Organic Heterocyclothiazenes. Part 3.[1] Synthesis and Structure of 1,3,5,2,4-Trithiadiazepines

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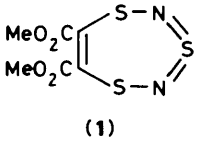
1,3λ⁴δ²,5,2,4-Trithiadiazepine (**10**) has been prepared from 1-chloroethane-1,2-bis(sulphenyl chloride) (**11**) and bis(trimethylsilyl)sulphurdi-imide (**3**) and also by dehydrogenation of the 6,7-dihydro derivative (**9**). Trithiadiazepine (**10**) is a planar, delocalised, stable 10π aromatic system. Its benzo derivative (**4**), an analogous 14π aromatic system, has been prepared from benzene-1,2-bis(sulphenyl chloride) (**2**) and sulphurdi-imide (**3**). In 6,7-dihydro-1,3λ⁴δ²,5,2,4-trithiadiazepine (**9**), similarly prepared from ethane-1,2-bis(sulphenyl chloride) (**8**) and sulphurdi-imide (**3**), the five heteroatoms are accurately co-planar, with the out of plane methylene protons rapidly interconverting at room temperature. Reaction of S_4N_4 with di-t-butyl acetylenedicarboxylate in boiling toluene gave di-t-butyl 1,3λ⁴δ²,5,2,4-trithiadiazepine-6,7-dicarboxylate (**14**) and t-butyl 1,3λ⁴δ²,5,2,4,6-trithiatriazepine-7-carboxylate (**15**) in low yield.

In Part 1 of this series we showed that the reaction of tetrasulphur tetranitride, S_4N_4, with dimethyl acetylenedicarboxylate in boiling toluene gave the very stable dimethyl 1,3λ⁴δ²,5,2,4-trithiadiazepine-6,7-dicarboxylate (**1**) as a minor product.[2] This compound was the first example of the novel trithiadiazepine ring system; with 10π electrons delocalised over seven atoms, its electron-rich heterocyclothiazene ring[3] is presumably stabilised by the ester groups. It was, therefore, of interest to synthesize the unsubstituted compound, to determine its stability and to see if its chemical reactivity is comparable with that of simpler aromatic and heteroaromatic species. We now describe the synthesis and properties of the parent trithiadiazepine together with its benzo and dihydro derivatives.[4]



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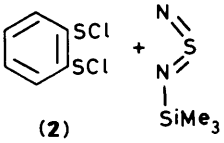
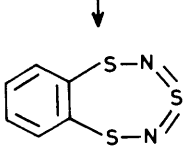


(**2**) (**3**)



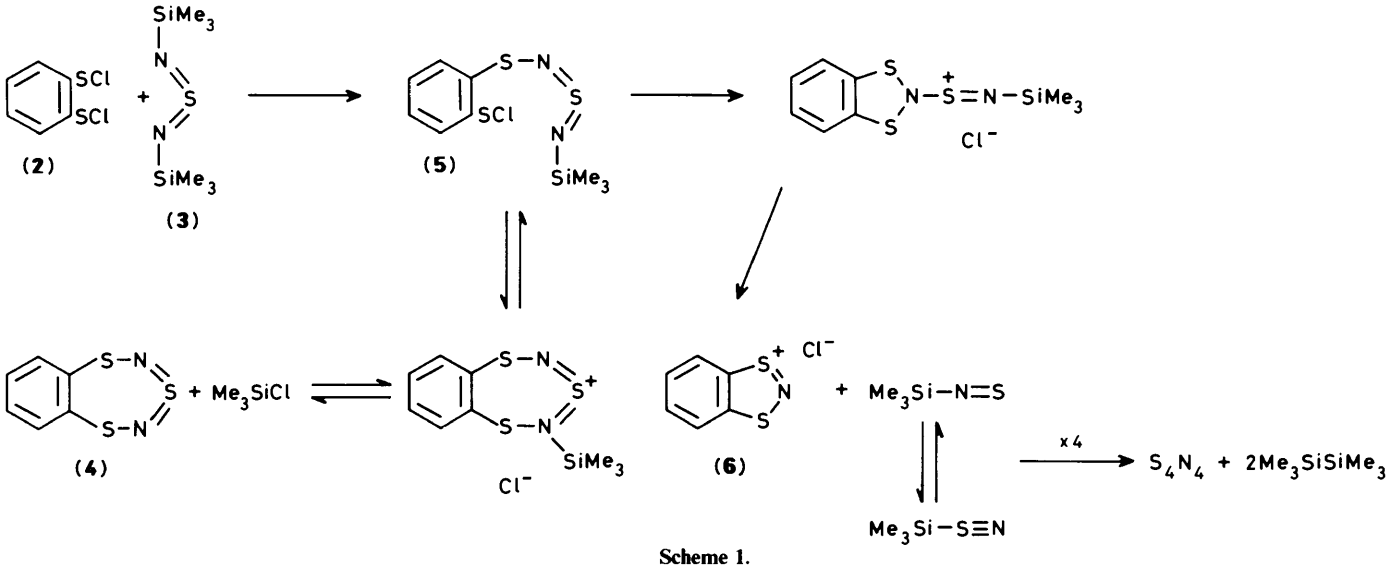
(**4**)

1,3λ⁴δ²,5,2,4-*Benzotrithiadiazepine* (**4**).—Since the hydrolysis of the diester (**1**) proved to be unexpectedly difficult and since (**1**) was available only in low yield from the S_4N_4 reaction, an alternative, more rational synthesis was required. One was initially devised for the benzo derivative (**4**) based upon the reaction of arenesulphenyl chlorides with bis(trimethylsilyl)-sulphurdi-imide (**3**).[5] Benzene-1,2-dithiol was converted quantitatively into the bis(sulphenyl chloride) (**2**) with chlorine in tetrachloromethane, and then dilute solutions of this and of the sulphurdi-imide (**3**) in dichloromethane were added slowly and synchronously from mechanically driven syringes to a large volume of vigorously stirred dichloromethane under nitrogen. The high dilution conditions successfully minimised polycondensation reactions. A yellow precipitate (see below) was removed and chromatography then gave 1,3λ⁴δ²,5,2,4-benzotrithiadiazepine (**4**) (50%) as bright yellow, air-stable needles, m.p. 78 °C, together with a small amount of S_4N_4. Compound (**4**) is readily soluble in organic solvents and is relatively non-polar with an R_F value of 0.31 (light petroleum–silica); the diester (**1**) has an R_F value of zero in the same system.

The structure of the benzo derivatives (**4**) was confirmed by *X*-ray crystallography.[6] It is planar with a crystallographic two-fold axis passing through S(3) and bisecting the benzene ring. Although it can be considered as a 14π electron aromatic system, the measured bond lengths provide evidence of some bond alternation in the rings. In particular, the C–S bonds are longer (1.73 Å) than those of the monocylic compound (**10**) below (1.68 and 1.69 Å); however, they are still much shorter than a C–S single bond like those (1.80 Å) in 6,7-dihydrotrithiadiazepine (**9**). There is also pronounced bond alternation in the carbocyclic ring, with bond lengths, starting with the common bond, of 1.39, 1.42, 1.35, and 1.40 Å. The ring bond angles at nitrogen are abnormally large (139°) as a consequence of the molecular planarity. The molecules adopt a parallel stacking arrangement in the crystal, the 7-membered ring of one directly overlying the six-membered ring of another, and *vice versa*. The interplanar separation is small at 3.54 Å.[6]

The 250 MHz ^{1}H n.m.r. spectrum of the benzotrithiadiazepine (**4**) is an 18 line AA'BB' pattern centred at δ 7.51. Computer simulation of the spectrum was achieved with $J_{AA'}$ 0.54, $J_{AB'}$ 1.17, $J_{BB'}$ 6.80, and J_{AB} 8.70 Hz. The chemical shift of the heterocyclic ring carbon atoms is δ_C 147.2. In the mass spectrum the molecular ion is observed at *m/z* 200 and the major fragment at 154 ($M^+ - 46$) is attributed to the loss of NS. A long wavelength π→π* absorption has its maximum at 379 nm in the u.v. spectrum, and the principal i.r. absorption at 1 150 cm^{-1} is characteristic of an asymmetric sulphurdi-imide stretching vibration.

In this preparation of the benzotrithiadiazepine (**4**) 2 other, unexpected, products were isolated, S_4N_4 and a flocculent yellow precipitate which proved to be 1,3,2-benzodithiazolium chloride (**6**). The latter was identified by comparison of its spectral data and properties with those of the corresponding bromide perbromide salt whose structure was elucidated by *X*-ray crystallography.[7] The formation of all three products in the reaction of benzene-1,2-bis(sulphenyl chloride) (**2**) and bis(trimethylsilyl)sulphurdi-imide (**3**) can be rationalised as

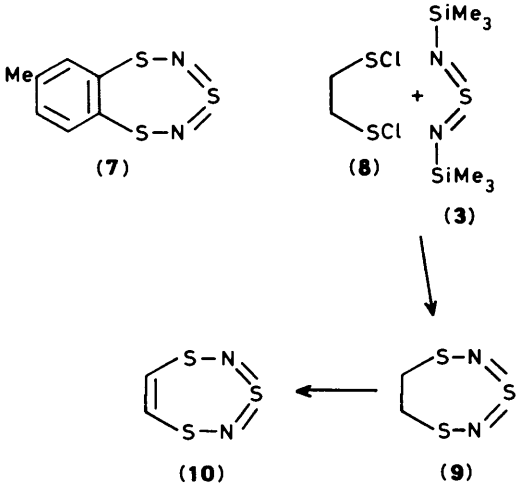


Scheme 1.

shown in Scheme 1. The first product, the monosulphenyl chloride (**5**), can cyclise by nucleophilic attack on the sulphenyl chloride by either nitrogen atom of the sulphurdi-imide group, to give five-and seven-membered ring intermediates; these can lead, as shown, to the 1,3,2-benzodithiazolium salt (**6**) and the desired benzotrithiadiazepine (**4**), respectively. The intermediate (**5**) could also be produced by a reversible reaction of product (**4**) with the trimethylsilyl chloride formed as the reaction proceeds. Liberation of the reactive intermediate, $Me_3Si–N{=}S$, or its isomer, $Me_3Si–S{\equiv}N$, could be responsible for the formation of the small amount of S_4N_4 observed since this is known to be a tetramer of SN. Benzodithiazolium chloride (**6**) has recently been prepared from the bis(sulphenyl chloride) (**2**) and trimethylsilyl azide.[8]

7-Methyl-1,3$\lambda^4\delta^2$,5,2,4-benzotrithiadiazepine (**7**) was prepared from toluene-3,4-dithiol, in somewhat better yield (65%), exactly as for the benzo compound; it too is a bright yellow crystalline solid, m.p. 88—90 °C, with similar spectroscopic properties to (**4**), absorbing at $\lambda_{max.}$ 382 nm and $\nu_{max.}$ 1 150 cm^{-1}.

6,7-*Dihydro*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* (**9**).—A direct extension of the above route to the preparation of the monocyclic trithiadiazepine (**10**) would require *cis*-ethene-1,2-bis(sulphenyl chloride). However the instability of the precursor, *cis*-ethene-1,2-dithiol,[9] and the associated problems of its chlorination make this method impractical. Ethane-1,2-dithiol, on the other hand, is stable, cheap, and readily converted into the bis(sulphenyl chloride (**8**) in quantitative yield.[10] Condensation of this with sulphurdi-imide (**3**) should give the dihydro derivative (**9**), dehydrogenation of which would complete the synthesis of the aromatic trithiadiazepine (**10**).



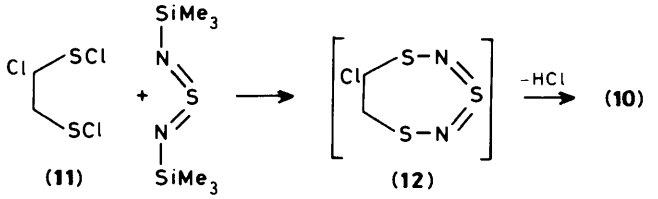
Treatment of the sulphenyl chloride (**8**) with sulphurdi-imide (**3**) in dichloromethane in high dilution did indeed give 6,7-dihydro-1,3$\lambda^4\delta^2$,5,2,4-trithiadiazepine (**9**) (22%) as a deep orange liquid which could be distilled at 45 °C, 0.3 mmHg to give low melting orange crystals, m.p. 29.5—31 °C. The yield was significantly lower than in the preparation of the benzo derivative (**4**), presumably because of the greater conformational flexibility of the saturated bis(sulphenyl chloride) (**8**), compared with (**2**), and hence the greater propensity for polycondensation reactions.

The dihydro compound (**9**) is more polar than benzotrithiadiazepine, with an R_F of 0.07 (light petroleum–silica). It is noticeably less stable than the benzo compound, decomposing slowly over several weeks, when stored at 4 °C under nitrogen. Although satisfactory elemental analysis could not be obtained for the dihydro compound (**9**), its structure was confirmed by *X*-ray crystallography.[6] The SNSNS portion of the ring is accurately planar, maximum deviation from the least squares plane for these atoms being 0.028 Å, and the molecule has a crystallographic two-fold axis. The S(1)–N(2)/S(5)–N(4) bonds (1.65 Å) have less double character than those of the benzo derivative (1.61 Å), and the C–S bonds are single (1.80 Å). The preferred planar conformation of the heteroatoms again results in an enlargement of the ring bond angle at nitrogen (137°). The two sp^3 carbon atoms lie symmetrically 0.47 Å above the below the SNSNS plane. The 250 MHz ^1H n.m.r. spectrum at room temperature is a sharp singlet at δ 3.71 indicating rapid hydrogen interconversion. The energy barrier for this interconversion is low (<40 kJ mol^{-1}) since characteristics of a partially exchange-broadened AA′BB′ spin system only become evident on cooling to 190 K. The chemical shift of the two equivalent carbon atoms is δ_C 55.9. In the mass spectrum the molecular ion is observed at *m/z* 152 and major peaks appear at $M^+ - 28$, $M^+ - 46$, and $M^+ - 60$, from the loss of C_2H_4, NS, and N_2S respectively. Surprisingly the dihydro compound absorbs at longer wavelengths ($\lambda_{max.}$ 408 nm) than the benzo compound ($\lambda_{max.}$ 379); it also exhibits a lower energy NSN stretching frequency at 1 138 cm^{-1} in the i.r. spectrum.

1,3λ⁴δ²,5,2,4-*Trithiadiazepine* (**10**).—Assuming this to be a stable aromatic system, we expected that the dihydro derivative (**9**) would dehydrogenate readily; treatment of (**9**) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (2 equiv.) in boiling dioxane for 16 h allowed conversion into the parent compound (**10**) (70%). Trithiadiazepine (**10**) crystallised from light petroleum as stable, volatile, colourless plates, m.p. 57—58 °C. Like benzotrithiadiazepine (**4**) it is readily soluble in organic solvents and has a similar R_F value of 0.30 (light petroleum–silica).

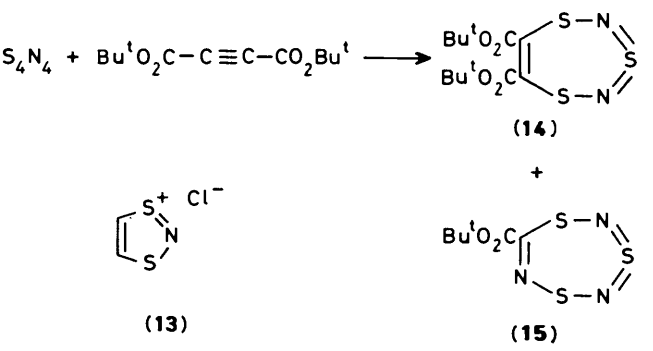
The *X*-ray crystal structure[6] confirms that the ring is planar, with maximum deviation from the least squares plane of 0.04 Å. Although the molecule is essentially symmetric, like its 6,7-diester (**1**),[11] it has no crystallographic two-fold axis. The ring bond lengths are all intermediate between single and double bonds, supporting a delocalised 10π system, and the bond angles at nitrogen are again enlarged (138° and 137°). In contrast with the benzo derivative (**4**), the smaller molecules of the monocyclic compound (**10**) do not pack in parallel planes in the crystal.

The ^{1}H n.m.r. spectrum of the trithiadiazepine (**10**) is a singlet at δ 7.76, and the ^{13}C spectrum shows that the carbon atoms are also firmly in the aromatic region, appearing as a singlet at δ_C 127.8 p.p.m. The mass spectrum contains the molecular ion at *m/z* 150 and major fragments at $M^+ - 26$ and $M^+ - 46$, for the loss of C_2H_2 and NS respectively. Only two large bands are observed in the solution i.r. spectrum below 2 500 cm^{-1}; these are 1 152 cm^{-1} (asymmetric NSN vibration) and 635 cm^{-1} (NSN bending vibration). Interestingly, the trithiadiazepine (**10**) absorbs at a much shorter wavelength ($\lambda_{max.}$ 330 nm) than the dihydro derivative (**9**) ($\lambda_{max.}$ 408 nm).

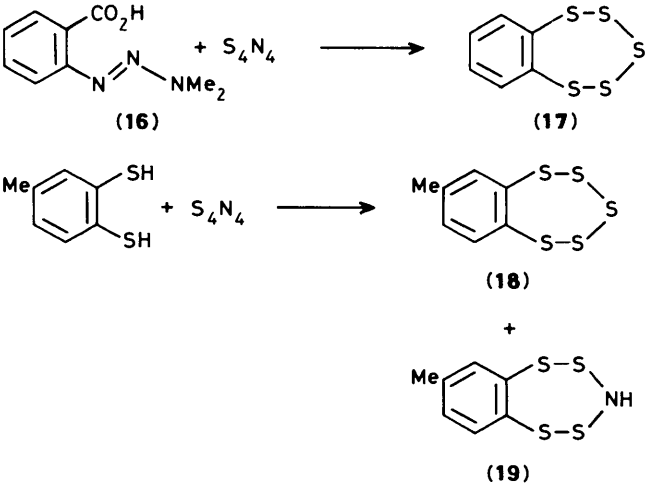


In view of the low yield of the dihydro compound (**9**) obtained from the bis(sulphenyl chloride) (**8**) and the sulphurdi-imide (**3**), and of the need to dehydrogenate the dihydro compound to produce the aromatic trithiadiazepine (**10**), a modified synthesis of (**10**) was devised which involved only two steps from ethane-1,2-dithiol. Ethane-1,2-bis(sulphenyl chloride) (**8**) could be prepared from the dithiol with chlorine gas in tetrachloromethane at −20 °C. However, when the chlorination was performed at 0 °C, with careful ^{1}H n.m.r. monitoring, a 70—90% conversion of ethanedithiol into the trichloro derivative (**11**) could be effected. Reaction of the trichloro compound (**11**) with sulphurdi-imide (**3**) in dichloromethane at high dilution gave the parent trithiadiazepine (**10**) directly, in 30% overall yield from ethane-1,2-dithiol. Presumably the chloro derivative (**12**) is an intermediate in this reaction, though it has not been isolated. The ease with which hydrogen chloride is (spontaneously) lost from (**12**) indicates a strong driving force for aromatisation. During this reaction a dark brown precipitate was formed; this is probably 1,3,2-dithiazolium chloride (**13**). The salt could not be obtained pure, but structure (**13**) was suggested by the ^{1}H n.m.r. spectrum (250 MHz; D_2O) which is a sharp singlet at δ 11.28 and by the mass spectrum (f.a.b.) which showed a molecular ion at *m/z* 104.

Reactions of S_4N_4 *directed towards the Synthesis of* 1,3,5,2,4-*Trithiadiazepines.*—Finally, we describe some attempted routes to various trithiadiazepines, starting from S_4N_4. The first was based on the reaction of S_4N_4 with dimethyl acetylenedicarboxylate, which gave the trithiadiazepine diester (**1**) and a trithiatriazepine mono-ester as minor products.[2] We thought that increasing the bulk of the ester groups might alter the ratio of the two products and thus we investigated the reaction which occurred when S_4N_4 and di-t-butyl acetylenedicarboxylate were heated in boiling toluene. Since all of the S_4N_4 was consumed within 3.5 h, the reaction is faster than with the dimethyl ester which required 6 h. The two analogous products (**14**) and (**15**) were isolated and characterised; however their chromatographic separation was very tedious because of their almost identical R_F values, and the reaction was thus of little practical value. The yields of both esters were also slightly lower [4% for (**14**) and 10% for (**15**)] than for the methyl esters.



We next investigated the reaction of S_4N_4 with the highly reactive 'alkyne', benzyne, since by cycloaddition across S(1) and S(5) this could furnish the benzotrithiadiazepine (**4**), though in the event none of this was detected. When S_4N_4 was treated with a 10-fold excess of benzenediazonium-2-carboxylate in 1,2-dichloroethane at reflux for 15 min, much S_4N_4 remained and the product mixture was very complex (t.l.c.). When 3,3-dimethyl-1-(2-carboxyphenyl)triazene (**16**), which decomposes at a higher temperature than the diazonium carboxylate, was used as benzyne precursor in refluxing xylene, the S_4N_4 was consumed in 3 h and benzopentathiepine (**17**) was isolated (29%). Structure (**17**) was assigned from the mass spectrum, which showed the molecular ion and the loss of 2, 3, and 4 sulphur atoms, and the ^{1}H n.m.r. spectrum, an AA′BB′ pattern centred on δ 7.58. This compound has also been prepared from benzene-1,2-dithiol and trisulphur dichloride.[12] The S_4N_4 has clearly been extensively degraded in this unexpected reaction.



1,2,5-Thiadiazoles are sometimes major products in S_4N_4 reactions, the NSN unit being abstracted from S_4N_4. It thus seemed possible that a trithiadiazepine ring could be constructed from an S–C(R)=C(R)–S unit, by such an NSN abstraction. With this in mind we treated toluene-3,4-dithiol with S_4N_4 in boiling xylene for 3 h. The reaction proceeded cleanly to give two products, related to the pentathiepine (**17**). The major product was 7-methylbenzopentathiepine (**18**) (58%), very similar in properties to (**17**). According to the spectral data the minor product was probably either the 3-aza compound (**19**) or its 2- or 4-aza isomer. The mass spectrum shows the molecular ion at *m/z* 233, with the major fragment at $M^+ - 47$ corresponding to the loss of HNS. An N–H stretch is present in the i.r. spectrum at 3 220 cm^{-1}, and a broad singlet at δ 4.8 in the 250 MHz ^1H n.m.r. spectrum also supports its presence. Whatever the precise structures of the products in the last two reactions, the decomposition of S_4N_4 was much too extensive to be of use in the construction of trithiadiazepines. When toluene 3,4-dithiol was replaced by its bis(sulphenyl chloride) in the reaction with S_4N_4, very little decomposition occurred, save for the slow decomposition of the sulphenyl chloride.

Experimental

For general points see reference 2. Light petroleum refers to the fraction b.p. 40—60 °C unless stated otherwise.

1,3λ^{4}δ^2,5,2,4-*Benzotrithiadiazepine* (**4**).—Benzene-1,2-bis(sulphenyl chloride) (**2**) was prepared as follows (*cf.* reference 13). Benzene-1,2-dithiol (1.42 g, 10 mmol) was dissolved in dry tetrachloromethane (50 ml) and chlorine gas was bubbled through the solution at 0 °C for approximately 10 min until the initial white precipitate had redissolved and an orange homogeneous solution was obtained. The passage of chlorine gas was stopped, the cooling bath removed, and nitrogen was bubbled through the solution as it warmed to room temperature. The solvent was removed under reduced pressure and the crude residue was dissolved in dry dichloromethane (30 ml).

Bis(trimethylsilyl)sulphurdi-imide (**3**)[5] (1.8 ml, 2.06 g, 10 mmol) was similarly dissolved in dry dichloromethane (30 ml). The two dichloromethane solutions were added synchronously over 48 h *via* mechanically driven syringe drives to a large flask containing dry dichloromethane (1.5 l), with vigorous stirring under nitrogen at room temperature. When the addition was complete the reaction mixture was stirred for a further 2 days to ensure complete reaction. A flocculent yellow precipitate was filtered off, the solvent was evaporated, and the residue chromatographed on silica gel. Elution with light petroleum gave 1,3λ^{4}δ^2,5,2,4-*benzotrithiadiazepine* (**4**) (1.00 g, 50%) as bright yellow needles, m.p. 78 °C (from light petroleum) (Found: C, 35.9; H, 1.9; N, 13.95. $C_6H_4N_2S_3$ requires C, 36.0; H, 2.0; N, 14.0%); $\lambda_{max.}$(EtOH) 223sh (log ε 4.08), 250 (4.25), 294 (4.02), and 379 nm (3.63); $\nu_{max.}$($CHCl_3$) 1 460s, 1 150s, and 640 cm^{-1}; $\nu_{max.}$(KBr) 592, 525, 435, and 395 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.27 (2 H, BB′ protons) and 7.75 (2 H, AA′ protons, $J_{AA'}$ 0.54, $J_{AB'}$ 1.17, $J_{BB'}$ 6.80, and J_{AB} 8.70 Hz); δ_C (62.9 MHz; $CDCl_3$) 121.8, 123.0, and 147.2; *m/z* 200 (M^+, 33%), 154 (100), 110 (14), 108 (14), and 78 (9). Further elution with light petroleum gave tetrasulphur tetranitride (5%), identical with authentic material.

The yellow precipitate was washed with dry dichloromethane to give pure 1,3,2-*benzodithiazolium chloride* (**6**) (0.70 g, 37%), m.p. 218—220 °C (Found: C, 37.8; H, 2.1; Cl, 19.05; N, 7.3. $C_6H_4ClNS_2$ requires C, 38.0; H, 2.1; Cl, 18.7; N, 7.4%); $\lambda_{max.}$(EtOH) 248 (log ε 3.79), 332 (3.23), and 396 nm (3.02); $\nu_{max.}$(KBr) 1 520, 1 400br, 1 322, 756s, 744, 729s, 489, 448s, 396, and 315 cm^{-1}; δ_H (90 MHz; D_2O) 8.18 (2 H, m, BB′ protons) and 9.11 (2 H, m, AA′ protons); *m/z* (f.a.b.) 154 (M^+).

7-*Methyl*-1,3λ^{4}δ^2,5,2,4-*benzotrithiadiazepine* (**7**).—This was prepared from toluene-3,4-dithiol by the above method described for benzo-1,3,5,2,4-trithiadiazepine (**4**). Chromatography, also as previously described, gave the title compound (**7**) (65%) as bright yellow needles, m.p. 88—90 °C (from light petroleum) (Found: C, 39.15; H, 2.85; N, 12.75. $C_7H_6N_2S_3$ requires C, 39.25; H, 2.8; N, 13.2%); $\lambda_{max.}$(EtOH) 232sh (log ε 4.01), 251 (4.15), 294 (3.85), and 382 nm (3.49); $\nu_{max.}$($CHCl_3$) 2 920, 2 860, 1 604s, 1 460s, 1 356, 1 150s, 856, and 645 cm^{-1}; $\nu_{max.}$(KBr) 598, 520, and 435 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 2.44 (3 H, s), 7.09 (1 H, dd, *J* 2 and 8.5 Hz), 7.52 (1 H, m), and 7.64 (1 H, d, *J* 8.5 Hz); δ_C (62.9 MHz; $CDCl_3$) 20.9, 122.2, 123.2, 123.9, 132.1, 144.5, and 147.6; *m/z* 214 (M^+, 80%), 168 (100), and 122 (25).

6,7-*Dihydro*-1,3λ^{4}δ^2,5,2,4-*trithiadiazepine* (**9**).—Ethane-1,2-bis(sulphenyl chloride) (**8**) was prepared in quantitative yield from ethane-1,2-dithiol as follows (*cf.* reference 10). Ethane-1,2-dithiol (2.0 ml, 2.25 g, 23.9 mmol) was stirred at room temperature under nitrogen with dry tetrachloromethane (10 ml), and sulphuryl chloride (4.2 ml, 7.06 g, 52.3 mmol) was added dropwise over 30 min. The solution was stirred at room temperature overnight. Since after this time a small amount of precipitated polysulphide was still present in the yellow reaction mixture, a few more drops of sulphuryl chloride were added and the mixture was stirred for a further 2 h until it became homogeneous. Evaporation of the solvent gave ethane-1,2-bis(sulphenyl chloride) (**8**) (3.90 g, 100%), as a pale yellow oil, which crystallised on cooling to −12 °C, δ_H (90 MHz; $CDCl_3$) 3.53 (s). The sulphenyl chloride (**8**) was either used directly or stored at −12 °C, under nitrogen, for up to 3 months.

Ethane-1,2-bis(sulphenyl chloride) (**8**) (1.95 g, 12.0 mmol) dissolved in dry dichloromethane (30 ml) and bis(trimethylsilyl)-sulphurdi-imide (**3**)[5] (2.9 ml, 2.47 g, 12.0 mmol) dissolved in dry dichloromethane (30 ml) were added synchronously over 48 h *via* mechanically driven syringe drives to a large flask containing dry dichloromethane (1.5 l), which was vigorously stirred under nitrogen at room temperature. When the addition was complete the mixture, a cloudy orange-brown solution, was stirred for 2 days to ensure complete reaction. The solvent was then evaporated and the residue chromatographed on silica gel. Elution with dichloromethane (5%) in light petroleum gave 6,7-*dihydro*-1,3λ^{4}δ^2,5,2,4-*trithiadiazepine* (**9**) (22%) (0.40 g, 2.6 mmol) as an orange oil. Distillation under reduced pressure (45 °C/0.3 mmHg) gave orange crystals, m.p. 28—30 °C, which on recrystallisation from light petroleum at 4 °C gave orange plates, m.p. 29.5—31 °C (Found: M^+, 151.9538. $C_2H_4N_2S_3$ requires 151.9537); $\lambda_{max.}$(EtOH) 260 (log ε 3.15), 305 (2.76), and 408 nm (3.26); $\nu_{max.}$(film) 2 920, 2 880, 2 100, 1 390s, 1 270, 1 250, 1 190, 1 138s, 945s, 875s, 705, 685, and 605 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 3.71 (s); δ_C (62.9 MHz; $CDCl_3$) 55.9; *m/z* 152 (M^+, 76%), 124 (97), 106 (15), 92 (23), 78 (100), 64 (58), and 46 (78).

1,3λ^{4}δ^2,5,2,4-*Trithiadiazepine* (**10**).—(a) *By dehydrogenation of* 6,7-*dihydro*-1,3,5,2,4-*trithiadiazepine* (**9**). Compound (**9**) (152 mg, 1.0 mmol) was dissolved in dry dioxane (5.0 ml) and 2,3-dichloro-5,6-dicyanobenzoquinone (454 mg, 2.0 mmol) was added in 1 portion. The mixture was then heated at reflux under nitrogen for 16 h. After cooling, insoluble material was filtered off, the solvent evaporated under reduced pressure, and the residue chromatographed on silica gel. Elution with light petroleum gave 1,3λ^{4}δ^2,5,2,4-*trithiadiazepine* (**10**) (105 mg, 70%) as colourless plates, m.p. 57—58 °C (from light petroleum) (Found: C, 16.2; H, 1.25; N, 18.7. $C_2H_2N_2S_3$ requires C, 16.0; H, 1.3; N, 18.7%); $\lambda_{max.}$(EtOH) 224 (log ε 3.76) and 330 nm (3.64);

$\nu_{max.}$($CHCl_3$) 2 930, 2 855, 1 152s, and 635 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 7.76 (s); δ_C (62.9 MHz; $CDCl_3$) 127.8; *m/z* 150 (M^+, 100%), 124 (8), 104 (23), and 78 (46).

(b) via 1-*Chloroethane*-1,2-*bis*(*sulphenyl chloride*) (**11**). Ethane-1,2-dithiol (1.0 ml, 0.94 g, 10 mmol) was dissolved in dry tetrachloromethane (50 ml) and chlorine gas was bubbled through the solution at 0 °C. The initially formed white precipitate was seen to redissolve forming a homogeneous yellow solution and a few minutes later a second precipitate began to form. When the bulk of the mixture was once again solid, chlorination was discontinued and dry nitrogen was passed through the reaction mixture as it warmed to room temperature. Stirring, with gentle warming if necessary, was continued until the solution became homogeneous once more. A small sample of the reaction mixture was removed for ^1H n.m.r. analysis in order to determine the ratio of ethane-1,2-bis(sulphenyl chloride) to 1-chloroethane-1,2-bis(sulphenyl chloride). If the proportion of 1-chloroethane-1,2-bis(sulphenyl chloride) (**11**) [$\delta_H(CCl_4)$ 3.76 (1 H, d), 3.86 (1 H, d), and 5.52 (1 H, t)] was greater than 70% then the solvent was evaporated and the crude product was redissolved in dry dichloromethane (30 ml) for direct use in the next stage. If the proportion of trichloride (**11**) was less than 70% then the solution was recooled to 0 °C and chlorination was continued as before until a sufficient yield of trichloride (**11**) was obtained.

Bis(trimethylsilyl)sulphurdi-imide (**3**)[5] (1.8 ml, 2.06 g, 10 mmol) was similarly dissolved in dry dichloromethane (30 ml). The two dichloromethane solutions were added synchronously over 48 h *via* mechanically driven syringe drives to a large flask containing dry dichloromethane (1.5 l) vigorously stirred under nitrogen at room temperature. When the addition was complete the reaction mixture, a cloudy brown solution, was stirred for a further 2 days to ensure complete reaction. Insoluble material was filtered off, the solvent evaporated, and the residue chromatographed on silica gel; elution with light petroleum gave 1,3,5,2,4-trithiadiazepine (**10**) (454 mg, 30% from ethane-1,2-dithiol), identical with that described earlier.

Reactions of Tetrasulphur Tetranitride, S_4N_4.—(a) *With di-t-butyl acetylenedicarboxylate*. S_4N_4 (360 mg, 1.96 mmol) and di-t-butyl acetylenedicarboxylate (885 mg, 3.92 mmol) were heated at reflux in dry toluene (10 ml) under nitrogen for 3.5 h, after which time all the S_4N_4 had been consumed (t.l.c.). Evaporation of the solvent and chromatography of the residue on silica gel, eluting with 5% dichloromethane in light petroleum gave a mixture of two components. These were separated by preparative t.l.c. eluting twice with 5% dichloromethane in light petroleum to give firstly *t-butyl* 1,3$\lambda^4\delta^2$,5,2,4,6-*trithiatriazepine*-7-*carboxylate* (**15**) (50 mg, 10%) as colourless needles, m.p. 82.5—83 °C (from light petroleum) (Found: C, 29.1; H, 3.5; N, 16.85. $C_6H_9N_3O_2S_3$ requires C, 28.7; H, 3.6; N, 16.7%); $\lambda_{max.}$(EtOH) 266 (log ε 3.87), and 332 nm (3.20); $\nu_{max.}$($CHCl_3$) 2 920, 1 725s, 1 690s, 1 365, 1 290—1 140s, 970, and 825 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.65 (s); *m/z* 251 (M^+, 37%), 78 (21), 57 (100), and 46 (6), and secondly *di-t-butyl* 1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine*-6,7-*dicarboxylate* (**14**) (29 mg, 4%), as pale yellow needles, m.p. 92—92.5 °C (from light petroleum) (Found: C, 41.2; H, 5.2; N, 7.9. $C_{12}H_{18}N_2O_4S_3$ requires C, 41.15; H, 5.15; N, 8.0%) $\lambda_{max.}$(EtOH) 274 (log ε 3.80) and 335 nm (3.13); $\nu_{max.}$($CHCl_3$) 2 930, 1 720s, 1 705s, 1 470, 1 450, 1 390, 1 365s, 1 270—1 140s, and 830—740br cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.61 (s); δ_C (62.9MHz; $CDCl_3$) 27.9, 84.6, 142.5, and 160.8; *m/z* 350 (M^+, 5%), 294 (3), 238 (11), 194 (4), 175 (2), 148 (3), and 57 (100). Two other products of the reaction, detected by t.l.c. and presumed to be di-t-butyl 1,2,5-thiadiazole-3,4-dicarboxylate and di-t-butyl 1,2,4-thiadiazole-3,5-dicarboxylate, were not isolated.

(b) *With benzyne*. S_4N_4 (112 mg, 0.61 mmol) and 3,3-dimethyl-1-(2-carboxyphenyl)triazene (**16**) (140 mg, 0.73 mmol) were dissolved in dry xylene (10 ml) and heated at reflux under nitrogen for 3.5 h, after which time all of the S_4N_4 had been consumed. The solvent was evaporated and the residue chromatographed on silica gel. Elution with light petroleum gave firstly sulphur then 1,2,3,4,5-benzopentathiepine (**17**) (42 mg, 29%), m.p. 130—140 °C (Found: M^+, 235.8910. Calc. for $C_6H_4S_5$. 235.8916); δ_H (90 MHz; $CDCl_3$) 7.21—7.43 (2 H, m, BB′ protons) and 7.72—7.95 (2 H, m, AA′ protons); *m/z* 236 (M^+, 16%) 172 (100), 140 (19), 108 (32), and 96 (15).

(c) *With toluene*-3,4-*dithiol*. S_4N_4 (260 mg, 1.41 mmol) and toluene-3,4-dithiol (400 mg, 2.56 mmol) were dissolved in dry xylene (50 ml) and heated at reflux under nitrogen for 3 h. The solvent was evaporated and the residue chromatographed on silica gel. Elution with light petroleum gave 7-*methyl*-1,2,3,4,5-*benzopentathiepine* (**18**) (370 mg, 58%) as a waxy yellow solid, m.p. 61—62 °C (Found: C, 33.8; H, 2.4. $C_7H_6S_5$ requires C, 33.6; H, 2.4%); $\lambda_{max.}$(cyclohexane) 232 (log ε 4.02), 257sh (3.60), and 320sh nm (3.26); $\nu_{max.}$(KBr) 2 920, 2 855, 1 579, 1 455, 1 440, 888, 821s, 560, 475, 465, and 450 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 2.36 (3 H, s), 7.12 (1 H, ddd, *J* 0.8, 1.7, and 7.6 Hz), 7.65 (1 H, d, *J* 1.7 Hz), and 7.71 (1 H, d, 7.6 Hz); *m/z* 250 (M^+, 23%), 188 (14), 187 (10), 186 (100), 154 (12), 153 (14), 122 (16), and 121 (20). Elution with 50% dichloromethane in light petroleum gave, as a pale blue solid, a compound which was tentatively assigned the structure of 7-*methyl*-1,2,4,5,3-*benzotetrathiazepine* (**19**) (90 mg, 15%), m.p. 146—148 °C (Found: M^+, 232.9467. $C_7H_7NS_4$ requires 232.9461); $\lambda_{max.}$(cyclohexane) 235 (log ε 4.16), and 302 nm (3.49); $\nu_{max.}$(KBr) 3 220, 1 582s, 1 452s, 1 440s, 1 374, 1 252, 1 208, 1 030, 815s, 775, 585, 555, and 470s cm^{-1}; δ_H (250 MHz; $CDCl_3$) 2.34 (3 H, s), 4.78 (1 H, s, br), 7.08 (1 H, ddd, *J* 0.75, 2.0, and 8.0 Hz), 7.57 (1 H, d, *J* 2.0 Hz), and 7.62 (1 H, d, *J* 8.0 Hz); *m/z* 233 (M^+, 10%), 186 (100), 153 (13), 121 (16), 78 (7), and 64 (10).

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