Organic Heterocyclothiazenes. Part 12.[1] 1,3,5,2,4-Trithiadiazines

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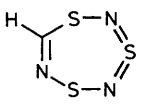
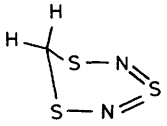
Diazomethane and its alkyl and aryl derivatives react as ylides with tetrasulphur tetranitride in boiling dichloromethane to give the red crystalline 1,3$\lambda^4\delta^2$,5,2,4-trithiadiazines (**2**), (**5**), and (**7**). The five contiguous heteroatoms in this new ring system form a planar U-shaped S_3N_2 unit, very similar to that in S_4N_2 (**3**) and the dihydrotrithiadiazepine (**4**).

We have shown that electron-deficient alkynes react with tetrasulphur tetranitride, S_4N_4, to give two novel heteroaromatic ring systems, the trithiadiazepines and the trithiatriazepines.[2] We have also described an independent synthesis of the former ring, but not of the latter.[3] In an attempted synthesis of trithiatriazepine (**1**) we treated S_4N_4 with diazomethane in the hope of introducing a methylene group into S_4N_4 followed by an aromatising loss of HNS. However trithiatriazepine was not formed in this reaction, but the product proved to be a new, six-membered ring, 1,3$\lambda^4\delta^2$,5,2,4-trithiadiazine (**2**),[4] and we now give details of this route to trithiadiazines.

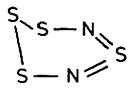
Reaction of Tetrasulphur Tetranitride with Diazoalkanes.— When ethereal diazomethane was added to S_4N_4 in dichloromethane at room temperature the yellow solution immediately became black and then slowly changed over 30 min to a bright red colour. T.l.c. showed one, intense red, component together with S_4N_4 and baseline material. Chromatography gave a highly crystalline red product, m.p. 43—45 °C, with a garlic like odour and molecular formula $CH_2N_2S_3$. Thus methylene had become incorporated into S_4N_4 but with the loss of a N_2S fragment. In the mass spectrum the isotopic abundance of ^{34}S showed the presence of three sulphur atoms, and there was sequential loss of two NS fragments suggesting that the alternating arrangement of nitrogen and sulphur in the starting material had been preserved, in an SNSNS unit. The i.r. spectrum was extremely simple indicating a highly symmetrical structure, and the n.m.r. spectra showed a δ_H singlet at 4.18 and



(**1**)



(**2**)



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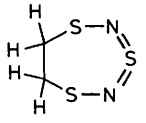


(**4**)

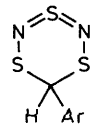
δ_C at 28.8 p.p.m., consistent with SCH_2S. The cyclic structure (**2**) thus seemed most reasonable for the red product and this was confirmed by single crystal *X*-ray diffraction.[4] Formation of this new and unexpected 1,3,5,2,4-trithiadiazine ring system was interesting because both six-membered and non-aromatic rings are rarely formed in S_4N_4 reactions with organic substrates.[5a]

Compound (**2**) is structurally analogous to tetrasulphur dinitride (**3**)[6] which is red, and dihydrotrithiadiazepine (**4**)[3] which is orange. In all three the S–N=S=N–S unit is U-shaped and almost exactly planar, with the rest of the molecule out of this plane; the methylene groups in (**2**) and (**4**) are rapidly inverting on the n.m.r. time scale.[4]

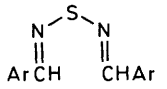
The rapid reaction between diazomethane and S_4N_4 was studied in some detail, with variation in solvent, reaction temperature, and mole ratio and rate of mixing of the starting materials. These variables were optimised in di-, tri-, and tetrachloromethane, from 0 to 77 °C, by the single factor procedure.[7] The best conditions, yielding about 40% of trithiadiazine (**2**) reproducibly, were addition of four equivalents of ethereal diazomethane to S_4N_4 in dichloromethane at gentle reflux. Curiously, some S_4N_4 always remained however large the excess of diazomethane. The preparation was improved by much slower addition, over 1.5 h, of the diazomethane as it was formed. Although the yield (40%) was not improved the S_4N_4 was almost all consumed and the chromatographic isolation was easier, and isolation of the diazomethane solution was avoided. In the presence of copper acetonylacetonate, as a catalyst for diazomethane decomposition, the reaction was much less clean with the yield of trithiadiazine (**2**) reduced (12%).

The reaction of S_4N_4 with three monoaryldiazomethanes, $ArCHN_2$ (Ar = phenyl, 4-methoxyphenyl, and 4-nitrophenyl), was studied next under the same conditions. Phenyldiazomethane gave 6-phenyltrithiadiazine (**5a**) in 37% yield (80% conversion, based on recovered S_4N_4) as a highly crystalline red compound, m.p. 82—84 °C, with spectroscopic properties analogous to those of the parent compound (**2**). The reaction mixture again turned black before fading to the bright red colour of the product. 4-Nitrophenyldiazomethane gave the somewhat less stable 6-(4-nitrophenyl)trithiadiazine (**5b**) (19% yield, 27% conversion), together with a bright yellow, highly crystalline compound, m.p. 236—240 °C, $C_{14}H_{10}N_4O_4S$ (37%). This was assigned structure (**6**) on the basis of its spectroscopic properties, though the compound showed no imine stretch in the i.r. region, probably because of its extensively delocalised nature ($\lambda_{max.}$ 405 nm, log ε 4.34). Compound (**6**) is interesting in that it demonstrates the likely fate of the three heteroatoms of S_4N_4 which remain after formation of the trithiadiazine, and provides a clue to the reaction pathway (see below). 4-Methoxyphenyldiazomethane, the least stable of the monoaryldiazomethanes prepared, gave the most stable trithiadiazine (**5b**) (26%) on reaction with S_4N_4.

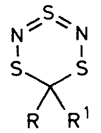
Thus monoaryl trithiadiazines are readily prepared from aryldiazomethanes as red, crystalline, sublimable solids which are relatively non-polar (R_F 0.3 to 0.5, silica, light petroleum) and moderately stable. The order of stability of these compounds, (**2**) > (**5c**) > (**5a**) > (**5b**), suggests that their instability could be associated with the acidity of the ring proton, the most



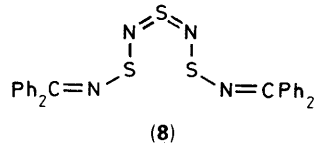
(5)a; Ar = Ph
b; Ar = $C_6H_4NO_2$-*p*
c; Ar = C_6H_4OMe-*p*



(6) Ar = $C_6H_4NO_2$-*p*



(7)a; R = R^1 = Ph
b; R = Ph, R^1 = CH_2Ph
c; R = Me, R^1 = $C_6H_4NO_2$-*p*
d; R = R^1 = Me
e; R = H, R^1 = CO_2Et
f; R = R^1 = CO_2Et



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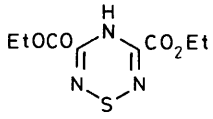

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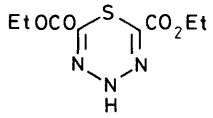


(10)

acidic being the least stable. Differences in the ^1H n.m.r. chemical shifts, although small, agree qualitatively with this trend (δ 4.18, 4.49, 4.52, and 4.62 respectively). Disubstitution of the ring carbon should thus enhance stability, and this was found to be so with the trithiadiazines (**7**).

The only reactions of simple diazo compounds with S_4N_4 reported in the literature are those of diaryldiazomethanes;[5b] diphenyldiazomethane gave the acyclic compound (**8**) with seven contiguous heteroatoms, and no trithiadiazines were reported. We have repeated this reaction (Ph_2CN_2, S_4N_4, diethyl ether, room temperature, 12 h) and confirm that compound (**8**),[8] with its somewhat surprising structure, is indeed the major product (60%). It was isolated by crystallisation from the complex reaction mixture since it decomposed on chromatography. No 6,6-diphenyltrithiadiazine was observed, but when the reaction was repeated under our favoured conditions (boiling dichloromethane) the trithiadiazine (**7a**) was isolated in low yield (6%). Compound (**8**) was still the major product but it did not survive column chromatography. The disubstituted trithiadiazine (**7a**) was more stable than the monophenyl compound (**5a**) and could be stored for long periods in the cold. 6-Benzyl-6-phenyltrithiadiazine (**7b**) was similarly formed, in much better yield (45%), and was also stable. We wished to prepare 6-methyl-6-(4-nitrophenyl)trithiadiazine (**7c**) for comparison with the unmethylated compound (**5c**). This was formed, and readily isolated, from the corresponding diazo compound, though only as a minor product (3% yield; 8% conversion) in a complex reaction. As expected, this was considerably more stable than (**5c**); it showed the properties characteristic of a trithiadiazine: a red colour with a weak long-wavelength absorption (420—450 nm) in the visible region, a moderately strong i.r. band in the range 1 070—1 090 cm^{-1}, and a strong M^+ with sequential loss of two NS units in the mass spectrum.

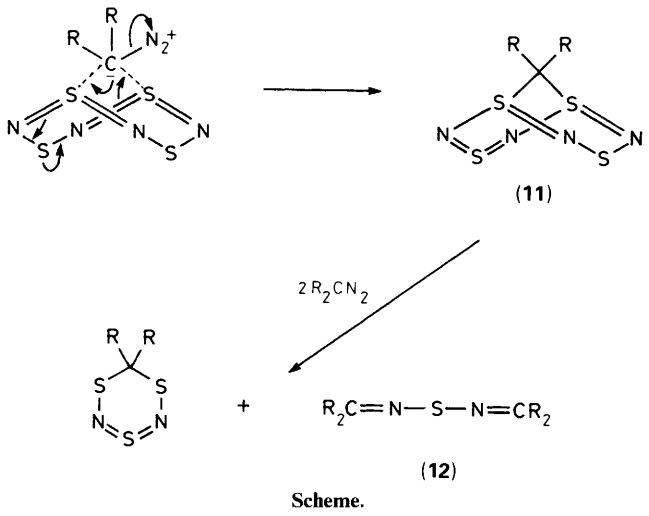
Thus the reaction of disubstituted diazomethanes with S_4N_4 all produce trithiadiazines though in variable and sometimes low yield; much of the S_4N_4 is consumed in alternative reactions and with diphenyldiazomethane the major product was the acyclic compound (**8**). Since products analogous to (**8**) were not observed with the monoaryldiazomethanes, we wondered if this pathway was a feature of disubstituted diazomethanes in general, possibly associated with the stability of the type (**8**) products. Accordingly, 2-diazopropane, prepared by oxidation of the hydrazone with alkaline mercuric oxide[9] and conveniently co-distilled with ether from the reaction mixture under reduced pressure, was added to S_4N_4 in hot dichloromethane. The reaction was cleaner than with diphenyldiazomethane, and it gave 6,6-dimethyltrithiadiazine (**7d**), m.p. 29 °C, as the major product (52%) with none of the acyclic compound analogous to (**8**). Trithiadiazine (**7d**) appeared to be indefinitely stable at 4 °C, though it did have the same intensely objectionable smell as propane-2,2-dithiol, which may indicate the occurrence of some very slight hydrolysis.

Thus trithiadiazines can be formed from diazomethane, dialkyldiazomethanes, and monoaryldiazomethanes. Disubstituted diazomethanes in which one of the substituents is aryl give more complex reaction mixtures containing low and variable yields of trithiadiazines. We now hoped to extend this reaction to the synthesis of functionalised trithiadiazines.

When S_4N_4 was treated with ethyl diazoacetate in boiling dichloromethane, benzene, or toluene no reaction occurred, but boiling chlorobenzene gave a complex mixture from which none of the corresponding trithiadiazine (**7e**) could be isolated. The only pure product was an intense purple oil, $C_8H_{11}N_3O_4S$, (16%). I.r. spectroscopy indicated the presence of an NH (3 355 cm^{-1}), an ester carbonyl (1 730 cm^{-1}) and an imine (1 675 cm^{-1}), and ^1H n.m.r. showed one NH and two ethyl ester groups. ^{13}C N.m.r. spectroscopy showed the molecule to be symmetrical with only four signals, at δ 14, 64, 143, and 157. These data seem to limit the structure to thiatriazine (**9**) or (**10**), and closer inspection of the mass spectrum showed two fragmentation pathways both involving the loss of *m/z* 46 (NS) which is characteristic of compounds with adjacent sulphur and nitrogen atoms. Therefore structure (**9**), a rare ring system with sulphur at the divalent oxidation level, is tentatively assigned to the product. Since ethyl diazoacetate did not react with S_4N_4 until heated to a temperature at which it loses nitrogen to form a carbene, we attempted to lower the reaction temperature by adding copper bronze, copper(I) salts, and rhodium acetate. However this gave no improvement in the incorporation of sulphur and nitrogen into the organic reaction products.

The non-isolation of the trithiadiazine mono-ester (**7e**) may have resulted from its instability in view of the likely acidity of the ring proton. We therefore treated S_4N_4 with diethyl diazomalonate since this could give the diester (**7f**). Again no reaction was observed at temperatures up to 80 °C (benzene). At 110 °C (toluene) the S_4N_4 decomposed completely over 24 h but the diethyl diazomalonate was unaffected. When S_4N_4 was treated with azibenzil, $PhCOC(N_2)Ph$, in boiling dichloromethane or benzene the only products isolated were thiobenzophenone (*ca.* 10%) and a trace of tetrasulphur dinitride (**3**). Thiobenzophenone is known to be formed from S_4N_4 and diphenylketene,[10] and presumably Wolff rearrangement of azibenzil to diphenylketene is the initial process here.

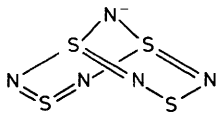
Clearly the formation of trithiadiazines from S_4N_4 and alkyl



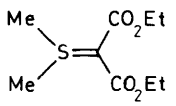
Scheme.

and aryl diazomethanes cannot be extended to the more stable α-carbonyl diazo compounds.

Mechanism of the Reaction of S_4N_4 *and Diazoalkanes.*—This last observation, together with the deleterious effect of carbene-promoting catalysts, suggest that in the formation of trithiadiazines the diazoalkanes are acting as ylides. We propose (Scheme) initial attack on sulphur by the diazo compound as a carbon nucleophile, followed by cyclisation across the weakly bonded 1,5-sulphur atoms, with loss of nitrogen, to give the intermediate (**11**). This intermediate may be responsible for the transient black colour since it is a completely symmetrical and potentially delocalised 10π system. Salts of the related ions $S_4N_5^-$ (**13**) and $S_4N_5^+$ are delocalised and coloured.[5c] Attempts to isolate the black intermediate by using a deficiency



(**13**)



(**14**)

of diazo compound led only to lower yields of the trithiadiazine. The intermediate (**11**) may cleave to give the trithiadiazine and an N_2S fragment which is intercepted by two further molecules of diazo compound to give a thiadiazapentadiene (**12**), which was isolated in the *p*-nitrophenyl case (**6**); alternatively the intermediate (**11**) could react with two molecules of diazo compound and then cleave directly to the trithiadiazine and thiadiazapentadiene (**12**). This would explain the need for excess of diazo compound for maximum yields of trithiadiazine. The formation of the acyclic compound (**8**) is more readily explained by an alternative attack by the diazoalkane on 2,4-related nitrogen atoms followed by loss of the connecting sulphur atom. This may dominate in the diphenyldiazomethane reaction because of the extensive conjugation of the phenyl groups with the delocalised chain of heteroatoms.

Some support for the mechanism proposed in the Scheme was obtained by the reaction of S_4N_4 with other more reactive ylides, which was found to extend the scope of this method. Dimethylsulphoxonium methylide[11] in THF was added slowly to S_4N_4 in THF at −78 °C. Immediate reaction occurred and again a transient black colour was observed. The parent trithiadiazine (**2**) was formed, though in low yield (7%), together with much unchanged S_4N_4 (58%), which is only very poorly soluble in THF at −78 °C. The fact that any trithiadiazine was formed at such a low temperature prompted the use of a more stabilised ylide.[12] We therefore prepared the ylide diester (**14**) by photolysis of diethyl diazomalonate in dimethyl sulphide. Treatment of S_4N_4 with this ylide in boiling trichloromethane gave the trithiadiazine diester (**7f**) (which was not formed from diethyl diazomalonate itself) as a bright orange oil in good yield (66%).

Experimental

For general points see refs. 1 and 2. Light petroleum refers to the fraction b.p. 40—60 °C.

1,3,5,2,4-*Trithiadiazine* (**2**).—An ethereal solution of diazomethane, prepared from Diazald (2.4 g, 11.2 mmol), was added to a stirred solution of tetrasulphur tetranitride, (0.360 g, 1.95 mmol) in chloroform (100 cm^3) heated at reflux, *via* the condenser over a period of 5 min. The reaction mixture immediately changed from light yellow to black (transiently) and dark red. Reflux was maintained for 30 min, and then the reaction mixture was cooled and evaporated to dryness. The products were removed from most of the remaining tetrasulphur tetranitride by washing with 10% dichloromethane in light petroleum. The combined washings were evaporated and the product isolated by chromatography (light petroleum) to give 1,3λ^{4}δ^2,5,2,4-*trithiadiazine* (**2**) (0.099 g, 37%) as deep red needles, m.p. 43—45 °C (from light petroleum, b.p. 60—80 °C) (Found: C, 8.6; H, 1.35; N, 20.1. $CH_2N_2S_3$ requires C, 8.7; H, 1.45; N, 20.3%); $\lambda_{max.}$(cyclohexane) 255 (log ε 3.58), 286 (3.46), and 455 nm (2.93); $\nu_{max.}$(CS_2) 2 955 and 2 910 (CH), 1 368, 1 147, 1 075 (NSN), 825, and 640 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 4.18 (s); δ_C(62.9 MHz; $CDCl_3$) 28.81; *m*/*z* (70 ev, 80 °C), 138 (M^+, 87%), 92 (65), 78 (41), and 46 (100).

Trithiadiazine (**2**) *from Dimethylsulphoxonium Methylide.*—Tetrasulphur tetranitride (0.184 g, 1.0 mmol) was dissolved in THF (20 cm^3). The solution was flushed with nitrogen and cooled to −78 °C. Dimethylsulphoxonium methylide (1 mmol) in THF was added dropwise over 2 min. As each drop was added the solution became temporarily black, until addition was complete and the black colour persisted. The mixture was allowed to warm slowly to room temperature overnight. The following morning a cherry red solution had formed. The mixture was evaporated and chromatography (light petroleum–dichloromethane) gave firstly 1,3λ^{4}δ^2,5,2,4-trithiadiazine (**2**) (10 mg, 7%) identical with material previously described, and secondly unaltered tetrasulphur tetranitride (107 mg, 58%).

6-*Phenyl*-1,3,5,2,4-*trithiadiazine* (**5a**).—To stirred solution of tetrasulphur tetranitride (0.4891 g, 2.66 mmol) in dichloromethane (135 cm^3) heated at reflux was added phenyldiazomethane (0.641 g, 5.43 mmol) in dichloromethane (20 cm^3) over 15 min. The solution became deep red to black during the addition. The reaction mixture was maintained at reflux overnight and became cherry red in colour. The reaction mixture was evaporated to dryness and the organic products were extracted from the unchanged tetrasulphur tetranitride (0.26 g, 53%) with light petroleum–10% dichloromethane. The organic extracts were evaporated to dryness and chromatographed (light petroleum–dichloromethane) to give 6-*phenyl*-1,3λ^{4}δ^2,-5,2,4-*trithiadiazine* (**5a**) (0.213 g, 38%) as bright red plates, m.p. 82—84 °C (from light petroleum) (Found: C, 39.3; H, 2.7; N, 13.0. $C_7H_6N_2S_3$ requires C, 39.2; H, 2.8; N, 13.1%); $\lambda_{max.}$(cyclohexane) 290 (log ε 2.79) and 438 nm (3.30); $\nu_{max.}$($CHCl_3$) 1 495, 1 450, 1 070, and 645 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 4.52 (1 H, s), 7.28 (2 H, br), and (3 H, br); δ_C(62.9 MHz; $CDCl_3$) 44.7, 129.69, 130.19, 130.33, and 132.73; *m*/*z* (70 eV, 100 °C) 214 (M^+, 16%), 168 (24), 122 (37), 121 (100), and 77 (13).

6-(4-*Nitrophenyl*)-1,3,5,2,4-*trithiadiazine* (**5b**) *and* 1,5-*Bis*(4-*nitrophenyl*)-3-*thia*-2,4-*diazapenta*-1,4-*diene* (**6**).—To a solution of tetrasulphur tetranitride (99.5 mg, 0.54 mmol), in dichloromethane (50 cm^3) heated at reflux, was added a solution of 4-nitrophenyldiazomethane (0.175 g, 1.1 mmol) in dichloromethane (10 cm^3) in 6 portions over 10 min. The yellow reaction mixture became darker during the course of the addition to give a red solution. The mixture was then maintained at reflux overnight. The reaction mixture was evaporated to dryness under reduced pressure. The organic products were extracted from the unchanged tetrasulphur tetranitride (0.029 g, 29%) with light petroleum–20% dichloromethane. The extracts were evaporated to dryness and chromatographed (light petroleum) to give (i) 6-(4-*nitrophenyl*)-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazine* (**5b**) (0.0186 g, 13%) as red plates, m.p. 78—79 °C (Found: C, 31.7; H, 1.85. $C_7H_5N_3O_2S_3$ requires C, 32.4; H, 1.9%); $\nu_{max.}$($CHCl_3$) 3 090, 2 960, 2 940, 1 610, 1 525s, 1 485, 1 350s, 1 085s (NSN), 865s, and 650 cm^{-1}; δ_H(250 MHz; $CHCl_3$) 4.62 (1 H, s), 7.45 (2 H, d, *J* 7.6 Hz) and 8.3 (2 H, d, *J* 7.6 Hz); δ_C(62.9 MHz; $CDCl_3$) 43.6, 124.8, 131.3, 139.9, and 149.3. And (ii) 1,5-*bis*(4-*nitrophenyl*)-3-*thia*-2,4-*diazapenta*-1,4-*diene* (**6**) (0.066 g, 37%) as yellow plates, m.p. 236—240 °C (from light petroleum) (Found: C, 50.7; H, 3.0; N, 17.0. $C_{14}H_{10}N_4O_4S$ requires C, 50.9; H, 3.05; N, 17.0%); $\lambda_{max.}$(EtOH) 294 (log ε 4.14) and 405 nm (4.34); $\nu_{max.}$($CHCl_3$) 1 605, 1 526, 1 350s, and 1 210 cm^{-1}; δ_H(250 MHz; $CDCl_3$), 7.93 (4 H, d, *J* 9 Hz) 8.32 (4, d, *J* 9 Hz), and 8.75 (2, s); *m*/*z* (70 eV, 200 °C) 330 (M^+, 46%), 284 (5.8), and 135 (100).

6-(4-*Methoxyphenyl*)-1,3,5,2,4-*trithiadiazine* (**5c**).—To a solution of tetrasulphur tetranitride (0.1556 g, 0.845 mmol) in dichloromethane (100 cm^3) stirred at reflux was added 4-methoxyphenyldiazomethane (0.2502 g, 1.69 mmol) in dichloromethane (5 cm^3) over 5 min. The reaction mixture changed from yellow to black during the course of the addition. Reflux was maintained overnight. The reaction mixture was evaporated to dryness and the organic products were extracted from most of the unaltered tetrasulphur tetranitride with 20% dichloromethane–light petroleum. The extracts were evaporated to dryness. Chromatography on silica with dichloromethane–light petroleum gave 6-(4-*methoxyphenyl*)-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazine* (**5c**) (0.054 g, 26%) as red plates, m.p. 93—95 °C (Found: C, 39.5; H, 3.2; N, 11.45. $C_8H_8N_2OS_3$ requires C, 39.3; H, 3.3; N, 11.5%); $\lambda_{max.}$(cyclohexane) 242 (log ε 4.28), 283 (3.85), and 442 nm (3.18); $\nu_{max.}$($CHCl_3$) 2 910, 2 840, 1 590, 1 580, 1 495, 1 460, 1 305, 1 070 (NSN), 835, and 635 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 3.85 (3 H, s), 4.49 (1 H, s), 6.98 (2 H, d, *J* 7 Hz), and 7.18 (2 H, d, *J* 7 Hz); δ_C(69 MHz; $CDCl_3$) 45, 55.5, 115.5, 125, 132, and 161; *m*/*z* (70 eV, 110 °C) 244 (M^+, 24%), 198 (32), 152 (62), and 151 (100).

6,6-*Diphenyl*-1,3,5,2,4-*trithiadiazine* (**7a**).—To a solution of tetrasulphur tetranitride (0.102 g, 0.55 mmol) in dichloromethane (50 cm^3) heated at reflux was added a solution of diphenyldiazomethane (0.201 g, 1.04 mmol) in dichloromethane (5 cm^3) over 5 min. The colour changed from yellow to deep red during the addition. The mixture was then maintained at reflux for 12 h and then evaporated to dryness under reduced pressure. The organic products were extracted from the unchanged tetrasulphur tetranitride with 15% dichloromethane in light petroleum. The extracts were evaporated and chromatographed (light petroleum) to give 6,6-*diphenyl*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazine* (**7a**) (10 mg, 6%) as deep red plates, m.p. 125—128 °C (from sublimation) (Found: C, 53.5; H, 3.4; N, 9.6. $C_{13}H_{10}N_2S_3$ requires C, 53.7; H, 3.4; N, 9.6%); $\lambda_{max.}$(cyclohexane) 230 (log ε 3.18), 295 (2.66), and 486 nm (2.90); $\nu_{max.}$(CCl_4) 3 080, 1 495, 1 450, 1 320, 1 080, 1 035, 960, 690, 660, and 640 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 7.39 (br); *m*/*z* (70 eV, 130 °C) 290 (M^+, 14.5%), 244 (49), 298 (100), 165 (79), and 121 (58).

6-*Benzyl*-6-*phenyl*-1,3,5,2,4-*trithiadiazine* (**7b**).—To a refluxing solution of tetrasulphur tetranitride (0.191 g, 1.04 mmol) in dichloromethane (100 cm^3) was added 1,2-diphenyldiazoethane (0.867 g, 4.17 mmol) dropwise over 5 min. The reaction mixture became black. The mixture was maintained at reflux for 30 min, and then stirred at room temperature overnight. The reaction mixture was evaporated under reduced pressure and chromatographed (light petroleum–dichloromethane) to give 6-*benzyl*-6-*phenyl*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazine* (**7b**) (0.145 g, 45%) as red plates, m.p. 105—106 °C (Found: C, 55.1; H, 3.9; N, 9.15. $C_{14}H_{12}N_2S_3$ requires C, 55.2; H, 4.0; N, 9.2%); $\lambda_{max.}$(cyclohexane) 216 (log ε 4.14), 294 (3.38), and 463 nm (2.85); $\nu_{max.}$(CCl_4) 3 090, 3 070, 3 040, 1 075, (NSN), 1 035, 956, 918, 700, 655, and 635 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 3.72 (2 H, s), 7.2 (5 H, m), 7.45 (3 H, m), and 7.55 (2 H, m); *m*/*z* (70 eV, 130 °C) 304 (M^+, 29%), 258 (7.1), 225 (13), 212 (17), 193 (9), 179 (20), 121 (100), and 77 (10).

6-*Methyl*-6-(4-*nitrophenyl*)-1,3,5,2,4-*trithiadiazine* (**7c**).—Tetrasulphur tetranitride (0.184 g, 1 mmol), 1-(4-nitrophenyl)diazoethane (0.708 g, 4.2 mmol) and benzene (30 cm^3) were mixed and stirred at reflux. After 30 min the mixture had become black, and was maintained at reflux for a further 2 h. The reaction mixture was evaporated under reduced pressure. Chromatography (light petroleum–dichloromethane) gave firstly 6-*methyl*-6-(4-*nitrophenyl*)-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazine* (**7c**) (8.9 mg, 3.2%), m.p. 96 °C (from light petroleum–dichloromethane) (Found: M^+, 272.9709. $C_8H_7N_3O_2S_3$ requires 272.9700); $\nu_{max.}$(CCl_4) 1 530vs, 1 348vs, 1 072 (NSN), and 859 cm^{-1}; δ_H (90 MHz; $CDCl_3$, TMS) 2.1 (3 H, s), 7.6 (2 H, d, *J* 9 Hz), and 8.3 (2 H, d, *J* 9 Hz); *m*/*z* (70 eV, 120 °C), 273 (M^+, 56%), 227 (85), 181 (100), 166 (99), 148 (81). and 120 (28.1), and secondly unaltered tetranitride (96.1 mg, 52%).

6,6-*Dimethyl*-1,3,5,2,4-*trithiadiazine* (**7d**).—To a solution of tetrasulphur tetranitride (0.368 g, 2.0 mmol) in dichloromethane (100 cm^3) at just below reflux was added an ethereal solution of 2-diazopropane (0.77 g, 11 mmol). The solution immediately changed from yellow to red. The solution was maintained at reflux for 30 min and then stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness under reduced pressure. The product was then extracted from the unaltered tetrasulphur tetranitride with light petroleum. The combined extracts were evaporated and chromatographed (light petroleum) to give 6,6-*dimethyl*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazine* (**7d**) (0.1717 g, 52%) as red plates, m.p. 29 °C (sublimation) (Found: M^+, 165.9687. $C_3H_6N_2S_3$ requires 165.9693); $\lambda_{max.}$(cyclohexane) 293 (log ε 3.48) and 470 nm (3.00); $\nu_{max.}$(CCl_4) 2 975, 2 930, 2 860, 1 455, 1 368, 1 075 (NSN), 655, and 640 cm^{-1}); δ_H(250 MHz; $CDCl_3$) 2.7 (s); *m*/*z* (70 eV, 80 °C) 166 (M^-, 68%), 120 (75), 74 (92), and 59 (100).

Diethyl 1,2,4,6-*Thiatriazine*-3,5-*dicarboxylate* (**9**).—To a stirred solution of tetrasulphur tetranitride (0.191 g, 1.03 mmol) in dry chlorobenzene (40 cm^3) at reflux, was added a solution of ethyl diazoacetate (0.7132 g, 6.3 mmol) in chlorobenzene (3 cm^3), portionwise over 1 h. The mixture was mintained at reflux for 1 h during which time the colour changed from yellow to dark red. Thin layer chromatography (dichloromethane) showed many spots of varying colour. The mixture was evaporated and chromatography (light petroleum–dichloromethane) gave a purple oil which was tentatively assigned as *diethyl* 1,2,4,6-*thiatriazine*-3,5-*dicarboxylate* (**9**) (40.1 mg, 16%) (Found: M^+, 245.0474. $C_8H_{11}N_3O_4S$ requires 245.0470); $\lambda_{max.}$(CH_2Cl_2) 280 and 475 nm; $\nu_{max.}$(film) 3 555 (NH), 2 930, 1 730 (CO), 1 675 (C=N), 1 370, 1 260 (CO), 1 115, and 1 010 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.38 (6 H, t, *J* 6.5 Hz), 4.35 (4 H, q, *J* 6.5 Hz), and 7.68 (1 H, s, br); δ_C(62.9 MHz; $CDCl_3$) 13.9, 63.8, 143.8, and 157.3; *m*/*z*

(70 eV, 110 °C) 245 (M^+, 60%) 217 (23), 189 (64), 171 (16), 143 (28), 115 (3), 99 (10), 46 (18), and 29 (100), as the only product characterised.

Diethyl 1,3,5,2,4-*Trithiadiazine*-6,6-*dicarboxylate* (**7f**).—To a solution of tetrasulphur tetranitride (20 mg, 0.11 mmol) in trichloromethane (4 cm^3) was added a solution of diethyl bismethoxycarbonylmethylide (158 mg, 0.71 mmol) in trichloromethane (2 cm^3). The mixture was heated at reflux for 2 h, when t.l.c. showed no remaining tetrasulphur tetranitride. The mixture was evaporated and chromatography (light petroleum–dichloromethane) gave *diethyl* 1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazine*-6,6-*dicarboxylate* (**7f**) (20.5 mg, 66%) as a bright orange oil (Found: C, 29.95; H, 3.8; N, 9.8. $C_7H_{10}N_2O_4S_3$ requires C, 29.8; H, 3.6; N, 9.9%); $\lambda_{max.}$(cyclohexane) 284 (log ε 3.53) and 428 nm (3.05); $\nu_{max.}$(CCl_4) 2 980, 1 729 (CO), 1 240, 1 220, 1 190, and 1 095 (NSN), and 645 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 1.32 (3 H, t, *J* 7.1 Hz) and 4.32 (2 H, q, *J* 7.1 Hz); δ_C(126 MHz; $CDCl_3$) 13.75, 47.74, 63.74, and 163.49; *m*/*z* (70 eV, 120 °C), 282 (M^+, 25%), 236 (3), 149 (19), 128 (20), 122 (19), 94 (62), and 29 (100).

Treatment of Diethyl Diazomalonate with Tetrasulphur Tetranitride.—Tetrasulphur tetranitride (116 mg, 0.63 mmol) and diethyl diazomalonate (460 mg, 2.5 mmol) were heated in toluene (30 cm^3) at reflux for 24 h. Thin layer chromatography (light petroleum–dichloromethane) showed sulphur, a little remaining tetrasulphur tetranitride, and unaltered diethyl diazomalonate.

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