Organic Heterocyclothiazenes. Part 4.[1] Chemistry of 1,3,5,2,4-Trithiadiazepines

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The chemical, like the physical, properties of 1,3,5,2,4-trithiadiazepines broadly support their 10π aromatic nature. The parent compound (**1**) is thermally stable, though photochemically labile, does not undergo cycloaddition reactions characteristic of sulphur di-imides, is inert towards acids, amines, iodomethane, catalytic hydrogenation, and reacts only slowly with *m*-chloroperbenzoic acid. It undergoes electrophilic aromatic substitution smoothly to give mono- and di-nitro and mono- and di-bromo derivatives, though it could not be acylated. It is, however, sensitive to hydroxide and t-butoxide ions; treatment with potassium t-butoxide and iodomethane gives 3,4-bis(methylthio)-1,2,5-thiadiazole (**4**). Triphenylphosphine similarly causes ring contraction of trithiadiazepine (**3**) to the 1,2,5-thiadiazole (**5**). The properties of the benzo compound (**2**) are similar to those of the monocyclic compound (**1**), though it is generally less stable and more reactive than (**1**), in agreement with some bond alternation in the bicyclic structure. Treatment of compound (**2**) with bromine gives bis(1,3,2-benzodithiazolium)bromide tribromide (**11**). Mechanisms are proposed (Schemes 1, 2, and 4) for the various trithiadiazepine ring contractions reported.

In earlier Parts of this series we have reported the synthesis of 1,3λ⁴δ²,5,4,2-trithiadiazepine (**1**),[1] its benzo derivative (**2**),[1] and the diester (**3**).[2] The spectral properties and *X*-ray diffraction analysis of these compounds support their delocalised, aromatic nature; their chemical properties, which we now describe, are equally in accord with this.[3]

Thermal and Photochemical Stability.—Trithiadiazepine (**1**) has remarkable thermal stability for a ring with such a high proportion of heteroatoms; it undergoes negligible decomposition on heating under nitrogen in *o*-dichlorobenzene at 150 °C for 32 h followed by refluxing (180 °C) for 48 h. Benzotrithiadiazepine (**2**) on the other hand is totally decomposed within 2 h in boiling decalin (decahydronaphthalene) (190 °C) or on prolonged heating (77 h) in xylene (140 °C). The thermolysis of (**2**) gave sulphur and at least three other products (not identified), which were more polar than the starting material; 2,1,3-benzothiadiazole could not be detected (t.l.c.) even though dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**5**) is formed on thermolysis of the diester (**3**) in boiling decalin.[2] Both trithiadiazepines (**1**) and (**2**) are photochemically labile; irradiation at 300 or 350 nm in light petroleum led to their rapid and extensive degradation.

Attempted Cycloaddition Reactions.—Sulphur di-imides undergo a variety of cycloaddition reactions, in which they act as 2π (N=S) or 4π ($\bar{N}$–$\overset{+}{S}$=N) components.[4] Trithiadiazepines (**1**) and (**2**), however, did not react with a variety of electron-rich and electron-poor 2π and 4π cycloaddition reagents, under the conditions indicated in Table 1. In every case starting materials were recovered in high yield and no products were detected.

This general lack of reactivity supports the delocalised nature of the heteroaromatic ring and the absence of sulphur di-imide functionality. The inertness of trithiadiazepine (**1**) towards norbornadiene also emphasises the difference between this system and S_4N_4 which rapidly forms a 1:2 adduct with norbornadiene and other strained alkenes.[5] However, it has recently been shown that the more reactive benzotrithiadiazepine (**2**) does form a 1:1 adduct with norbornadiene, by cycloaddition across S(1)–S(3).[6]

The inertness of the electron-rich trithiadiazepines towards tetracyanoethylene and dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate is particularly striking. Furthermore the trithiadiazepines (**1**) and (**2**) did not form charge-transfer complexes with tetracyanoethylene, nor with picric acid, trinitrobenzene, and the powerful acceptor, (2,4,7-trinitro-9-fluorenylidene)-malononitrile. Since (**1**) and (**2**) do not complex with these electron acceptors, we wondered if they would do so with electron donors, by virtue of their low-lying vacant π* orbitals, but no charge-transfer complexation could be detected between them and the donor molecule, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.

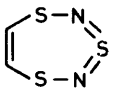
Table 1. Inertness of the trithiadiazepines in cycloaddition reactions

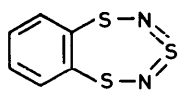
(a) Trithiadiazepine (**1**):

(i) Tetraphenylcyclopentadienone (1 equiv.), boiling toluene, 21 h.
(ii) Dimethyl acetylenedicarboxylate (2 equiv.), boiling toluene, 65 h.
(iii) Dihydropyran (excess), boiling tetrahydrofuran, 5 h.
(iv) 1-Acetoxybutadiene (excess), boiling tetrahydrofuran, 3 h.
(v) Dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (1 equiv.), boiling dioxane, 30 h.
(vi) Tetracyanoethylene (1 equiv.), boiling tetrahydrofuran, 8 h.
(vii) Norbornadiene (excess) at reflux, 6 h.
(viii) 2,5-Bis(trimethylsilyoxy)furan (excess), boiling tetrachloromethane, 48 h.

(b) Benzotrithiadizepine (**2**):

(i) Dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (1 equiv.), boiling toluene, 20 h.
(ii) 2,5-Bis(trimethylsilyloxy)furan (excess), boiling tetrachloromethane, 48 h.
(iii) 1-Acetoxybutadiene (1 equiv.), boiling tetrahydrofuran, 16 h.


(**1**)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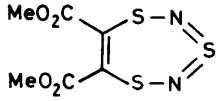
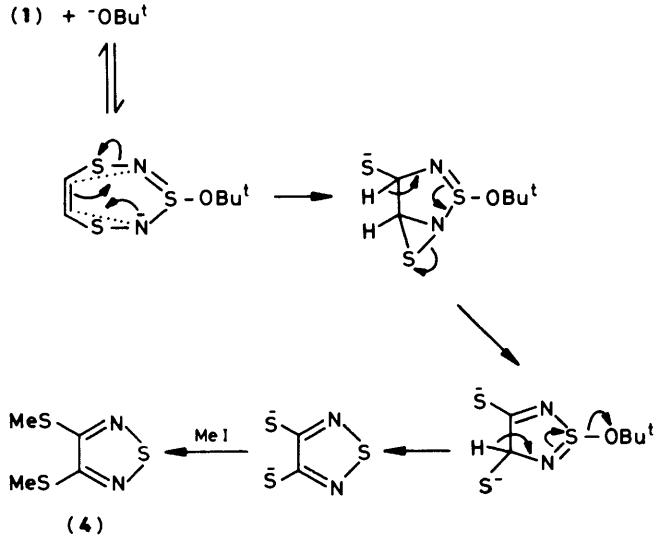


(**3**)

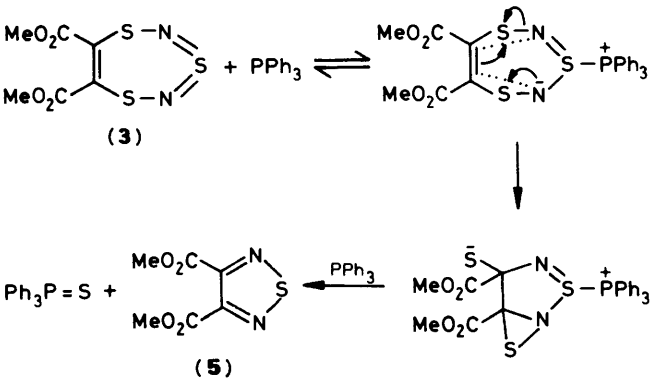
Stability Towards Acids, Bases, Electrophiles, and Nucleophiles.—Trithiadiazepine (**1**) is stable towards a variety of mineral and Lewis acids including hydrochloric acid, trifluoroacetic acid, aluminium trichloride, boron trifluoride, and tin tetrachloride. It is also resistant to triethylamine and benzylamine, but is rapidly decomposed by 1M sodium hydroxide in aqueous dioxane.



Scheme 1.

On addition of potassium t-butoxide to a solution of trithiadiazepine (**1**) in dry tetrahydrofuran (THF) the trithiadiazepine was rapidly consumed and an orange precipitate formed. Addition of iodomethane converted the precipitate into pale cream crystals which were identified as 3,4-bis(methylthio)-1,2,5-thiadiazole (**4**) (50%). This unexpected product results from a rearrangement in which two of the ring sulphur atoms have become exocyclic. A possible mechanism (Scheme 1) involves reversible co-ordination of t-butoxide to the most electropositive sulphur, which could initiate the tranformations shown, though the precise sequence is speculative. It seems reasonable that a similar mechanism could account for the decomposition of trithiadiazepine (**1**) by sodium hydroxide. However, when (**1**) was treated with 1M sodium hydroxide in aqueous dioxane and then with iodomethane, there was no trace of 3,4-bis(methylthio)-1,2,5-thiadiazole (**4**). Similarly, when the iodomethane treatment was replaced by acidification with hydrochloric acid, 1,2,5-thiadiazole-3,4-dithiol could not be detected. This difference between hydroxide and t-butoxide may be explained by the greater nucleophilicity of the hydroxide compared with t-butoxide. The latter could attack the trithiadiazepine selectively at the most electropositive centre, S(3), whilst the former could attack indiscriminantly at all three sulphur atoms, leading to rapid decomposition.

On treatment with triphenylphosphine (1 equiv.) in boiling toluene, dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (**3**) slowly gave dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**5**). After 5 h only 28% of the trithiadiazepine (**3**) had reacted but the yield of thiadiazole (**5**) based on this was high (88%). A ring



Scheme 2.

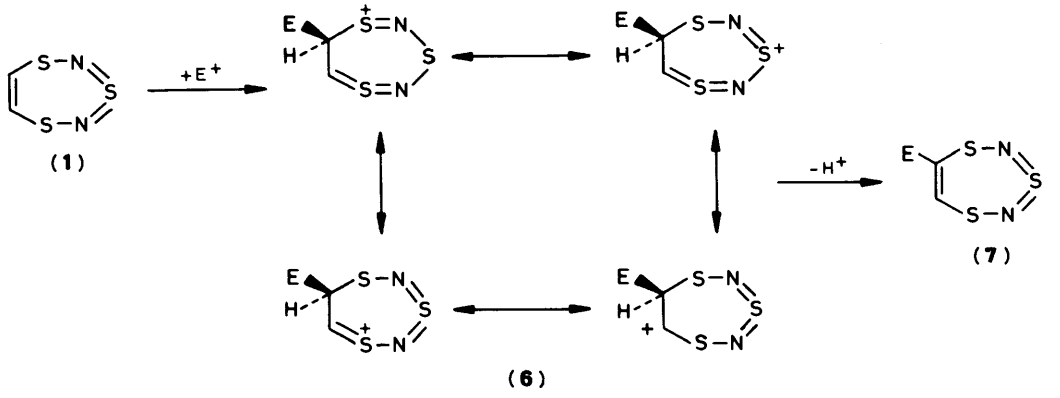
contraction mechanism similar to that proposed in Scheme 1 may operate, but with two of the sulphur atoms now being removed from the molecule as triphenylphosphine sulphide (Scheme 2). Again the reaction is initiated by reversible nucleophilic attack on S(3), more slowly with triphenylphosphine than with t-butoxide ions, but the extruded sulphur atoms are now abstracted by triphenylphosphine.

In contrast with the diester (**3**), benzotrithiadiazepine (**2**) was rapidly decomposed by triphenylphosphine in toluene at room temperature, to give an unidentified orange precipitate; 2,1,3-benzothiadiazole was not a product. The parent trithiadiazepine (**1**) was inert under these conditions but, like the diester, it reacted slowly when heated at reflux. After 8 h much trithiadiazepine (**1**) remained and only a small amount of triphenylphosphine sulphide (9%) had been formed.

Dimethyl trithiadiazepine-6,7-dicarboxylate (**3**) underwent negligible reaction with *m*-chloroperbenzoic acid (1 equiv.) in dichloromethane at room temperature. Under the same conditions the parent compound (**1**) slowly reacted to form a cloudy suspension, although after 20 h 47% of the starting material was recovered. Again the benzo derivative (**2**) was much more reactive; on addition of the peracid to a dichloromethane solution the colour changed immediately from yellow to deep orange. All the benzo compound had decomposed but the polar products could not be identified.

Trithiadiazepine (**1**) did not react with iodomethane either when mixed neat and heated at reflux for 12 h or when stirred in dimethylformamide (DMF) solution for several days; DMF is generally a very effective solvent for the quaternisation of nitrogen heterocyclic compounds with iodomethane. Thus the nitrogen (and sulphur) lone pairs are not readily available for co-ordination, again demonstrating the reluctance of the trithiadiazepine heteroatoms to act as nucleophilic centres.

Both trithiadiazepines (**1**) and (**2**) were totally inert towards catalytic hydrogenation with 10% palladium on carbon in



Scheme 3.

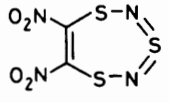
ethanol at 1 atm hydrogen and room temperature; the heterocyclic ring is an effective catalyst poison (see below).

Electrophilic Aromatic Substitution.—As a 10π aromatic system, trithiadiazepine (**1**) is expected to undergo electrophilic substitution reactions. With 10π electrons delocalised over 7 ring atoms the ring should be activated to electrophilic substitution relative to benzene; however its inertness towards some electron acceptors, and its susceptibility to nucleophilic attack, have already been demonstrated. Considering a general mechanism for electrophilic substitution (Scheme 3), the tetrahedral intermediate (**6**) could be stabilised by delocalisation of the positive charge onto the three sulphur atoms. Electrophilic attack could also occur at nitrogen but this process would probably be reversible.

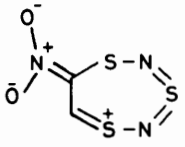
Nitration. Treatment of trithiadiazepine (**1**) with nitronium tetrafluoroborate in acetonitrile at −10 °C gave 6-nitro-1,3,5,2,4-trithiadiazepine (**7**; E = NO_2) as stable bright yellow needles, m.p. 86 °C, in 82% yield. The ^1H n.m.r. spectrum of the product, a singlet at δ 7.81, and an i.r. absorption at 1 160 cm^{-1} suggested that the heterocyclic ring was still intact. The presence of a nitro group was supported by strong i.r. absorptions at 1 495 and 1 306 cm^{-1}, and the mass spectrum and elemental analysis confirmed the molecular formula as $C_2HN_3O_2S_3$; the mass spectrum also showed the loss of fragments of mass 46 (NO_2 or NS) and 92 (both of these). Unusually, the 7-H of the nitro compound was shifted downfield by only 0.05 p.p.m. relative to the parent compound; by contrast the *o*-protons of nitrobenzene are shifted downfield by 1 p.p.m. relative to benzene. The ^{13}C signals for the nitro compound are shifted downfield, and appear at δ_C 151 and 135, compared to 128 for the parent compound.

The nitro compound (**7**; E = NO_2) was also prepared (94%) by treatment of compound (**1**) with an excess of copper(II) nitrate trihydrate in acetic anhydride at 0 °C. With an excess of nitronium tetrafluoroborate as a saturated solution in acetonitrile at +10 °C, the mononitro compound was converted into 6,7-dinitro-1,3,5,2,4-trithiadiazepine (**8**) (59%), deep yellow needles, m.p. 63—64 °C. The presence of 2 nitro groups now has a significant effect on the NSN stretching frequency, which is lowered to 1 122 cm^{-1}; the signal for the carbon atoms appears at δ_C 153.6 in the the ^{13}C n.m.r. spectrum. This ready introduction of the second nitro group, *ortho* to the first, is quite striking.

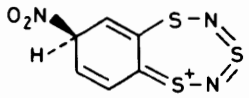
X-Ray crystallographic analysis[7] of the mono- and di-nitro compounds showed that in the crystalline state a single nitro group is almost coplanar with the ring, forming an angle of 5.9° with the ring plane, indicative of some charge delocalisation, but in the dinitro compound the two groups are in parallel planes inclined to the ring plane by 45°. In the mononitro compound the C(7)–S(1) bond (1.67 Å) is slightly shorter than the C(6)–S(5) bond (1.72 Å), again suggesting a contribution from such resonance forms as (**9**).



(**8**)



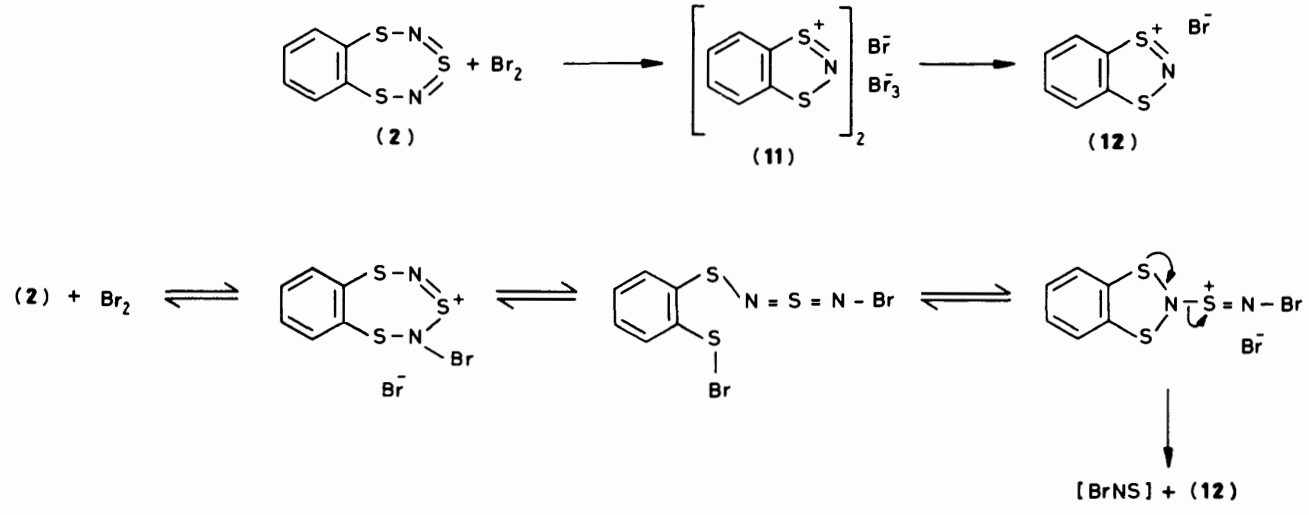
(**9**)



(**10**)

The benzo derivative (**2**) was markedly less stable than trithiadiazepine itself towards the nitration conditions. Although no reaction occurred on treatment with copper(II) nitrate trihydrate in acetic anhydride at 0 °C, if the solution was warmed to room temperature much decomposition of the benzo compound (**2**) was observed and only 15% of a mononitrated product was obtained. With nitronium tetrafluoroborate (1 equiv.) in acetonitrile at −30 °C the same product was isolated in 6% yield and the remainder of the starting material was destroyed. The spectroscopic properties of the nitro compound, particularly its ^1H n.m.r. spectrum, show it to be the 7-isomer; the two protons adjacent to the nitro group resonate 1.06 and 0.85 p.p.m. downfield, relative to benzotrithiadiazepine, and the remaining proton is shifted 0.20 p.p.m. downfield. *ortho*, *meta*, and *para* Proton couplings are observed with *J* values of 9.6, 2.0, and 0.7 Hz. Electronically the 6- and 7-positions seem to be about equally activated towards electrophilic substitution, though '*para*-quinonoid' intermediates like (**10**), which would give 7-substitution, are presumably favoured over analogous '*ortho*-quinonoid' structures. Similar regioselectivity is observed in 1,2-dimethoxybenzene which substitutes preferentially at C-4.

Bromination. Treatment of trithiadiazepine (**1**) with bromine in tetrachloromethane at room temperature gave a monobromo



Scheme 4.

Table 2. Attempted acetylation and formylation of trithiadiazepine (**1**)

Reaction and work-up conditions:	Result
(i) Ac_2O, CH_2Cl_2, BF_3·Et_2O, 20 °C, 2 h; H_2O, CH_2Cl_2	No reaction
(ii) CH_3COCl, $AlCl_3$, CS_2, heat, 2 h; ice, CH_2Cl_2	50% (**1**) recovered; rest decomposed
(iii) Me_2N·CHO, $POCl_3$, heat, 2 h; NaOAc (aq.), CH_2Cl_2	70% (**1**) recovered; rest decomposed
(iv) $BuOCHCl_2$, $SnCl_4$, CH_2Cl, −78 °C; H_2O, CH_2Cl_2	All (**1**) decomposed

compound in low yield (32%) accompanied by much decomposition. However, *N*-bromosuccinimide in acetonitrile at room temperature gave the same product, 6-bromo-1,3,5,2,4-trithiadiazepine (**7**; E = Br) in 88% yield. Characteristic peaks at $\nu_{max.}$ 1 155 cm^{-1} in the i.r. spectrum and at $M^+ - 46$ in the mass spectrum, and the sharp singlet at δ_H 7.75 in the ^1H n.m.r. spectrum, showed the trithiadiazepine ring had survived the bromination conditions. When a large excess of *N*-bromosuccinimide was added slowly to trithiadiazepine (**1**) in acetonitrile at room temperature, over several days, 6,7-dibromo-1,3,5,2,4-trithiadiazepine was obtained (77%); its u.v. spectrum ($\lambda_{max.}$ 347 nm) was similar to that of the monobromo derivative ($\lambda_{max.}$ 342 nm), and it had an NSN i.r. stretch at 1 145 cm^{-1}. Again the fragment $M^+ - 46$ was a predominant feature of the mass spectrum; the ^{13}C n.m.r. spectrum showed that the carbon atoms are shielded relative to those in the parent compound, being shifted upfield to δ 115.7 p.p.m.

Treatment of benzotrithiadiazepine (**2**) with *N*-bromosuccinimide in acetonitrile at room temperature led to its rapid decomposition, illustrating once again that it is more sensitive than the monocyclic compound (**1**). Treatment with bromine in dichloromethane gave a dark red, high melting, water soluble crystalline product. Its ^1H n.m.r. in D_2O revealed a symmetrical AA′BB′ pattern, similar to that of the starting material, centred on δ_H 7.48, its mass spectrum had a peak at *m/z* 154 ($C_6H_4NS_2^+$), there was no NSN stretch in the i.r. spectrum and the u.v. spectrum showed a long wavelength absorption at $\lambda_{max.}$ 392. The structure was solved by *X*-ray crystallography[7] which showed it to be bis(1,3,2-benzodithiazolium)bromide tribromide (**11**) (56%). Vacuum drying for 3 days at room temperature allowed conversion of this salt into the simpler 1,3,2-benzodithiazolium bromide (**12**), molecular bromine having sublimed off. The mechanism for this ring contraction is probably closely related to that reported in Part 3[1] for the formation of 1,3,2-benzodithiazolium chloride in the synthesis of benzotrithiadiazepine (**2**), but with bromine replacing trimethylsilyl chloride (Scheme 4). The reaction is initiated, it is proposed, by prior rapid and reversible electrophilic attack by bromine on a ring nitrogen atom. The chloride and the bromide tribromide (**11**) had very similar properties, including almost identical u.v. spectra, though the very similar AA′BB′ patterns in their ^1H n.m.r. spectra were well separated (by 1.2 p.p.m.).

6-Bromo-7-nitro-1,3,5,2,4-trithiadiazepine would be a useful synthetic intermediate in this series; it could not be made by bromination of the nitro compound, but was formed by nitration of 6-bromotrithiadiazepine (**7**; E = Br), though in low yield. With 2 equivalents of nitronium tetrafluoroborate in acetonitrile at room temperature, all of the bromo compound was consumed but only 16% of the bromo-nitro compound could be isolated. Nitration of the bromo compound with copper(II) nitrate–acetic anhydride was even less successful (7% yield); considerable variation of reaction conditions with either reagent did not result in improved yields.

Table 3. Attempted reduction of 6-nitro-1,3,5,2,4-trithiadiazepine. (All reactions are at room temperature unless stated otherwise)

Reaction conditions	Result
H_2 (1 atm), 10% Pd/C, EtOH, 1 h	N.r.
H_2 (1 atm), 5% Pd/C, EtOH, 20 h	N.r.
H_2 (1 atm), 5% Pd/C, H_2SO_4, EtOH, 5 h	N.r.
H_2 (1 atm), PtO, EtOH, 15 h	N.r.
H_2(130 atm), 10% Pd/C, EtOH, 50 °C, 5 h	All decomp.
H_2 (1 atm), PdS/C,[8] EtOH, 3 days	N.r.
H_2(50 atm), PdS/C, EtOH, 24 h	N.r.
H_2 (150 atm), PdS/C, EtOH, 16 h	Some decomp.
H_2 (200 atm), PdS/C, EtOH, 30 °C, 3 h	All decomp.
HCO_2NH_4, 10% PdS/C, MeOH, 26 h[9]	N.r.
Cyclohexene, 10% Pd/C, 90 °C, 10 h	N.r.
Cyclohexene, PdS/C, 90 °C, 10 h	N.r.
$SnCl_2$·$2H_2O$, EtOH, 70 °C, 1 h[10]	N.r.
Zn dust, Ac_2O, NaOAc, Et_2O, 20 min	N.r.
Fe dust, AcOH, reflux, 30 min[11]	70% Decomp.
Na_2S_x, H_2O reflux, 45 min	All decomp.
$Na_2S_2O_4$, H_2O, reflux, 45 min[12]	All decomp.
$NaBH_4$, $NiCl_2$·$6H_2O$, MeOH, 0 °C, to 20 °C[13]	All decomp.
$TiCl_3$ aq., THF, 1 h[14]	All decomp.
$TiCl_3$ as above, then AcCl	Complex mixture

N.r. = No reaction.

Attempted Acetylation and Formylation.—Despite the successful nitration and bromination of the trithiadiazepine ring, we failed to acetylate or formylate it (Table 2). Friedel-Crafts acylations of heterocyclic compounds are often unsuccessful because of co-ordination of the Lewis acid catalyst to the ring heteroatoms. This can sometimes be overcome by using a large excess of catalyst, but this did not help with our polyheteroatom system.

Attempted Reduction of 6-Nitro-1,3,5,2,4-trithiadiazepine.—6-Amino-1,3,5,2,4-trithiadiazepine (**7**; E = NH_2) would be an interesting compound in demonstrating the effect of an electron-releasing substitutent on the electron-rich heterocyclic ring, and it should also be a versatile synthetic intermediate. Unfortunately we have been unable to reduce the nitro compound to this amino compound by a variety of catalytic and other methods (Table 3).

We noted earlier the resistance of trithiadiazepines (**1**) and (**2**) towards catalytic hydrogenation; when the nitro compound proved equally resistant it seemed possible that the sulphur-rich ring was acting as a catalyst poison. Evidence to confirm this deduction was provided by the hydrogenation of *p*-nitroacetophenone in ethanol over 5% Pd/C, in the absence and presence of trithiadiazepine (**1**). In its absence the nitro compound was reduced almost quantitatively to the corresponding amino alcohol, whilst in its presence the hydrogenation was totally inhibited. Hydrogenation was equally unsuccessful with other catalysts, including palladium sulphide which can overcome catalyst poisoning by sulphur compounds.[8] Under mild conditions the nitro compound was recovered in high yield, whilst at high pressures it was extensively decomposed. Catalytic hydrogen-transfer and other reducing systems were also unsuccessful; again there was either no reaction or the nitro compound was destroyed. The amine, if formed, must be sensitive; it could not be intercepted by acetylation. Electron-releasing groups are known to destabilise planar eight-membered electron rich S–N rings, causing them to fold to permit transannular S–S bonding.[15] Since such compensating stabilisation is geometrically much less favoured with the present seven-membered ring, the amino compound could be inherently more reactive and hence readily decomposed.

Experimental

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

Thermolysis of 1,3,5,2,4-*Trithiadiazepine* (**1**).—1,3,5,2,4-Trithiadiazepine (**1**) (5 mg) was heated in 1,2-dichlorobenzene (3 ml) for 32 h at 150 °C, after which time t.l.c. analysis indicated that starting material only was present. The solution, which was now pale brown in colour, was then refluxed at 180 °C for 48 h, after which time, despite further darkening of the solution, much starting material remained (t.l.c.).

Photolysis of 1,3,5,2,4-*Trithiadiazepine* (**1**).—A solution of 1,3,5,2,4-trithiadiazepine (**1**) (20 mg, 0.13 mmol) in light petroleum (b.p. 60—80 °C) (100 ml) under nitrogen was irradiated at 300 nm in a Rayonet Photochemical Reactor. After 1 h a dark brown precipitate had formed and all the starting material had been consumed. The brown solid was insoluble in dichloromethane, ethyl acetate, methanol, and water and was not identified. No other products were isolated. A similar result was obtained when the photolysis was carried out at 350 nm.

Treatment of 1,3,5,2,4-*Trithiadiazepine* (**1**) *with Hydrogen and Palladium on Charcoal.*—1,3,5,2,4-Trithiadiazepine (**1**) (25 mg, 0.17 mmol) was dissolved in absolute ethanol (10 ml) and 5% palladium on charcoal (15 mg) was added. The mixture was shaken in an atmosphere of hydrogen (1 atm) at room temperature for 24 h. The catalyst was then removed by filtration through Celite and t.l.c. indicated that only starting material was present. Evaporation of the solvent gave recovered 1,3,5,2,4-trithiadiazepine (22 mg, 88%).

Hydrogenation of p-*Nitroacetophenone.*—(a) *In the presence of* 1,3,5,2,4-*trithiadiazepine.* 1,3,5,2,4-Trithiadiazepine (**1**) (21 mg, 0.14 mmol) was dissolved in absolute ethanol (10 ml) and 5% palladium on charcoal (5 mg) was added. The mixture was shaken in an atmosphere of hydrogen (1 atm) for 5 min, then *p*-nitroacetophenone (33 mg, 0.20 mmol) was added and shaking under hydrogen was continued for 24 h. After this time t.l.c. indicated that both the trithiadiazepine and the nitro compound were still present and no products had been formed.

(b) *In the absence of* 1,3,5,2,4-*trithiadiazepine. p*-Nitroacetophenone (35 mg, 0.21 mmol) was dissolved in absolute ethanol (10 ml) and 5% palladium on charcoal (5 mg) was added. The mixture was shaken in an atmosphere of hydrogen (1 atm) for 20 h, after which time t.l.c. indicated that all of the starting nitro compound had been consumed to give one product. The catalyst was removed by filtration through Celite and the solvent was evaporated to give an almost quantitative yield of 1-(*p*-aminophenyl)-ethanol, $\nu_{max.}(CCl_4)$ 3 610, 3 480, 3 470, 3 390, 3 020, 3 000, 2 970, 2 925, 2 885, 2 665, 1 615s, 1 505, 1 270s, 1 175, 1 065, and 895 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.18 (2 H, d, *J* 9 Hz), 6.60 (2 H, d, *J* 9 Hz), 4.74 (1 H, q, *J* 7 Hz), 2.65—3.20 (3 H, br), and 1.40 (3 H, d, *J* 7.5 Hz).

Treatment of 1,3,5,2,4-*Trithiadiazepine* (**1**) *with Triphenylphosphine.*—1,3,5,2,4-Trithiadiazepine (**1**) (33 mg, 0.22 mmol) was stirred under nitrogen in dry toluene (3 ml) and a solution of triphenylphosphine (58 mg, 0.22 mmol) in toluene (3 ml) was added dropwise. The mixture was stirred at room temperature for 28 h during which time a slight cloudiness appeared, but t.l.c. analysis indicated no significant reaction had occurred. The mixture was therefore heated at reflux under nitrogen for 8 h. Subsequent evaporation of the solvent, followed by chromatography on silica gel, gave, on elution with light petroleum, firstly triphenylphosphine sulphide (6 mg, 0.02 mmol, 9%) and then a mixed fraction (31 mg) containing 1,3,5,2,4-trithiadiazepine contaminated with triphenylphosphine.

Treatment of 1,3,5,2,4-*Trithiadiazepine* (**1**) *with* m-*Chloroperbenzoic acid.*—A solution of 1,3,5,2,4-trithiadiazepine (**1**) (36 mg, 0.24 mmol) in dichloromethane (2 ml) was stirred under nitrogen and a solution of *m*-chloroperbenzoic acid (MCPBA) (41 mg, 0.24 mmol) in dichloromethane (3 ml) was added dropwise at room temperature. The mixture was stirred at room temperature for 20 h during which time a gradual yellow colouration and cloudiness of the solution was observed, followed by the formation of an orange precipitate. The solvent was evaporated and the residue chromatographed on silica gel, eluting with light petroleum, to give unchanged 1,3,5,2,4-trithiadiazepine (17 mg, 47%).

Treatment of 1,3,5,2,4-*Trithiadiazepine* (**1**) *with Iodomethane.*—1,3,5,2,4-Trithiadiazepine (**1**) (13 mg, 0.09 mmol) was dissolved in iodomethane (3 ml) and heated at reflux for 12 h under nitrogen, after which time no reaction had occurred.

The reaction was repeated using dimethylformamide (DMF) as solvent. 1,3,5,2,4-Trithiadiazepine (**1**) (41 mg, 0.27 mmol) and iodomethane (0.75 ml) were stirred under nitrogen at room temperature in DMF (1.5 ml) for 10 days. Again there was no reaction.

Treatment of 1,3,5,2,4-*Trithiadiazepine* (**1**) *with Potassium t-Butoxide and Iodomethane.*—To a solution of 1,3,5,2,4-trithiadiazepine (**1**) (17 mg, 0.11 mmol) stirred in dry THF (3 ml) under nitrogen was added dropwise a solution of potassium t-butoxide (25 mg, 0.22 mmol) in dry THF (2 ml). An orange precipitate was formed as the addition proceeded. Stirring was continued for 5 min then iodomethane (5 ml) was added. The mixture was left at room temperature overnight and then the solvent and the excess of iodomethane were evaporated and the residue was dissolved in dichloromethane for application to a p.t.l.c. plate. Elution of the plate with 10% dichloromethane in light petroleum gave, as the sole product, 3,4-*bis*(*methylthio*)-1,2,5-*thiadiazole* (**4**) (10 mg, 50%) as pale cream crystals, m.p. 44—45 °C (from light petroleum) (Found: C, 26.95; H, 3.15; N, 16.0%; M^+, 177.9687 $C_4H_6N_2S_3$ requires C, 26.95; H, 3.4; N, 15.7%; M^+, 177.9693); $\lambda_{max.}$(EtOH) 260 (log ε 3.49) and 318 nm (4.02); $\nu_{max.}(CHCl_3)$ 2 930, 1 444, 1 312, 1 020, and 965 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.72 (s); δ_C (62.9 MHz; $CDCl_3$) 14.9 and 155.5; *m/z* 178 (M^+, 100%), 163 (25), 145 (38), 144 (13), 105 (63), and 90 (24).

Nitration of 1,3,5,2,4-*Trithiadiazepine* (**1**).—(a) *With nitronium tetrafluoroborate.* A solution of 1,3,5,2,4-trithiadiazepine (**1**) (44 mg, 0.29 mmol) in dry acetonitrile (5 ml) was stirred under nitrogen at −10 °C and a solution of nitronium tetrafluoroborate (45 mg, 0.34 mmol) in dry acetonitrile (2 ml), also cooled to −10 °C, was added dropwise *via* a double-ended needle. The reaction mixture was allowed to warm slowly to room temperature, and as it did so the solution gradually became pale yellow. The mixture was stirred at room temperature for a further 4 h after which the solvent was removed and the residue chromatographed on silica gel to give, on elution with 5% dichloromethane in light petroleum, 6-*nitro*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* (**7**; E = NO_2) (46 mg, 82%) as bright yellow needles, m.p. 86 °C (from light petroleum) (Found: C, 12.4; H, 0.5; N, 21.25. $C_2HN_3O_2S_3$ requires C, 12.3; H, 0.5; N, 21.5%); $\lambda_{max.}$(EtOH) 293 (log ε 4.40), and 356 nm (3.95); $\nu_{max.}(CHCl_3)$ 1 536, 1 495, 1 304vs, 1 160, and 970s cm^{-1}; $\nu_{max.}$(KBr) 595 and 405 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.81 (s); δ_C (62.9 MHz; [$^2H_6$]acetone) 135.1 and 150.9; *m/z* 195 (M^+, 100%), 149 (11), 105 (43), 103 (39), and 78 (95).

(b) *With copper*(II) *nitrate trihydrate.* 1,3,5,2,4-Trithiadiazepine (**1**) (28 mg, 0.19 mmol) was dissolved in acetic anhydride (2 ml) at 0 °C under nitrogen and an excess of powdered copper(II) nitrate trihydrate (90 mg, 0.38 mmol) was added in one portion, with stirring. Stirring was continued at 0 °C for 2 h and then ether (5 ml) and ice (2 g) were added. After 10 min the aqueous layer was separated and extracted

with ether (2 × 5 ml). The combined ether extracts were washed several times with saturated aqueous sodium hydrogen carbonate until there was no further reaction, and then with water. The resulting ethereal solution was dried ($MgSO_4$), evaporated under reduced pressure and the residue chromatographed on silica gel; elution with 5% dichloromethane in light petroleum gave 6-nitro-1,3,5,2,4-trithiadiazepine (35 mg, 94%), identical with that previously described.

6,7-*Dinitro*-1,3,5,2,4-*trithiadiazepine* (**8**).—A solution of 6-nitro-1,3,5,2,4-trithiadiazepine (107 mg, 0.55 mmol) in dry acetonitrile (2 ml) was added dropwise to a freshly prepared solution of nitronium tetrafluoroborate (366 mg, 2.75 mmol) in dry acetonitrile (1 ml) which was stirred under nitrogen at 10 °C. Stirring was continued at room temperature for 4 h after which the solvent was evaporated and the residue chromatographed on silica gel. Elution with 5% dichloromethane in light petroleum gave 6,7-*dinitro*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* (**8**) (78 mg, 59%) as bright yellow needles, m.p. 63—64 °C (from light petroleum) (Found: C, 10.4; N, 22.9. $C_2N_4O_4S_3$ requires C, 10.0; N, 23.3%); $\lambda_{max.}$(EtOH) 299 (log ε 4.28) and 384 nm (3.68); $\nu_{max.}$($CHCl_3$) 1 650vs, 1 550vs, 1 325s, 1 295s, 1 270, 1 122, 915, 892, 876, and 838 cm^{-1}; $\nu_{max.}$(KBr) 660s, 585, and 388 cm^{-1}; δ_C (62.9 MHz; $CDCl_3$) 153.6; *m/z* 240 (M^+, 66%), 148 (15), 124 (10), 118 (7), 102 (41), 92 (41), 90 (15), 87 (21), 86 (23), 80 (10), and 78 (100).

Bromination of 1,3,5,2,4-*Trithiadiazepine* (**1**).—(a) *With* N-*bromosuccinimide* (NBS). 1,3,5,2,4-Trithiadiazepine (**1**) (50 mg, 0.33 mmol) was dissolved in dry acetonitrile (4 ml) and stirred at room temperature under nitrogen. *N*-Bromosuccinimide (64 mg, 0.36 mmol) was added in one portion and stirring was continued overnight. T.l.c. analysis at this stage indicated that a small amount of starting material was still present; therefore a further portion of NBS (15 mg, 0.08 mmol) was added and stirring was continued until the reaction was complete (*ca.* 24 h). The solvent was then removed and the residue chromatographed on silica gel, eluting with light petroleum, to give the product initially as a pale yellow oil, which solidified with time, and was subsequently recrystallised from light petroleum to give 6-*bromo*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* (**7**; E = Br) (66 mg, 88%) as pale cream needles, m.p. 31—31.5 °C (Found: M^+, 227.8482. $C_2HBrN_2S_3$ requires 227.8485); $\lambda_{max.}$(cyclohexane) 225 (log ε 4.01) and 342 nm (3.70); $\nu_{max.}$($CHCl_3$) 3 003, 2 970, 1 498vs, 1 155vs, 1 000, 872, 772, 738, 680, and 655 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 7.75 (s); *m/z* 230 (M^+, 71%), 288 (M^+, 63), 184 (34), 182 (31), 138 (10), 136 (8), 124 (27), 105 (10), 103 (10), 78 (100), 57 (36), and 46 (46).

(b) *With bromine*. A solution of bromine in dry tetrachloromethane (0.38M) was added dropwise to a stirred solution of 1,3,5,2,4-trithiadiazepine (**1**) (20 mg, 0.13 mmol) in dry tetrachloromethane (1.5 ml) under nitrogen until all the starting material was consumed (t.l.c.). Approximately 1 ml of the bromine solution was added over 1.5 h. Stirring was continued for a further 30 min, then the solvent was evaporated and the residue chromatographed on silica gel. Elution with light petroleum gave 6-bromo-1,3,5,2,4-trithiadiazepine (10 mg, 32%), identical with that previously described.

6,7-*Dibromo*-1,3,5,2,4-*trithiadiazepine*.—1,3,5,2,4-Trithiadiazepine (**1**) (173 mg, 1.15 mmol) was stirred at room temperature under nitrogen in dry acetonitrile (20 ml). NBS (0.82 g, 4.6 mmol) was added in one portion and stirring was continued for 20 h. T.l.c. analysis indicated a significant amount of monobrominated material was still present. Further portions of NBS (0.1 g each) were added at intervals of *ca.* 8 h, until all the monobromide had been consumed and only one product was observed by t.l.c.; in total a further 1.4 g (7.8 mmol) of NBS was required. The solvent was removed and the residue chromatographed on silica gel, eluting with light petroleum, to give 6,7-*dibromo*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* (272 mg, 77%) as pale cream crystals, m.p. 88—89 °C (from light petroleum) (Found: C, 7.95; N, 8.95. $C_2Br_2N_2S_3$ requires C, 7.8; N, 9.1%); $\lambda_{max.}$(cyclohexane) 238 (log ε 3.50) and 347 nm (3.21); $\nu_{max.}$($CHCl_3$) 2 910, 2 850, 1 590, 1 455, and 1 145 cm^{-1}; δ_C (62.9 MHz; $CDCl_3$) 115.7; *m/z* 306 (M^+, 19%), 308 (M^+, 41%), 310 (M^+, 23%), 262 (33), 216 (7), 184 (3), 137 (18), 135 (17), 125 (11), 124 (34), 123 (10), 102 (27), 88 (15), and 78 (100).

Nitration of 6-*Bromo*-1,3,5,2,4-*trithiadiazepine*.—(a) *With nitronium tetrafluoroborate*. 6-Bromo-1,3,5,2,3-trithiadiazepine (32 mg, 0.14 mmol) was dissolved in dry acetonitrile (2 ml) and stirred under nitrogen at −20 °C. A solution of nitronium tetrafluoroborate (18 mg, 0.14 mmol) in dry acetonitrile (0.25 ml) was added and the mixture was allowed to warm slowly to room temperature. After being stirred for 2 h at room temperature a considerable amount of starting material was still present (t.l.c.). The solution was therefore recooled to −20 °C and a further portion of nitronium tetrafluoroborate (18 mg, 0.14 mmol) in dry acetonitrile (0.25 ml) was added. Stirring at room temperature was continued for 2 h after which the solvent was evaporated and the residue chromatographed on silica gel. Elution with light petroleum gave 6-*bromo*-7-*nitro*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* (7 mg, 16%) as a yellow oil (Found: M^+, 272.8331. $C_2BrN_3O_2S_3$ requires 272.8336); $\lambda_{max.}$(EtOH) 227, 287, and 348 nm; *m/z* 275 (M^+, 46%), 273 (M^+, 43%), 229 (12), 227 (8), 175 (24), 173 (33), 137 (15), 135 (13), 125 (17), 123 (18), 102 (96), and 78 (100).

(b) *With copper*(II) *nitrate trihydrate*. 6-Bromo-1,3,5,2,4-trithiadiazepine (55 mg, 0.24 mmol) was dissolved in acetic anhydride (5 ml) and stirred at 0 °C under nitrogen; copper(II) nitrate trihydrate (116 mg, 0.48 mmol) was then added in one portion. The reaction mixture was stirred at room temperature for 5 days and then ether (15 ml) and ice (5 g) were added. After a further 30 min the aqueous layer was separated and extracted twice more with ether (15 ml). The combined ether extracts were washed several times with saturated sodium hydrogen carbonate until there was no further reaction, and then with water, and dried ($MgSO_4$). The ether was evaporated under reduced pressure and the residue applied to a preparative t.l.c. plate. Elution of the plate twice, with 5% dichloromethane in light petroleum, gave 6-bromo-1,3,5,2,4-trithiadiazepine (21 mg, 39% recovery) and the slightly more polar 6-bromo-7-nitro-1,3,5,2,4-trithiadiazepine (5 mg, 7%), identical with that described earlier.

Thermolysis of 1,3,5,2,4-*Benzotrithiadiazepine* (**2**).—1,3,5,2,4-Benzotrithiadiazepine (**2**) (12 mg) was heated at reflux temperature (137—140 °C) in dry xylene (3 ml) for 32 h, after which time t.l.c. analysis indicated that a substantial amount of starting material was still present. Heating was continued for a further 45 h, after which time only a trace of starting material remained. Decomposition had occurred to give sulphur and three other, more polar, products which could not be identified, together with baseline material. Comparative t.l.c. indicated that 2,1,3-benzothiadiazole was not a product of this reaction. When the thermolysis was repeated in decalin (decahydronaphthalene) at reflux temperature (193 °C) 1,3,5,2,4-benzotrithiadiazepine was completely decomposed within 2 h.

Photolysis of 1,3,5,2,4-*Benzotrithiadiazepine* (**2**).—1,3,5,2,4-Benzotrithiadiazepine (**2**) (16 mg) was dissolved in light petroleum (b.p. 60—80 °C) (50 ml) under nitrogen and irradiated at 300 nm in a Rayonet Photochemical Reactor. A flocculent yellow precipitate was formed as irradiation proceeded. After 1 h all the starting material had been consumed.

Elemental sulphur and the yellow precipitate, which was not identified, were the only products. A similar result was obtained when the photolysis was carried out at 350 nm.

Treatment of 1,3,5,2,4-*Benzotrithiadiazepine* (**2**) *with Triphenylphosphine.*—1,3,5,2,4-Benzotrithiadiazepine (**2**) (10 mg, 0.05 mmol) was dissolved in light petroleum (b.p. 60—80 °C) (3 ml) and a solution of triphenylphosphine (14 mg, 0.05 mmol) was added dropwise, with stirring. As the addition proceeded the bright yellow colour of 1,3,5,2,4-benzotrithiadiazepine rapidly faded to give a colourless solution and an orange precipitate. T.l.c. analysis of the solution showed that all the trithiadiazepine had been consumed to give baseline products only. The orange precipitate, m.p. 85—95 °C, was not identified.

Treatment of 1,3,5,2,4-*Benzotrithiadiazepine* (**2**) *with* m-*Chloroperbenzoic acid.*—A solution of 1,3,5,2,4-benzotrithiadiazepine (**2**) (10 mg, 0.05 mmol) in dichloromethane (2 ml) was stirred under nitrogen and a solution of *m*-chloroperbenzoic acid (9 mg, 0.05 mmol) in dichloromethane (1 ml) was added dropwise at room temperature. The solution rapidly changed colour from bright yellow to deep orange/red. Stirring was continued for 1 h, when analysis by t.l.c. indicated that most of the starting trithiadiazepine had been consumed to give baseline products only.

Nitration of 1,3,5,2,4-*Benzotrithiadiazepine* (**2**).—(a) *With nitronium tetrafluoroborate.* A solution of 1,3,5,2,4-benzotrithiadiazepine (**2**) (40 mg, 0.2 mmol) in dry acetonitrile (5 ml) was stirred at −30 °C under nitrogen and a solution of nitronium tetrafluoroborate (27 mg, 0.2 mmol) in dry acetonitrile (2 ml), also cooled to −30 °C under nitrogen, was added dropwise *via* a double-ended needle. The reaction mixture became dark green with the formation of a dark green precipitate. The mixture was allowed to warm slowly to room temperature and then stirred overnight. During this time the green colour disappeared and gave rise to a yellow solution and an orange precipitate. The solvent was evaporated and the residue chromatographed on silica gel to give, on elution with light petroleum, firstly 1,3,5,2,4-benzotrithiadiazepine (**2**) (1 mg, 2% recovery), then 7-*nitro*-1,3$\lambda^4\delta^2$,5,2,4-*benzotrithiadiazepine* (3 mg, 6%) as a yellow solid, m.p. 170—172 °C (Found: M^+, 244.9392. $C_6H_3N_3O_2S_3$ requires 244.9387); $\lambda_{max.}$(EtOH) 220, 294, and 332 nm; $\nu_{max.}$($CHCl_3$) 1 340 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 7.95 (1 H, dd, *J* 0.7 and 9.6 Hz), 8.12 (1 H, dd, *J* 2.0 and 9.6 Hz), and 8.81 (1 H, dd, *J* 0.7 and 2.0 Hz); *m/z* 245 (M^+, 52%), 199 (26), 183 (6), 169 (6), 153 (51), 149 (12), 111 (19), 97 (29), 85 (43), 71 (63), and 57 (100).

(b) *With copper*(II) *nitrate.* 1,3,5,2,4-Benzotrithiadiazepine (**2**) (26 mg, 0.13 mmol) was dissolved in acetic anhydride (2 ml) at 0 °C under nitrogen and powdered copper(II) nitrate trihydrate (32 mg, 0.13 mmol) was added in one portion, with stirring. Stirring was continued at 0 °C for 2 h and then ether (5 ml) and ice (2 g) were added. After 10 min the aqueous layer was separated and extracted twice with ether (5 ml). The combined ether extracts were washed several times with saturated aqueous sodium hydrogen carbonate until there was no further reaction, and then with water. The resulting ethereal solution was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was dissolved in light petroleum and filtered through silica gel to give a quantitative recovery of 1,3,5,2,4-benzotrithiadiazepine (**2**).

The reaction with copper(II) nitrate trihydrate was repeated exactly as described above, except that it was carried out at room temperature and the reaction mixture was stirred for 17 h before the addition of ether and ice. The residue, after evaporation of the ether, was chromatographed on silica gel; elution with 5% dichloromethane in light petroleum gave 7-nitro-1,3,5,2,4-benzotrithiadiazepine (5 mg, 15%), identical with that previously described. All of the starting material had been consumed; thus 85% had undergone decomposition to give baseline products only.

Attempted Bromination of 1,3,5,2,4-*Benzotrithiadiazepine* (**2**).—(a) *With* N-*bromosuccinimide.* 1,3,5,2,4-Benzotrithiadiazepine (**2**) (38 mg, 0.19 mmol) was dissolved in dry acetonitrile (4 ml) and stirred at room temperature under nitrogen. *N*-Bromosuccinimide (38 mg, 0.21 mmol) was added in one portion and stirring was continued overnight. T.l.c. analysis of the resulting deep red solution indicated that all the starting material had been consumed. No identifiable products could be isolated from the reaction mixture.

(b) *With bromine.* 1,3,5,2,4-Benzotrithiadiazepine (**2**) (30 mg, 0.15 mmol) was dissolved in dry dichloromethane (15 ml) and a solution of bromine in dry dichloromethane (0.033M; 5 ml, 0.17 mmol Br_2) was added with stirring, under nitrogen in the dark. The mixture was set aside in the dark at room temperature for 24 h. The dark red dichloromethane solution was then decanted from the residue in the flask and the residue was washed several times with dichloromethane (until the washings were almost colourless). The combined dichloromethane solutions were evaporated and the residue was recrystallised from methanol to give dark red crystals which were shown by *X*-ray crystallography [7] to be *bis*-(1,3,2-*benzodithiazolium*) *bromide tribromide* (**11**) (26 mg, 56%), m.p. 218—222 °C; the same sample after being dried *in vacuo* for 3 days at room temperature had an analysis consistent with its formulation as 1,3,2-*benzodithiazolium bromide* (**12**) (Found: C, 30.6; H, 1.65; N, 6.0. $C_6H_4BrNS_2$ requires C, 30.75; H, 1.7; N, 6.0%); $\lambda_{max.}$(EtOH) 248 (log ε 4.79), 330 (4.23), and 392 nm (4.05); $\nu_{max.}$(KBr) 1 428, 1 312, 930, 735s, 438, and 390 cm^{-1}; δ_H (250 MHz; D_2O) 7.03 (2 H, m, BB′ protons) and 7.94 (2 H, m, AA′ protons); *m/z* (f.a.b.) 154 (M^+, 67%), 140 (14), and 115 (100).

Acknowledgements

We thanks the S.E.R.C. for a studentship (J. L. M.). Dr. D. J. Williams and Mr. R. Jones for the *X*-ray crystallographic results referred to, and Mr. D. J. Rigg for invaluable experimental assistance.

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Received 18th April 1986; *Paper* 6/749