $CDCl_3$) 3.60 (6 H, s).

4a,5,6,7,8,8a-*Hexahydro*-2,3-*dimethyl*-5,8-*methano*-1,4-*benzodithiine* **19**.—Following the procedure for compound **16**, a solution of the 1,4,2-dithiazine **1a** (251 mg, 1 mmol) and norbornene (2.82 g, 30 mmol) in dry toluene (1 cm^3) was irradiated for 23 h to afford *compound* **19** (*ca.* 70 mg, 33%) as a yellow oil; [*m/z* (EI) 212.0426. $C_{11}H_{16}S_2$ requires *m/z* 212.0693]; ν_{max}(thin film)/cm^{-1} 2952, 2869, 1448, 1368, 1198, 1083, 909 and 733; δ_H(250 MHz; $CDCl_3$) 3.28 (s) and 2.6–1.1 (complex pattern due to overlap, and possibly the presence of a small amount of unreacted norbornene).

Dimethyl 1,4-*Dithiine*-2,3-*dicarboxylate* **21**.—Following the procedure for compound **16**, a solution of the 1,4,2-dithiazine **2a** (344 mg, 2.11 mmol) in DMAD (3 cm^3, 24 mmol) was irradiated for 24 h to afford *compound* **21** (*ca.* 20 mg, 4%) as a yellow oil; [*m/z* (EI) 232.0263. $C_8H_8O_4S_2$ requires 231.9864]; ν_{max}(thin film)/cm^{-1} 2980, 1680, 1434, 1265, 1106, 904, 728 and 660; δ_H(250 MHz; $CDCl_3$) 6.41 (2 H, s) and 3.83 (6 H, s).

2-*Phenylsulfanylbut*-2-*ene*-3-*thiol* **25a**.—This procedure is representative of the reactions carried out between 1,4,2-dithiazines and Grignard reagents. To a stirred solution of the 1,4,2-dithiazine **1a** (251 mg, 1 mmol) in dry diethyl ether (20 cm^3) was added phenylmagnesium bromide solution (3.0 mol dm^{-3} in diethyl ether; 1.7 cm^3, 5 mmol) and the mixture stirred for 18 h at 20 °C. Hydrochloric acid solution (*ca.* 0.1 mol dm^{-3}; 100 cm^3) was added to the mixture which was then extracted with dichloromethane (3 × 50 cm^3). The combined extracts were washed with water (2 × 100 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure and the residue was chromatographed on a silica column, eluting with dichloromethane–hexane (1:3 v/v), to afford *compound* **25a** as a pale orange oil (170 mg, 87%) [Found: C, 62.0; H, 6.2%; *m/z* (EI) 196.0226. $C_{10}H_{12}S_2$ requires C, 61.2; H, 6.2%; *m/z* 196.0381]; ν_{max}(thin film)/cm^{-1} 3070, 2920, 1585, 1480, 1440, 1025, 740 and 685; δ_H(250 MHz; $CDCl_3$) 7.38–7.14 (5 H, m), 3.94 (1 H, s), 2.15 (3 H, s) and 1.97 (3 H, s).

2-tert-*Butylsulfanylbut*-2-*ene*-3-*thiol* **25b**.—Following the procedure for compound **25a**, a solution of the 1,4,2-dithiazine **1a** (251 mg, 1 mmol) in dry diethyl ether (20 cm^3) and *tert*-butylmagnesium chloride solution (2.0 mol dm^{-3} in diethyl ether; 5.0 cm^3, 10 mmol) was stirred for 95 h at 20 °C to afford *compound* **25a** (40 mg, 23%) as a pale yellow waxy solid [Found: C, 53.2; H, 8.3%; *m/z* (EI) 176.0666. $C_8H_{16}S_2$ requires C, 54.5; H, 9.1%; *m/z* 176.0693]; ν_{max}(thin film)/cm^{-1} 2950, 2910, 1580, 1455, 1365, 1215, 1150 and 1065; δ_H(250 MHz; $CDCl_3$) 2.15 (3 H, s), 2.09 (3 H, s) and 1.40 (9 H, s).

2,3-*Dihydro*-5-*phenylsulfanyl*-1,4-*dithiine*-6-*thiol* **26**.—Following the procedure for compound **25a**, a solution of the 1,4,2-dithiazine **2b** (290 mg, 1.14 mmol) in dry diethyl ether (20 cm^3) and phenylmagnesium bromide solution (3.0 mol dm^{-3} in diethyl ether; 1.9 cm^3, 5.7 mmol) was stirred for 23 h at 20 °C to afford *compound* **26** (220 mg, 75%) as a viscous orange oil; [*m/z* (EI) 257.9642. $C_{10}H_{10}S_4$ requires 257.9665]; δ_H(250 MHz; $CDCl_3$) 7.44–7.15 (5 H, m) and 3.44–3.21 (4 H, m).

Reaction of the 1,2-*Dithiolium Cation Salts with Iodine and Ammonia.—General Procedure.* The reaction of salt **27a** is representative. To a stirred solution of the 1,2-dithiolium cation salt **27a**[20] (180 mg, 0.5 mmol) and iodine (320 mg, 2.5 mmol) in acetonitrile (100 cm^3) was added dropwise ammonia solution (33%; 0.29 cm^3, 5 mmol). Stirring was continued for 1 h at 20 °C, after which time the mixture was diluted with water (200 cm^3) and extracted with dichloromethane (3 × 70 cm^3). The combined extracts were washed with water (200 cm^3), dried ($MgSO_4$) and evaporated at reduced pressure at ≤25 °C. The resultant oil was chromatographed on a silica column, eluting with dichloromethane–hexane (1:3 v/v). The fraction containing an orange band was evaporated under reduced pressure at ≤25 °C, to afford 4,5,6-*tris*(*methylsulfanyl*)-1,2,3-*dithiazine* **28a** (50 mg, 39%) as a red oil; [*m/z* (DEI, toluene) 254.9464. $C_6H_9NS_5$ requires 254.9339]; ν_{max}(thin film)/cm^{-1} 2920, 1490, 1445, 1310, 1270, 1110, 870 and 730; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 473w, 336, 283, 257 and 236; δ_H(250 MHz; $CDCl_3$) 2.56 (3 H, s), 2.36 (3 H, s) and 2.28 (3 H, s). Continued elution gave a yellow fraction which, when evaporated under reduced pressure at ≤25 °C, afforded 3,4,5-*tris*(*methylsulfanyl*)*isothiazole* **29a** (10 mg, 9%) as an orange oil; [*m/z* (EI) 222.9745. $C_6H_9NS_4$ requires 222.9618]; ν_{max}(Nujol mull)/cm 1605, 1580, 1290, 1270, 1120, 1070, 1040 and 955; δ_H(250 MHz; $CDCl_3$) 2.60 (6 H, s) and 2.29 (3 H, s). Compound **29a** could also be obtained, in quantitative yield, by evaporation of a chloroform solution of compound **28a**, stored for 48 h at 20 °C.

Following the general procedure the salt **27b**[19] (370 mg, 1 mmol), ammonia solution (33%; 0.59 cm^3, 10 mmol) and iodine (630 mg, 5 mmol) in acetonitrile (130 cm^3) were allowed to react for 3.5 h at 0 °C; column chromatography on silica of the product, eluting with dichloromethane–hexane (1:1 v/v) gave 4-*methylsulfanyl*-6,7-*dihydro*[1,4]*dithiino*[2,3-e]-1,2,3-*dithiazine* **28b** (35 mg, 14%) as an unstable red solid, m.p. 122–125 °C [Found: C, 30.5; H, 3.0; N, 5.2%; *m/z* (EI) 252.9505. $C_6H_7NS_5$ requires C, 28.4; H, 2.8; N, 5.5%; *m/z* 252.9182]; ν_{max}(KBr)/cm^{-1} 2925, 1495, 1460, 1410, 1265, 1105, 850 and 710; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 490w, 379, 284 and 231; δ_H(250 MHz; $CDCl_3$) 3.40 (2 H, t, *J* 6), 3.18 (2 H, t, *J* 6) and 2.37 (3 H, s). Continued elution of the column gave 3-*methylsulfanyl*-5,6-*dihydroisothiazolo*[4,5-b][1,4]*dithiine* **29b** (20 mg, 9%) as a yellow solid, m.p. 56–58 °C [Found: C, 31.2; H, 3.0; N, 5.3%; *m/z* (EI) 220.9440. $C_6H_7NS_4$ requires C, 32.6; H, 3.2; N, 6.3%; *m/z* 220.9461]; ν_{max}(thin film)/cm^{-1} 2925, 1470, 1430, 1355, 1265, 1055, 930 and 880; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 436, 295, 265 and 230; δ_H(250 MHz; $CDCl_3$) 3.32 (4 H, m) and 2.66 (3 H, s). Compound **29b** could also be obtained, in quantitative yield, by evaporation of a chloroform solution of compound **28b**, after storage for 30 h at 20 °C.

Following the general procedure, the salt **30** (m.p. 126–129 °C, lit.,[20] m.p. not recorded) (1.14 g, 4 mmol), ammonia solution (33%; 2.4 cm^3, 40 mmol) and iodine (2.54 g, 20 mmol) in acetonitrile (150 cm^3) were allowed to react for 2 h at 20 °C; chromatography of the product on silica (eluent dichloromethane–hexane; 1:3 v/v) gave 4-*methylsulfanylbenzo*[e]-1,2,3-*dithiazine* **31** (215 mg, 25%) as an orange oil; [*m/z* (DEI; toluene) 212.9672. $C_8H_7NS_3$ requires 212.9741]; ν_{max}(thin film)/cm^{-1} 3060, 2925, 1580, 1505, 1290, 1195, 955 and 755; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 426, 313, 267sh and 235; δ_H(250 MHz; $CDCl_3$) 7.76 (1 H, d, *J* 8), 7.49–7.28 (3 H, m) and 2.49 (3 H, s).

3-*Methylsulfanylbenzo*[d]*isothiazole* **32**.—A solution of the 1,2,3-dithiazine derivative **31** (215 mg, 1.0 mmol) in deuteriochloroform (2 cm^3) was stored at 20 °C for *ca.* 100 h, after which time a yellow precipitate of elemental sulfur was filtered off. Evaporation of filtrate afforded compound **32** (180 mg, 100%) as a yellow oil; [*m/z* (EI) 181.0218. $C_8H_7NS_2$ requires

181.0020]; ν_{max}(thin film)/cm^{-1} 3065, 2930, 1595, 1465, 1290, 1250, 995 and 760; λ_{max}(CH_2Cl_2–hexane; 1:1 v/v)/nm 427, 314 and 246; δ_H(500 MHz; $CDCl_3$) 7.88 (1 H, d, *J* 9), 7.83 (1 H, d, *J* 9), 7.47 (1 H, t, *J* 9), 7.37 (1 H, t, *J* 9) and 2.78 (3 H, s); δ_C(500 MHz; $CDCl_3$) 159.4, 151.7, 133.6, 128.0, 124.4, 122.7, 119.9 and 13.3.

2-Methylsulfanyl-1,3-dithianylium Tetrafluoroborate **44**.—A suspension of 1,3-dithiate-2-thione[21] (5.0 g, 33 mmol) in dimethyl sulfate (20 cm^3, 210 mmol) was heated and stirred for 0.3 h at 90 °C. The resultant solution was cooled before addition of tetrafluoroboric acid (54%; 13.6 cm^3, 100 mmol) to it with stirring. Slow addition of diethyl ether (300 cm^3) to the mixture gave a precipitate which was filtered off and washed with diethyl ether (4 × 50 cm^3). The precipitate was dried *in vacuo* to afford the salt **44** (6.8 g, 81%) as a pale cream powder, m.p. 125–129 °C; *m/z* (DEI, MeOH) 165 (M^+, cation); ν_{max}(thin film)/cm^{-1} 3030, 1670, 1422, 1282, 1235, 1024, 907 and 866. This material was used without further purification.

2-(N-Methylsulfanylimino)-1,3-dithiane **45**.—Following the procedure for the preparation of compound **6**, ammonia solution (33%; 5.9 cm^3, 100 mmol) was added to a solution of the 1,3-dithianylium salt **44** (2.52 g, 10 mmol) and iodine (3.17 g, 25 mmol) in acetonitrile (200 cm^3). The resultant mixture was stirred for 2.5 h at 20 °C to afford compound **45** (90 mg, 5%) as a pale yellow oil (Found: C, 33.7; H, 5.1; N, 7.5. $C_5H_9NS_3$ requires C, 33.5; H, 5.1; N, 7.8%); *m/z* (EI) 179 (M^+); (CI) 180 ($M^+ + 1$); ν_{max}(thin film)/cm^{-1} 2915, 1644, 1518, 1471, 1417, 1301, 935 and 743; δ_H(250 MHz; $CDCl_3$) 3.17 (2 H, t, *J* 7), 3.09 (2 H, t, *J* 7), 2.78 (3 H, s) and 2.19 (2 H, quintet, *J* 7); δ_C(200 MHz; $CDCl_3$) 154.1, 30.5, 29.8, 23.0 and 22.1. At higher stoichiometric equivalents of iodine no products were isolated.

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