Organic Heterocyclothiazenes. Part 10.[1] Reactions of the Tetrathiatriazepinium Cation with Acetylide Anions; New Mesoionic Thiones

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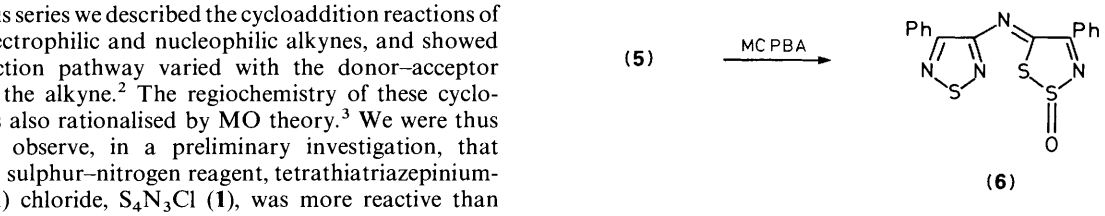
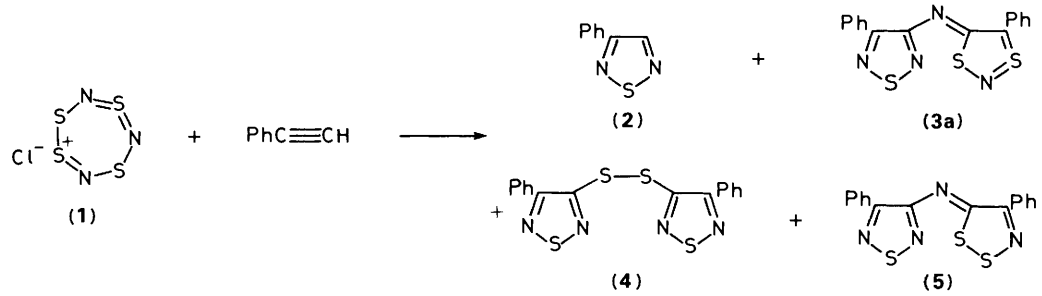
The reaction of tetrathiatriazepinium chloride (thiotrithiazyl chloride) (**1**) with phenylacetylene gives several products including the isomeric 1,3,2- and 1,2,3-dithiazole imines (**3a**) and (**5**). The salt (**1**) reacts much faster with phenylacetylide anions but again the reaction is complex and the products include S_4N_4, the imine (**3a**), and 5-phenyl-1,3,2-dithiazole-4-thione (**7a**), a new mesoionic thione. Analogous products are formed from other acetylides, together with the isomeric 4-t-butyl-1,2,3-dithiazole-5-thione (**8**) from t-butylacetylide. Mechanisms for the formation of (**7**) (Scheme 3) and (**8**) are proposed. 5-Phenyl-1,3,2-dithiazole-4-thione (**7a**) is converted into the 4-one (**11**) with lead tetra-acetate, the sulphine (**16**) with *m*-chloroperbenzoic acid, and the phenylimine (**17**) with iodomethane followed by aniline. 5-Phenyl-1,3,2-thiazol-4-one (**11**) is very light sensitive and photoisomerises to 4-phenyl-1,2,3-thiazole-5-one (**12**), probably *via* the bicyclic intermediate (**13**). Unlike the 1,3,2-imine (**3a**), the 1,2,3-imine (**5**) is oxidised by *m*-chloroperbenzoic acid in the dithiazole ring, to give (**6**), and this difference is rationalised in terms of electron delocalisation in the two systems.

In Part 5 of this series we described the cycloaddition reactions of S_4N_4 with electrophilic and nucleophilic alkynes, and showed how the reaction pathway varied with the donor–acceptor properties of the alkyne.[2] The regiochemistry of these cycloadditions was also rationalised by MO theory.[3] We were thus interested to observe, in a preliminary investigation, that an alternative sulphur–nitrogen reagent, tetrathiatriazepinium-(thiotrithiazyl) chloride, S_4N_3Cl (**1**), was more reactive than S_4N_4 towards both an electron-rich (PhC≡CH) and an electron-poor alkyne (MeO_2C–C≡C–CO_2Me). We now describe the results of a detailed investigation of the former reaction.

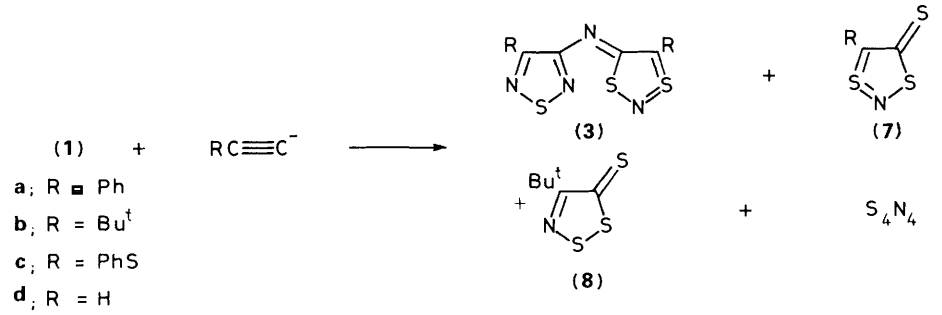
Very few reactions of S_4N_3Cl (**1**) with organic compounds have been reported.[4] It is readily prepared, *via* $S_3N_2Cl_2$, from disulphur dichloride and ammonium chloride.[5] It is relatively water stable, for a sulphur–nitrogen cation, and this probably results from its delocalised 10π aromatic nature. The degree of conjugation through the long disulphide bond has been a matter of debate,[6] but we hoped that the stability of the cation would be somewhat diminished and that it would be more reactive in cycloadditions than the fully aromatic trithiadiazepines and trithiatriazepines.[7]

Tetrathiatriazepinium Chloride and Phenylacetylene.—We first investigated the reaction of S_4N_3Cl (**1**) and phenylacetylene in refluxing toluene, which gave a complex mixture of products in low yields (Scheme 1). These included 3-phenyl-1,2,5-thiadiazole (**2**) (8%), the bicyclic imine (**3a**) (2%), identical with that from phenylacetylene and S_4N_4,[8] the colourless disulphide (**4**) (20%), and an orange compound assigned the 1,2,3-dithiazolyl imine structure (**5**) (4%). The disulphide (**4**) structure is based on elemental analysis, mass spectrometry, the symmetry of the molecule as shown by n.m.r., and the simple u.v. spectrum appropriate for a thiadiazole ring. The mass spectrum did not exhibit a fragment at *m/z* 121 for $(PhC{=}S)^+$ but did show a fragment at 103 for $(PhCN)^+$. Elemental analysis and mass spectrometry indicated that the orange product was an isomer of the imine (**3a**); the absence of a fragment at 121 for $(PhC{=}S)^+$ suggested a 1,2,3-dithiazole ring. Several attempts to obtain crystals for *X*-ray structure determination were unsuccessful. We had found before[1] with the bicyclic imine (**3a**) that the quality of the crystals was much improved on conversion into an *S*-oxide derivative, and this technique also worked well here. Oxidation of compound (**5**) with N_2O_4 was extremely slow, but *m*-chloroperbenzoic acid (MCPBA) in dichloromethane gave the *S*-oxide (**6**) in 60% yield. Its structure was proved by *X*-ray





Scheme 1.



Scheme 2.

diffraction [9] and this indicated strongly that the starting material was indeed the imino-1,2,3-dithiazole (**5**).

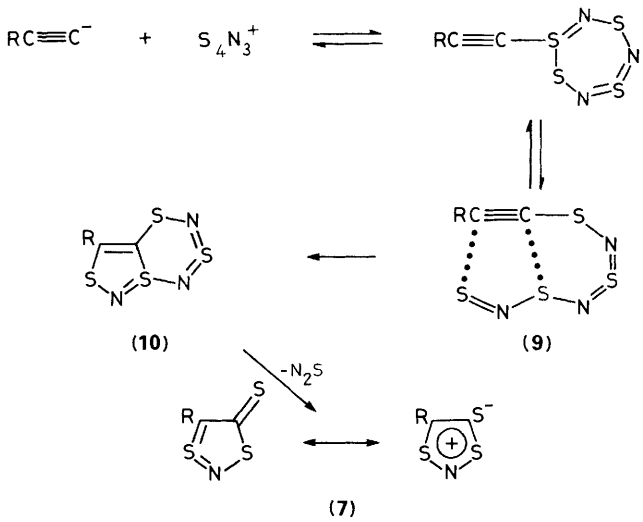
In view of the complexity of the phenylacetylene reaction we decided to treat the $S_4N_3^+$ salt with acetylide anions in the expectation of much faster reactions under milder conditions, and the hope of enhanced selectivity. In the event the reactions were much faster but not significantly simpler; the major product was usually S_4N_4 but some other interesting and novel products were formed (Scheme 2) and these are now described.

Tetrathiatriazepinium Chloride and Metal Acetylides.—Sodium phenylacetylide reacted immediately with S_4N_3Cl (**1**) in liquid ammonia to give S_4N_4 (30%), the bicyclic imine (**3a**)[8] (6%), and the new mesoionic thione (**7a**) (25%). This thione, a key 1,3,2-dithiazolium compound and potentially useful synthetic intermediate, was a very dark green metallic crystalline compound; its solution in dichloromethane was deep purple. Its i.r. spectrum showed a strong absorption at 1 191 cm^{-1} assigned to the C=S vibration. The mass spectrum showed a molecular ion at *m/z* 211 suggesting a molecular formula corresponding to phenylacetylide + NS_3, in agreement with the elemental analysis, and fragments at 165 (M^+ − NS) and 121 ($PhC{\equiv}S^+$). ^1H N.m.r. showed that the phenyl ring was still intact and ^{13}C n.m.r. showed the four benzenoid carbons and two additional resonances at 208 (C=S) and 174 p.p.m. The metallic appearance indicated that the molecules probably adopted a regular packing arrangement in the crystal lattice, and both this, and the molecular structure, were confirmed by *X*-ray analysis.[9]

The reaction of S_4N_3Cl (**1**) with lithium phenylacetylide in THF at −78 °C (10 min) also gave the thione (**7a**) (18%), the bicyclic imine (**3a**) (10%), and S_4N_4 (17%); whilst with copper(I) phenylacetylide (THF, room temp., 10 min) the bicyclic imine (**3a**) (5%), S_4N_4 (15%), and diphenylbutadiyne (8%) were formed, but none of the thione (**7a**). Diphenylbutadiyne (9%) and S_4N_4 (14%) were also isolated from the reaction of lithium phenylacetylide with thiodithiazyl chloride, $S_3N_2Cl_2$.

Other lithium acetylides were used to form the parent thione (**7d**), its alkyl and phenylthio derivatives, and a dialkyl bicyclic imine (**3b**). Thus the reaction of lithium t-butylacetylide with S_4N_3Cl in THF was similar to that of phenylacetylide, giving S_4N_4 (54%), the 1,3,2-dithiazole-4-thione (**7b**) (16%), and the bicyclic imine (**3b**) (4%), together with the isomeric 1,2,3-dithiazole-5-thione (**8**) (2%). Lithium phenylthioacetylide and lithium acetylide [10] with S_4N_3Cl gave the thiones (**7c**) (15%) and (**7d**) (5%) respectively.

The 1,3,2-dithiazole-4-thiones (**7**) have similar spectral properties. They exhibit a strong i.r. absorption between 1 290 and 1 190 cm^{-1}, attributed to the C=S vibration, a long wavelength u.v. absorption near 550 nm, and are deeply coloured. Their mass spectra all showed a strong molecular ion and an abundant fragment assigned to $(RC{=}S)^+$. The thiones (**7a**, **c**, **d**) showed a fragment corresponding to the loss of NS from the molecular ion; the t-butyl compound (**7b**) did not, possibly because of the very ready loss of the t-butyl group.



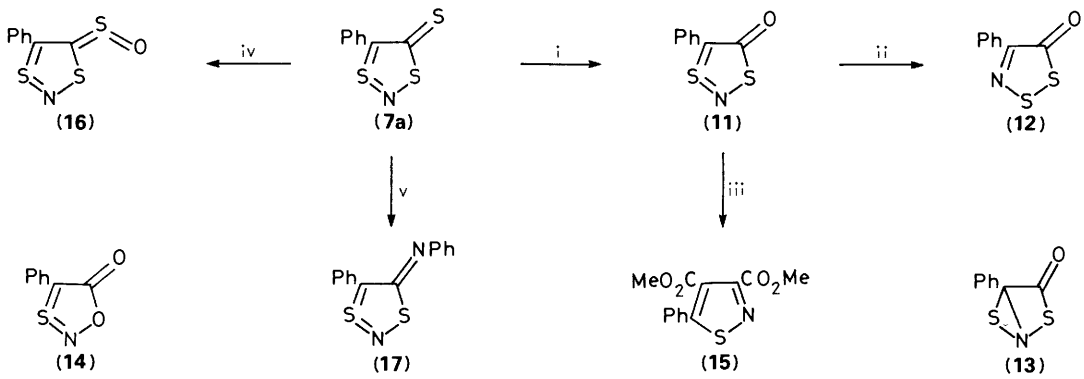
Scheme 3.

Unlike many products of the reactions of sulphur nitrides with organic substrates, the formation of thiones (**7**) is rather readily rationalised mechanistically (Scheme 3). Collapse of the acetylide anion onto the more electrophilic sulphur of $S_4N_3^+$ could be followed by cleavage of the disulphide bond to give the acyclic intermediate (**9**). This could undergo intramolecular 1,3-dipolar cycloaddition of the terminal SNS group to the alkyne to give the bicyclic intermediate (**10**). Extrusion of the elements of N_2S, which is quite common in closely related chemistry,[11] would lead to the observed products which are stablised, 6π aromatic, mesoionic thiolates (**7**). The first step in this mechanism is probably analogous to that in the reaction of $S_4N_3^+$ with aluminium azide which results in loss of nitrogen and ring expansion to form S_4N_4 in high yield.[12]

It is interesting to note that collapse of the acetylide anion onto the other sulphur atom of $S_4N_3^+$, followed by a similar sequence of ring opening, cycloaddition, and extrusion, leads to the isomeric 1,2,3-dithiazole-5-thione structure (**8**) which was also isolated, in very low yield, in the t-butylacetylide reaction (Scheme 2).

Chemistry of 5-Phenyl-1,3,2-dithiazol-4-thione (**7a**).—The thiones (**7**) are light sensitive; dilute solutions exposed to normal laboratory light are completely decomposed within 24 h. In the absence of light and oxygen the thiones are stable as solids and in solution.

5-Phenyl-1,3,2-dithiazole-4-thione (**7a**) is very rapidly oxidised by lead tetra-acetate in dichloromethane at −20 °C to give 5-phenyl-1,3,2-dithiazol-4-one (**11**) (70%), in which the C=S i.r. absorption has been replaced by a strong C=O band at 1 639 cm^{-1}. The mass spectrum exhibited a strong molecular ion at *m/z* 195 and the expected fragmentation of 167 (M^+ − CO),



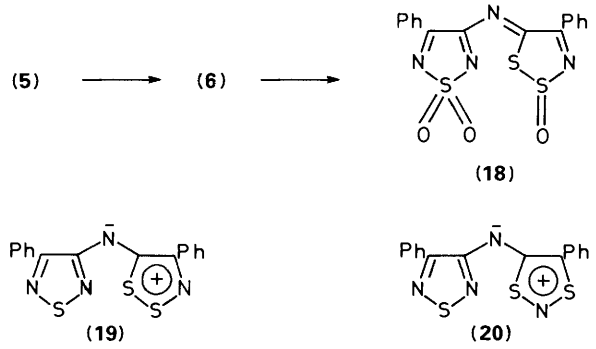
Scheme 4. *Reagents:* i, $Pb(OAc)_4$; ii, *hν*; iii, DMAD; iv, MCPBA; v, MeI, then $PhNH_2$

149 (M^+ – NS), and 121 ($PhC{=}S^+$). The 1,3,2-dithiazolone (**11**) is very light sensitive and unless protected isomerises rapidly to the 1,2,3-dithiazolone (**12**). The i.r. spectrum of (**12**) showed a new carbonyl absorption at 1 680 cm^{-1} indicating that the oxygen atom is still exocyclic. The main evidence for the rearranged ring system came from the mass spectrum which showed the complete absence of a fragment at *m/z* 121 for $(PhC{=}S)^+$, but rather the loss of CO to give $(PhCNSS)^+$ which lost the two sulphur atoms together (major path) and sequentially (minor path) to give $(PhCN)^+$. The photochemical rearrangement of (**11**) into (**12**) is also accompanied by the formation of benzonitrile and sulphur and probably involves the bicyclic intermediate (**13**). This is analogous to photochemical rearrangement and fragmentation in similar mesoionic systems,[13] particularly that of the closely related 1,3,2-oxathiazolone (**14**) which gives major amounts of benzonitrile and sulphur, and where the intermediate benzonitrile sulphide has also been intercepted.[14] The photochemical rearrangement of (**11**) to (**12**) can be conveniently monitored by performing the reaction in tetrachloromethane solution in an i.r. cell and measuring the relative intensities of the two carbonyl absorptions.

In contrast with the smooth cycloaddition of the oxathiazolone (**14**) to dimethyl acetylenedicarboxylate (DMAD) to give dimethyl 5-phenylisothiazole-3,4-dicarboxylate (**15**) and carbon dioxide, the analogous reaction of the dithiazolone (**11**) was much slower, and of the dithiazolethione (**7a**) was more complex. Oxidation of the dithiazolethione (**7a**) with *m*-chloroperbenzoic acid (1 equiv.) in CH_2Cl_2 at room temperature, until the deep purple solution had become turquoise, followed by rapid chromatography, gave a rather unstable compound which readily reverted to starting material (**7a**); this is tentatively assigned the sulphine structure (**16**).

Finally the condensation of the dithiazolethione (**7a**) with aniline was investigated as a model for the independent synthesis of the bicyclic imines (**3**) isolated from the S_4N_3Cl reactions. Treatment of the thione (**7a**) with aniline in refluxing ethanol under neutral or acidic (HCl, toluene-*p*-sulphonic acid) conditions gave only very slow decomposition. However if the thione was first treated with iodomethane to form the dark orange methiodide followed by aniline in refluxing ethanol, the deep violet imine (**17**) was formed, though in poor yield (26%). Reactions of 5-membered mesoionic rings with aniline can be accompanied by rearrangement,[15] but all the spectroscopic data are consistent with the unrearranged structure (**17**). Thus the mass spectrum showed fragments at *m/z* 121 (PhCS) and 224 (M^+ – NS) and the i.r. showed replacement of the C=S band by a strong imine absorption at 1 552 cm^{-1}. Unfortunately this condensation with aniline could not be extended to amidine-like amines such as 2-aminopyridine or 3-amino-4-phenyl-1,2,5-thiadiazole (in boiling ethanol) or their lithium salts (in boiling THF), and the bicyclic imines (**3**) have not yet been synthesised by this route.

The Imino-1,2,3-dithiazole (**5**).—It is instructive to compare the two isomeric imines (**3a**) and (**5**). The former is deep violet with a long wavelength $\lambda_{max.}$ 505 nm and the latter is orange with corresponding $\lambda_{max.}$ 409 nm. Oxidation of the former occurs exclusively on the thiadiazole ring[1] whilst oxidation of the latter, as noted above, gave an *S*-oxide (**6**) of the dithiazole ring. These observations suggest that the extensive delocalisation of electron density in (**3a**) from the dithiazole to the thiadiazole ring, which was discussed earlier,[1] is less marked in the isomer (**5**). This agrees with the expectation that π overlap will be weaker across the two adjacent sulphur atoms in (**5**) and thus the contribution of the mesoionic form to the overall structure will be distinctly less for (**19**) than for (**20**). Thus we



would expect the dithiazole ring of (**5**) to be more reactive and the thiadiazole ring to be less reactive towards electrophilic oxidation. However, treatment of the imine (**5**) or its oxide (**6**) with MCPBA gave the trioxide (**18**) where the further oxidation has occurred in the thiadiazole ring. Thiadiazoles are normally very resistant to oxidation and conversion into the 1,1-dioxide is only observed in the presence of electron-releasing substituents.[16] 4-Phenyl-1,2,5-thiadiazole, for example, is resistant to MCPBA in boiling dichloromethane. Thus the imino substituents in the thiadiazoles (**3a**) and (**5**) must both be quite strongly electron releasing, as invoked above.

Experimental

For general points see ref. 17. Light petroleum refers to the fraction, b.p. 40—60 °C.

Reactions of 1,2,4,6,3,5,7-*Tetrathiatriazepinium Chloride* (S_4N_3Cl) (**1**).—(i) *With phenylacetylene.* S_4N_3Cl (1.03 g, 5 mmol), phenylacetylene (0.51 g, 5 mmol), and toluene were heated at

reflux for 2.5 h. The reaction mixture was filtered, the filtrate evaporated, and the residue pre-adsorbed onto silica and separated by dry flash chromatography on silica (60 g). Dichloromethane (40—45%) in light petroleum eluted a crude orange compound which was repurified by a combination of flash and dry flash chromatography and recrystallisation to give N-(4-*phenyl*-1,2,5-*thiadiazol*-3-*yl*)-5-*imino*-4-*phenyl*-1,2,3-*dithiazole* (**5**) (4%) as bright yellow needles, m.p. 151—153 °C (dichloromethane–light petroleum) (Found C, 54.0; H, 2.9; N, 15.5; S, 27.4. $C_{16}H_{10}N_4S_3$ requires C, 54.2; H, 2.8; N, 15.8; S, 27.1%); $\lambda_{max.}$(EtOH) 265 (log ε 4.85), 320 (4.64), 400sh (4.55) and 409nm (4.64); $\nu_{max.}$($CHCl_3$) 3 064w, 1 526s, 1 501m, 1 496m, 1 461m, 1 439s, 1 395s, 1 238w, 904m, 828w, 714m, 695s, and 653w cm^{-1}; δ_H(90 MHz; $CDCl_3$) 7.30—7.60 (6 H, m) and 8.05—8.35 (4 H, m); *m/z* (190 °C) 356 (M^+ + 2, 16%), 354 (M^+, 100), 250 (33), 187 (M^+ − PhCNSS, 55), 167 ($PhCNSS^+$, 19), 135 ($PhCNS^+$, 22), 103 ($PhCN^+$, 29) and 64 (S_2^+, 75). Dichloromethane (52.5—55%) in light petroleum eluted 3-phenyl-1,2,5-thiadiazole (**2**) (66 mg, 8%). Dichloromethane (57.5—65%) in light petroleum eluted the bicyclic imine (**3a**) (14 mg, 2%) identical with an authentic specimen.[8] Dichloromethane (70—95%) in light petroleum eluted a mixture which was separated by rechromatography to give *bis*(4-*phenyl*-1,2,5-*thiadiazol*-3-*yl*) *disulphide* (**4**) (191 mg, 20%) as needles, m.p. 122—122.5 °C (light petroleum–dichloromethane) (Found: C, 49.4; H, 2.5; N, 14.4. $C_{16}H_{10}N_4S_4$ requires C, 49.7; H, 2.6; N, 14.5%); $\lambda_{max.}$(EtOH) 245 (log ε 4.26) and 298nm (4.12); $\nu_{max.}$(CCl_4) 3 069w, 1 462m, 1 441m, 1 355m, 1 254m, 1 146m, 974s, 746vs, 717m, and 694s cm^{-1}; δ_H(250 MHz; $CDCl_3$) 7.46—7.57 (6 H, m, 6 × ArH) and 7.87 (4 H, dd, 4 × ArH); *m/z* (130 °C) 388 (M^+ + 2, 9.8%), 386 (M^+, 48), 194 (100), 193 ($PhC_2N_2S_2^+$, 96), 135 ($PhCNS^+$, 59), and 103 ($PhCN^+$, 30).

(ii) *With sodium phenylacetylide.* Ammonia (20 ml) was collected into a flask fitted with a solid CO_2 condenser and drying tube. Sodamide (188 mg, 4.33 mmol at 90%) was added, followed by phenylacetylene (0.48 ml, 4.33 mmol) and the mixture stirred for 0.5 h at −33 °C. S_4N_3Cl (0.891 g, 4.33 mmol) was added (**CAUTION HYDROGEN EVOLVED**) and the ammonia allowed to evaporate over 2.5 h. The residue was dissolved in dichloromethane, and the solution filtered, pre-adsorbed onto silica, and separated by dry flash chromatography on silica (60 g) with gradient elution. Dichloromethane (0 to 17%) in light petroleum eluted sulphur. Dichloromethane (60 to 73%) in light petroleum eluted S_4N_4 (140 mg, 30%). Dichloromethane (77 to 80%) in light petroleum eluted a crude violet coloured mixture of products which was washed with acetone and recrystallised (dichloromethane–light petroleum) to give the bicyclic imine (**3a**) (45 mg, 6%). Dichloromethane (90 to 100%) in light petroleum eluted 5-*phenyl*-1,3,2-*dithiazole*-4-*thione* (**7a**) (230 mg, 25%) as very dark green metallic plates, m.p. 99—101 °C (dichloromethane) (Found: C, 45.6; H, 2.3; N, 6.5. $C_8H_5NS_3$ requires C, 45.5; H, 2.4; N, 6.6%); $\lambda_{max.}$(EtOH) 227sh (log ε 4.11), 321 (3.80), and 560 nm (3.12); $\nu_{max.}$(CCl_4) 3 067w, 1 495w, 1 447w, 1 327m, 1 285w, 1 191s, 1 091s, 970m, and 690s cm^{-1}; δ_H(90 MHz; $CDCl_3$) 7.40—7.60 (3 H, m, ArH) and 7.8—7.95 (2 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 126.4, 127.9, 129.2, 131.6, 174.0, and 208.4; *m/z* (130 °C) 213 (M^+ + 2, 7), 211 (M^+, 54), 210 (M^+ − H, 33), 165 (*M* − NS, 15), 121 ($PhCS^+$, 100), and 77 (Ph^+, 17).

(iii) *With lithium phenylacetylide.* Phenylacetylene (0.408 g, 4 mmol) in THF (12 ml) was treated with butyl-lithium (1.6M; 2.5 ml, 4 mmol) at — 78 °C; the mixture was stirred at 0 °C for 0.25h and then recooled to −78 °C. S_4N_3Cl (0.822 g, 4 mmol) was added and the reaction mixture stirred for 10 min at −78 °C. Water was then carefully added and the reaction mixture extracted with dichloromethane and the organic solution dried (Na_2SO_4) and evaporated. Chromatography as in the previous experiment gave sulphur, S_4N_4 (125 mg, 17%), the bicyclic imine (**3a**) (73 mg, 10%), and the thione (**7a**) (0.15 g, 18%).

(iv) *With copper*(I) *phenylacetylide.* S_4N_3Cl (103 mg, 0.5 mmol) and copper(I) phenylacetylide (82 mg, 0.5 mmol) were stirred in THF (2 ml) at 20 °C for 10 min. The dark reaction mixture was pre-adsorbed onto silica and separated by flash chromatography on silica (10 g). Light petroleum eluted diphenylbutadiyne (4 mg, 8%), dichloromethane–light petroleum (1:20) eluted S_4N_4 (7 mg, 15%), and dichloromethane–light petroleum (1:3) eluted the bicyclic imine (**3a**) (4.6 mg, 5%).

(v) *With lithium t-butylacetylide.* t-Butylacetylene (0.492 ml, 4 mmol) was treated with butyl-lithium (1.6M; 2.5 ml, 4 mmol) at −78 °C, and the mixture stirred at 0 °C for 0.25 h; it was then recooled to −78 °C. S_4N_3Cl (0.822 g, 4 mmol) was added and the reaction mixture stirred for 0.25 h at −78 °C; it was then allowed to warm to room temperature over 3 h. Water was carefully added and the mixture extracted with dichloromethane. The organic solution was dried (Na_2SO_4), pre-adsorbed onto silica, and separated by dry flash chromatography on silica (60 g). Dichloromethane (30 to 37%) in light petroleum eluted 4-(*t-butyl*)-1,2,3-*dithiazole*-5-*thione* (**8**) (17 mg, 2%) as red volatile needles, m.p. 70.5—71 °C [after sublimation (60 °C/20 mmHg)] (Found: C, 38.6; H, 4.8; N, 7.3%; M^+, 190.9897. $C_6H_9NS_3$ requires C, 37.7; H, 4.7; N, 7.3%; *M*, 190.9897); $\lambda_{max.}$ 233, 248, 257sh, 322, and 433nm; $\nu_{max.}$ 2 973m, 1 483w, 1 459m, 1 393w, 1 365m, 1 263w, 1 217w, 1 155s (C=S), 1 067s, and 871m cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.51 (s); *m/z* (120 °C) 193 (M^+ + 2, 14%), 191 (M^+, 100), 190 (M^+ − 1, 18), 176(7), 156(26), 127(14), 115(6), 112(9), 64(8), 57(20), and 41(9). Dichloromethane (53 to 63%) in light petroleum eluted a mixture of tetrasulphur tetranitride and a red product. The majority of the S_4N_4 was removed by crystallisation. The red product which remained in solution was repurified by flash chromatography on silica to give N-(4-*t-butyl*-1,2,5-*thiadiazol*-3-*yl*)-4-*imino*-5-*t-butyl*-1,3,2-*dithiazole* (**3b**) (25 mg, 4%) as deep needles, m.p. 140—150 °C (after sublimation) (Found: M^+, 314.0693. $C_{12}H_{18}N_4S_3$ requires *M*, 314.0694); $\lambda_{max.}$(EtOH) 233 (log ε 3.93), 254 (3.97), 294 (3.90), 341 (3.93), 353 (3.90), and 482 (3.47); $\nu_{max.}$(CCl_4) 2 967m, 1 474m, 1 441s, 1 410w, 1 363w, 1 262w, 949w, and 924w cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.56 (9 H, s, Bu^t) and 1.69 (9 H, s, Bu^t); *m/z* (120 °C) 316 (M^+ + 2, 11%), 314 (M^+, 69), 299 (M^+ − Me, 44), 268 (M^+ − NS, 50), 254 (26), 239 (77), 101 ($Bu^tC{=}S^+$, 100), 57 (Bu^{t+}, 65), and 41(59). Dichloromethane (77—83%) in light petroleum eluted S_4N_4 (0.201 g, 54%). Dichloromethane (87—93%) in light petroleum eluted 5-*t-butyl*-1,3,2-*dithiazole*-4-*thione* (**7b**) (0.125 g, 16%) as deep purple needles, m.p. 91—93 °C [after sublimation (80 °C/10 mmHg)]; $\lambda_{max.}$ 252 (log ε 3.72), 290 (3.78), and 543 nm (3.30); $\nu_{max.}$(CCl_4) 2 966m, 1 480w, 1 365m, 1 288s, 1 232m, 1 195s, 1 091m, 1 028m, 961m, 909m, and 854s cm^{-1}; δ_H(60 MHz; $CDCl_3$) 1.62; δ_C(62.9 MHz; $CDCl_3$) 27.8, 38.2, 187.4, and 210.0; *m/z* (120 °C) 193 (M^+ + 2, 14%), 191 (M^+, 100), 176 (M^+ − Me, 71), 149 (76), 101 (Bu^t $C{=}S^+$, 27), 57 (Bu^{t+}, 30), and 41 (40).

(vi) *With lithium phenylthioacetylide.* Phenylthioacetylene (201 mg, 1.5 mmol) in THF (10 ml) was treated with butyl-lithium (1.6M; 0.93 ml, 1.5 mmol) at −78 °C; the mixture was stirred at −20 °C for 0.25 h and then recooled to −78 °C. S_4N_3Cl (0.308 g, 1.50 mmol) was added and the reaction allowed to warm to room temperature over 1.5 h. The reaction mixture was pre-adsorbed onto silica and separated by dry flash chromatography on silica (60 g) using gradient elution. Dichloromethane (27—30%) in light petroleum eluted diphenyl disulphide (52 mg, 32%). Dichloromethane (43—67%) in light petroleum eluted S_4N_4 (80 mg, 58%). Dichloromethane (70—80%) in light petroleum eluted 5-*phenylthio*-1,3,2-*dithiazole*-4-*thione* (**7c**) (55 mg, 15%) as a deep violet oil (Found: M^+, 242.9312. $C_8H_5NS_4$ requires *M*, 242.9305); $\lambda_{max.}$(EtOH) 303, 335, and 550 nm; $\nu_{max.}$(CCl_4) 3 064w, 1 583w, 1 476m, 1 441m,

1 235s, 1 090m, 1 079m, 1 025w, 981m, 913w, 690m cm^{-1}; δ_H(90 MHz; $CDCl_3$) 7.1—7.8; *m/z* (150 °C) 245 (M^+ + 2, 18%), 243 (M^+, 100), 197 (M^+ − NS, 46), 153 ($PhSCS^+$, 61), 121 ($PhSC^+$, 23), 109 (PhS^+, 18), and 77 (Ph^+, 52).

(vii) *With lithium acetylide.*[10] Dry THF (8 ml), at −78 °C, was saturated with acetylene gas and butyl-lithium (1.6M; 2.5 ml, 4 mmol) was added over 20 min with continued passage of acetylene. The gas flow through the mixture was continued for a further 20 min. S_4N_3Cl (0.822 g, 4 mmol) was added and the reaction mixture allowed to warm to room temperature over 1 h. The mixture was pre-adsorbed onto silica and separated by dry flash chromatography on silica (60 g) using gradient elution. Dichloromethane (25—30%) in light petroleum eluted hepta-(sulphur imide) (8 mg). Dichloromethane (35 to 70%) in light petroleum eluted S_4N_4 (0.140 g, 38%). Ethyl acetate (10 to 20%) in dichloromethane eluted 1,3,2-*dithiazole*-4-*thione* (**7d**) (26 mg, 5%), as purple crystals,[18] m.p. 140 °C (Found: M^+, 134.9276. C_2HNS_3 requires *M*, 134.9271); $\lambda_{max.}$(EtOH) 253 (log ε 3.71), 300 (3.82), and 540 nm (3.25); $\nu_{max.}$(CCl_4) 3 083w, 1 293s (C=S), 1 146w, and 978m cm^{-1}; δ_H(90 MHz; $CDCl_3$) 9.01 (s); *m/z* (150 °C) 137 (M^+ + 2, 13.5%), 135 (M^+, 100), 89 (M^+ − NS, 87), and 45 (CHS^+, 67).

N-(4-*Phenyl*-1,2,5-*thiadiazol*-3-*yl*)-5-*imino*-4-*phenyl*-1,2,3-*dithiazole* 2-*Oxide* (**6**).—The imino-1,2,3-dithiazole (**5**) (23 mg, 0.065 mmol), MCPBA (85%; 13.2 mg, 0.065 mmol), and dichloromethane (4 ml) were stirred at −20 °C for 4 h. MCPBA (85%; 6.6 mg, 0.033 mmol) was added and the mixture stirred for 4 h at −20 °C. It was then allowed to warm to room temperature over 6 h. The reaction mixture was separated by dry flash chromatography. Dichloromethane (70 to 85%) in light petroleum eluted *the title compound* (**6**) (15.8 mg, 60%) as pale yellow needles, m.p. 180 °C (dichloromethane) (Found: C, 51.8; H, 2.6; N, 15.0. $C_{16}H_{10}N_4OS_3$ requires C, 51.8; H, 2.7; N, 15.1%); $\lambda_{max.}$(EtOH) 270 (log ε 4.19), 290 (4.18), and 390sh nm (3.27); $\nu_{max.}$ 3 065w, 1 573s, 1 445m, 1 381m, 1 282m, 1 133s, 1 085m, 1 074m, 906s, 703s, and 692m cm^{-1}; δ_H(250 MHz; $CDCl_3$) 7.31 (2 H, td, *J* 7.8 and 1.5 Hz, 2 × ArH), 7.37—7.43 (3 H, m, 3 × ArH), 7.67 (1 H, tt, *J* 7.5 and 1.4 Hz, 1 × ArH), 8.02 (2 H, dd, *J* 8.5 and 1.3 Hz, 2 × ArH), 8.12 (2 H, dd, *J* 8.5 and 1.5 Hz); *m/z* (170 °C) 370 (M^+, 1.2%) and 354 (M^+ − O, 4%).

5-*Phenyl*-1,3,2-*dithiazol*-4-*one* (**11**).—A solution of lead tetra-acetate (265 mg, 0.6 mmol) in dichloromethane (5 ml) was added dropwise over 5 min to the thione (**7a**) (85 mg, 0.4 mmol) in dichloromethane (5 ml) at −20 °C. The reaction mixture was purified by rapid dry flash chromatography on silica (20 g). Dichloromethane (60 to 95%) in light petroleum eluted the *title compound* (55 mg, 70%) as a yellow oil (Found: M^+, 194.9816. $C_8H_5NOS_2$ requires *M*, 194.9813); $\lambda_{max.}$(EtOH) 238 (log ε 3.69), 385sh (3.30), and 425 nm (3.49); $\nu_{max.}$(CCl_4) 1 639s (CO), 1 449w, 1 119w, and 689m cm^{-1}; δ_H(250 MHz; $CDCl_3$) 7.46 (3 H, m) and 7.80 (2 H, dd, *J* 7.7 and 2.3 Hz); *m/z* (150 °C) 197 (M^+ + 2, 3.6%), 195 (M^+, 37), 167 (M^+ − CO, 3), 149 (M^+ − NS, 2), 121 ($PhCS^+$, 100), and 77 (Ph^+, 18).

4-*Phenyl*-1,2,3-*dithiazol*-5-*one* (**12**).—The 1,3,2-dithiazol-4-one (**11**) (30 mg, 0.15 mmol) in dichloromethane (10 ml) was stirred under normal laboratory lighting for 7 days. After this the reaction mixture was pre-adsorbed onto silica and separated by dry flash chromatography on silica (10 g). Dichloromethane (5%) in light petroleum eluted sulphur; dichloromethane (30—35%) in light petroleum eluted the *title compound* (**12**) (13 mg, 43%) as a colourless oil (Found: M^+, 194.9816. $C_8H_5NOS_2$ requires *M*, 194.9813); $\lambda_{max.}$(EtOH) 252, 258, 305sh, and 363nm; $\nu_{max.}$(CCl_4) 1 681vs (CO), 1 445w, 1 262w, 700m, 690m, and 632m cm^{-1}; δ_H 7.43—7.50 (3 H, m), and 7.80 (2 H, dd, *J* 7.7 and 2.3 Hz); *m/z* (100 °C) 197 (M^+ + 2, 4%), 195 (M^+, 43), 167 ($PhCNSS^+$, 44), 135 ($PhCNS^+$, 7), 103 ($PhCN^+$, 35), and 64 (100). This light-induced rearrangement is much faster on a smaller scale, and can be readily monitored by i.r. spectroscopy.

Dimethyl 5-*Phenyl*-1,2-*thiazole*-3,4-*dicarboxylate* (**15**).—The 1,3,2-dithiazolone (**11**) (10 mg, 0.05 mmol), dimethyl acetylenedicarboxylate (DMAD) (13 μl, 0.1 mmol) and benzene (1 ml) were heated under reflux in the dark for 4 h; very little reaction had occurred (t.l.c.). The mixture was evaporated, DMAD (33 μl, 0.25 mmol) and toluene (1 ml) were added, and the mixture heated under reflux for 6 h. It was then separated by dry flash chromatography on silica (5 g). Dichloromethane (90—100%) in light petroleum eluted DMAD; dichloromethane eluted the title compound (**15**)[14] (30%) $\nu_{max.}$ 2 953m, 2 927m, 1 747s (CO), 1 736s (CO), 1 628w, 1 436m, 1 337m, 1 256s, 1 202s, and 1 166s cm^{-1}; *m/z* (180 °C) 277 (M^+, 8%), 193 (99), and 191 (100).

5-*Phenyl*-1,3,2-*dithiazole*-4-*thione* S-*Oxide* (**16**).—The thione (**7a**) (49 mg, 0.23 mmol) in dichloromethane (10 ml) was titrated with a solution of *m*-chloroperbenzoic acid (85%; 47 mg, 0.23 mmol) in dichloromethane (3 ml) until the deep purple solution had become turquoise and no starting material remained (t.l.c.). After pre-adsorption onto silica the mixture was immediately subjected to *rapid* dry flash chromatography on silica (15 g). Ethyl acetate (40—55%) in dichloromethane eluted a deep turquoise product (15 mg); $\lambda_{max.}$(EtOH) 233, 348, and 675 nm; $\nu_{max.}$(CCl_4) 2 925, 2 363, 1 743, 1 703, 1 577, 1 496, 1 370, 1 240, 982, 946, 721, and 688 cm^{-1}.

4-*Phenylimino*-5-*phenyl*-1,3,2-*dithiazole* (**17**).—The thione (**7a**) (16.4 mg, 0.078 mmol) and iodomethane (2 ml) were heated at reflux for 3 h after which the mixture was evaporated to give a dark orange solid. Ethanol (2 ml) and aniline (14.2 μl, 0.156 mmol) were added and the mixture was heated at reflux for 4 h. It was then evaporated and the residue pre-adsorbed onto silica and purified by dry flash chromatography on silica (10 g). Dichloromethane (70—80%) eluted the *title compound* (**17**) (5.5 mg, 26%) as a deep purple oil (Found: M^+, 270.0301. $C_{14}H_{10}N_2S_2$ requires *M*, 270.0285); $\lambda_{max.}$(EtOH) 253, 301, and 505 nm; $\nu_{max.}$(CCl_4) 3 065w, 1 552vs (C=N), 1 486m, 1 448w, 1 230w, 936w, 727m, and 691m cm^{-1}; δ_H(250 MHz; $CDCl_3$) 7.11 (2 H, dd, *J* 7.3 and 1.3 Hz, 2 × ArH), 7.39—7.51 (6 H, m, 6 × ArH), 8.00 (2 H, dd, *J* 7 and 3 Hz, 2 × ArH); *m/z* (180 °C) 270 (M^+, 15%), 224 (M^+ − NS, 10), 180 (100), 121 ($PhCS^+$, 95), and 77 (Ph^+, 52).

5-(1,1-*Dioxo*-4-*phenyl*-1,2,5-*thiadiazol*-3-*ylimino*)-4-*phenyl*-1,2,3-*dithiazole* 2-*Oxide* (**18**).—(i) *From the* 1,2,3-*dithiazole* (**5**). The dithiazole (**5**) (11 mg, 0.031 mmol), MCPBA (85%; 9.4 mg, 0.046 mmol), and dichloromethane (3 ml) were stirred at −20 °C for 14 h. Further MCPBA (26 mg, 0.128 mmol) was added and the mixture stirred for 24 h at 0 °C, rising to room temperature. Separation by dry flash chromatography gave the *trioxide* (**18**) (8.5 mg, 71%), m.p. 205 °C (light petroleum–dichloromethane) (Found: C, 48.1; H, 2.5; N, 13.6. $C_{16}H_{10}N_4O_3S_3$ requires C, 47.75; H, 2.5; N, 13.9%); $\lambda_{max.}$(EtOH) 235sh, 292, and 390 nm; $\nu_{max.}$($CHCl_3$) 1 590m, 1 356m, 1 284w, 1 169s, 1 163s, 1 087w, and 914m cm^{-1}; δ_H(250 MHz; $CDCl_3$) 7.34 (2 H, td, *J* 7.3 and 1.5 Hz), 7.46 (1 H, tt, *J* 7.2 and 1.3 Hz), 7.52 (2 H, td, *J* 7.8 and 1.7 Hz), 7.72 (1 H, tt, *J* 7.2 and 1.3 Hz), 8.00 (2 H, dd, *J* 8.3 and 1.5 Hz) and 8.15 (2 H, dd, *J* 8.3 and 1.5 Hz).

(ii) *From the* 1,2,3-*dithiazole* 2-*oxide* (**6**). The 2-oxide (**6**) (11.0 mg, 0.03 mmol) in dry dichloromethane (3 ml) was treated with MCPBA (26 mg, 0.128 mmol) and stirred for 3 h at 0 °C. Further MCPBA (20 mg, 0.1 mmol) was added and the stirring continued for 2 h. Separation by dry flash chromatography gave

the trioxide (**18**) (6.6 mg, 55%) identical with the above product.

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