Organic Heterocyclothiazenes. Part 1. The Trithiadiazepine and Trithiatriazepine Ring Systems

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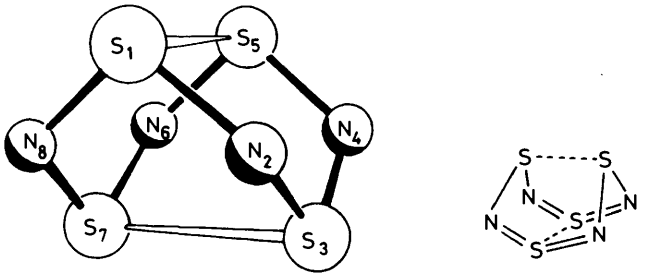
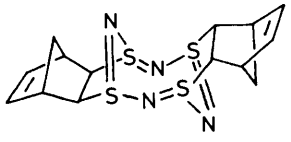
Reaction of S_4N_4 with dimethyl acetylenedicarboxylate in boiling toluene has been found to give dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**) as the major product, together with the rearranged dimethyl 1,2,4-thiadiazole-3,5-dicarboxylate (**4**), dimethyl 1,3$\lambda^4\delta^2$,5,2,4-trithiadiazepine-6,7-dicarboxylate (**7**), and methyl 1,3$\lambda^4\delta^2$,5,2,4,6-trithiatriazepine-7-carboxylate (**8**). The two seven-membered rings are new stable planar delocalised 10π electron aromatic systems. Mechanisms involving cycloaddition, rearrangement, and ring cleavage are proposed for the formation of the products.

Introduction to the Series.—This series of papers describes the chemistry of some novel ring systems, consisting mostly of sulphur and nitrogen but with at least one ring carbon, which thus lie at the borderline between inorganic and organic heterocyclic chemistry. The sulphur and nitrogen atoms are mostly two-co-ordinate and alternate around the rings, which are consequently electron-rich (π-excessive). The chemistry of closely related wholly inorganic cyclothiazenes has been very extensively studied and reviewed,[1] and it is now hoped to extend this into the organic domain by the presence of ring carbon and its associated substituents.



(1)

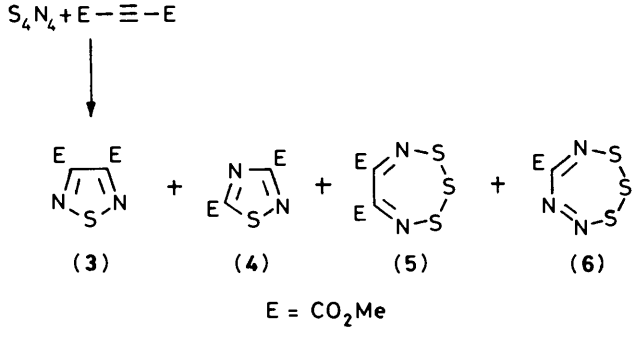
The starting point for the work was the organic chemistry of the intriguing compound tetrasulphur tetranitride (**1**), the best known of a whole family of sulphur nitrides and one of the most studied of all inorganic heterocyclic compounds. The atoms of S_4N_4 form a stable cage structure with the four nitrogen atoms in a square plane bisecting a tetrahedron of sulphur atoms, two above and two below the plane (**1**). The 12 π-electrons are completely delocalised, all the S–N bonds being of equal length and of intermediate bond order, and with substantial transannular bonding between adjacent pairs of sulphur atoms. Tetrasulphur tetranitride has a rich and varied inorganic chemistry, undergoing dissociation and addition reactions, oxidations and reductions, and reactions with electrophiles and nucleophiles and with Lewis acids and bases. So it is not surprising that there have been several investigations of its reactions with organic substrates, as potential routes to organic compounds rich in sulphur and nitrogen (see, *e.g.* references 2—5). But we believe that the scope of these reactions has not been fully appreciated, largely because their mechanisms are so poorly understood. The reactions usually give several diverse and unpredictable products in low yields, almost the only exceptions being the formation of 1:2 cycloadducts [*e.g.* (**2**)] from S_4N_4 and highly strained alkenes such as norbornadiene,[2] and of 1,2,5-thiadiazoles [*e.g.* (**3**)] from S_4N_4 and alkynes [3] or α-methylene ketones.[4]



(2)

The aims of the present work are to exploit the cycloaddition reactions of S_4N_4 and related species as practical routes to organic compounds rich in sulphur and nitrogen, to uncover the mechanisms of these reactions, and in the longer term to apply the new chemistry to modify the structure of the conducting polymer poly(sulphur nitride), $(SN)_x$,[6] to give more stable and useful conductors and superconductors.

Trithiadiazepines and Trithiatriazepines.—Our initial search for structurally new polyhetero atom species readily derived from S_4N_4, led us to reinvestigate [7] the reaction between S_4N_4 and dimethyl acetylenedicarboxylate (DMAD) in boiling toluene.[3] Four products had been reported for this reaction (Scheme 1): dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**) (60%), dimethyl 1,2,4-thiadiazole-3,5-dicarboxylate (**4**) (8%), and two other minor compounds (*ca.* 5%) with more of the S_4N_4 structure retained which were assigned structures (**5**) and (**6**).[3] Compounds (**4**) and (**6**) were interesting mechanistically

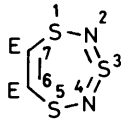


(3) (4) (5) (6)

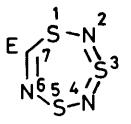
Scheme 1.

since their formation requires the DMAD to be cleaved at the triple bond; but more importantly the two trisulphide structures (**5**) and (**6**) did not seem to fit the thermal stability and the spectral data reported for them. We obtained the same four compounds in yields similar to those reported.[3] We confirm the thiadiazole structure (**3**) and (**4**) but not structures (**5**) and (**6**). For the latter compounds the u.v. spectra indicate highly

delocalised structures, the i.r. spectra do not show C=N absorptions, and the mass spectral fragmentation pattern suggests the presence of a C–S rather than C–N bonds in (**5**), and (**6**) shows no loss of N_2 or S. The structures of these products were solved by *X*-ray diffraction analysis and shown to be dimethyl 1,3$\lambda^4\delta^2$,-5,2,4-trithiadiazepine-6,7-dicarboxylate (**7**) and methyl 1,3$\lambda^4\delta^2$,5,2,4,6-trithiatriazepine-7-carboxylate (**8**) respectively.[7]

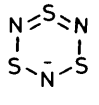


(**7**)

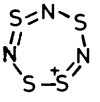


(**8**)

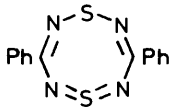
Both seven-membered rings are planar with maximum deviation from the least squares plane of 0.019 Å [C(6) in (**7**)] and 0.009 Å [N(6) in (**8**)]. Each ring has 10 electrons available to form a π system delocalised over the 7 atoms, and further evidence for delocalisation came from the long wavelength u.v. absorptions at 334 and 332 nm, respectively, and from the measured bond lengths which are intermediate between single and double bonds. The delocalised 10π aromatic nature of the rings was supported by their thermal and chemical stability, and by MNDO and *ab initio* MO calculations on the parent trithiadiazepine and trithiatriazepine.[8] These new ring systems are thus isoelectronic with cycloheptatrienyl trianion[9] and are comparable to the trisulphur trinitride anion, $S_3N_3^-$ (**9**),[10] the thiotrithiazyl cation, $S_4N_3^+$ (**10**),[11] and a related eight-membered ring compound, diphenyl dithiatetrazocine (**11**),[12] all of which are delocalised 10π aromatic systems. Indeed, the thermal and chemical stability of the organic compounds (**7**), (**8**), and (**11**) are very similar.



(**9**)

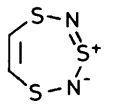


(**10**)

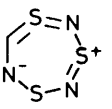


(**11**)

Compounds (**7**) and (**8**), like (**11**) but in contrast to S_4N_4, showed no decomposition on boiling in xylene (140 °C) for 24 h. In boiling decalin (decahydronaphthalene) (190 °C) the trithiadiazepine (**7**) was decomposed in 6 h, whilst some of the trithiatriazepine (**8**) still remained after 33 h. Both compounds were decomposed by irradiation at 300 nm in light petroleum, in rather complex reactions. The former gave sulphur and thiadiazole (**3**) whilst the latter gave sulphur and S_4N_4 as the only identified products; again the trithiatriazepine (**8**) decomposed significantly more slowly. Both compounds were strikingly inert towards *m*-chloroperbenzoic acid in boiling dichloromethane. Triazepine (**8**) was also inert to triphenylphosphine in boiling toluene, whilst the diazepine (**7**) was slowly decomposed under these conditions. This difference in stability and reactivity between compounds (**7**) and (**8**) is understandable if dipolar structures like (**12**) and (**13**) make significant contributions, since the trithiatriazepine ring has an extra nitrogen atom to bear the negative charge. The MO calculation[8] mentioned showed the two rings to be very similar, planar, [10]annulenes with bond lengths and angles in good agreement with the experimental values; the calculated charge distributions showed the importance of dipolar structures like (**12**) and (**13**) and reflected the greater contribution of structures with negative charge at position 6 when this was occupied by nitrogen rather than carbon. It is interesting to note that in spite of the extra heteroatoms the seven-membered ring compounds are less polar, as judged by their solubilities and R_F values, than the 1,2,4- and 1,2,5-thiadiazoles.



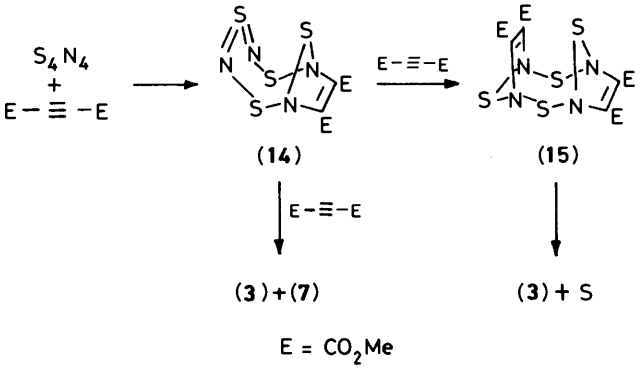
(**12**)



(**13**)

With 10π electrons delocalised over seven atoms, the rings of (**7**) and (**8**) are electron-rich and are presumably stabilised by the ester groups. It was thus of interest to determine the stability of the parent compounds and to see if their chemical properties generally were akin to the those of simpler aromatic species. Hydrolysis of the diester (**7**) proved unexpectedly difficult, however, and since it was only available in low yield from the S_4N_4 reaction, an alternative, more rational, synthesis of the ring system was required; this is described in Part 3 of this series.

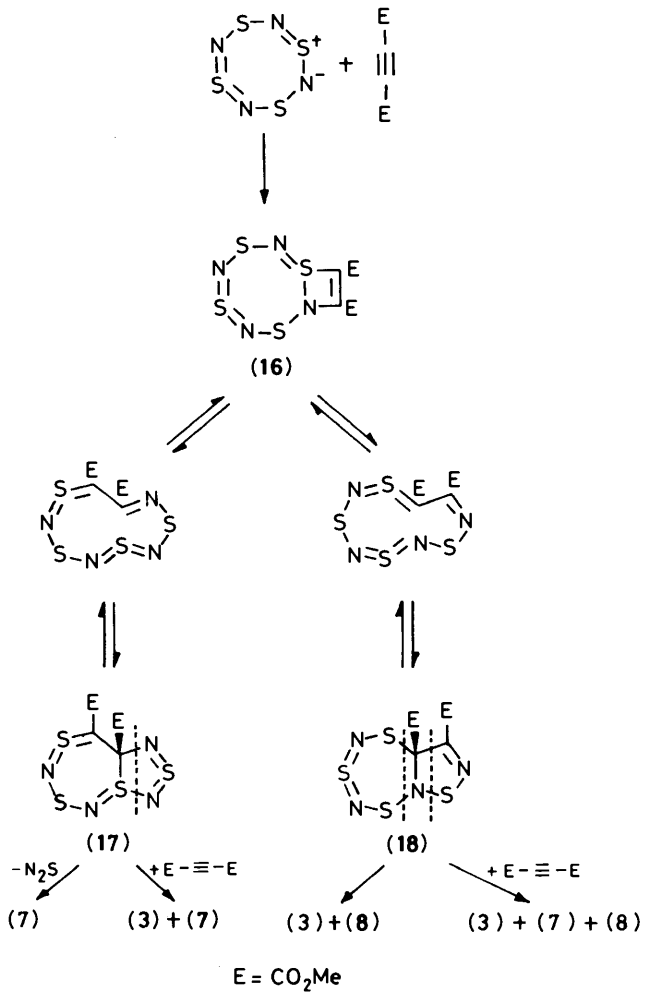
Reaction Mechanisms.—At present, mechanisms proposed for the formation of the four products from the S_4N_4–DMAD reaction are somewhat speculative, but serve as a basis for further experimentation. It is assumed that S_4N_4 itself, rather than any dissociation product, is the species reacting with DMAD in boiling toluene. It is known, from the structure of the 1:2 adducts [*e.g.* (**2**)] rapidly formed from S_4N_4 and strained alkenes, like norbornadiene,[2] that these cycloadditions occur across S(1)–S(3) and S(5)–S(7). The initial site of attack of triple bonds is not known, but formation of the major products, 3,4-disubstitued 1,2,5-thiadiazoles, is most simply explained (Scheme 2) by direct cycloaddition across N(2)—N(4) and



Scheme 2.

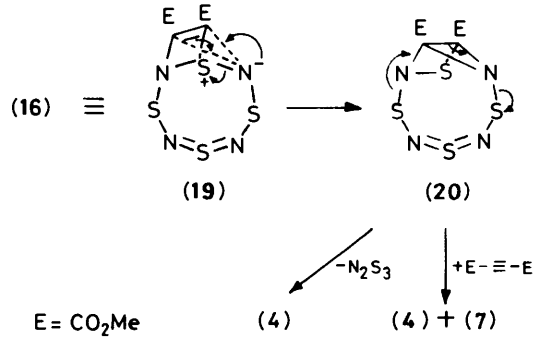
N(6)—N(8) to give, for example, (**14**) and then (**15**); the latter could readily extrude sulphur to give the very stable 1,2,5-thiadiazole (**3**). The high yields of 1,2,5-thiadiazoles sometimes observed require the formation of more than 1 mole of thiadiazole from 1 mole of S_4N_4, indicating the possible participation of 1:2 adducts like (**15**). The 1:1 adduct (**14**) could also react with a second mole of DMAD across S(1)—S(5), to give 1 mole of 1,2,5-thiadiazole (**3**) and 1 mole of trithiadiazepine (**7**) (Scheme 2).

Formation of the trithiatriazepine (**8**) requires a more complex pathway. A concise route to it is shown in Scheme 3; with slight modification this route also leads to the trithiadiazepine (**7**) and the thiadiazole (**3**). This involves initial, probably stepwise, [2 + 2]cycloaddition of DMAD to S_4N_4 to give (**16**) followed by opening of the four-membered ring; this is closely analogous to the reaction of DMAD with sulphimides.[13] Collapse of the 10-membered ring, so formed, to the 5,7-bicyclic systems (**17**) and (**18**) is finally followed by ring cleavage. This cleavage could be a spontaneous retro-cycloaddition, to give the very stable aromatic products, or it could result from reaction of (**17**) or (**18**) with a second mole of DMAD. The spontaneous



Scheme 3.

retro-cycloaddition of (**17**) or (**18**) would give trithiadiazepine (**7**) or thiadiazole (**3**) and trithiatriazepine (**8**), respectively. On further reaction with DMAD, (**17**) and (**18**) could both give products (**3**) and (**7**).



Scheme 4.

Formation of the 1,2,4-thiadiazole (**4**), in which all the DMAD structure has been retained but separated in half, requires a more deep-seated rearrangement. One possibility (Scheme 4) based on the same initial [2 + 2]cycloaddition involves rearrangement [arrows in (**19**)] of the intermediate (**16**) to the tricyclic species (**20**). Extrusion of S_3N_2 from (**20**), which again could be facilitated by further reaction with DMAD, accompanied by an aromatising rearrangement [arrows in (**20**)] would give thiadiazole (**4**). A somewhat similar rearrangement can be also written for transformation of the initial 1,3-dipolar cycloaddition adduct (**14**) into thiadiazole (**4**). With so many cycloaddition, rearrangement, and retro-cycloaddition pathways available in these S_4N_4 reactions, it is hardly surprising that several products are usually observed. We are now attempting to delimit these mechanistic possibilities and to increase the product selectivity.

Experimental

Light petroleum refers to the fraction b.p. 60—80 °C; it was redistilled before use. Benzene and toluene were dried over sodium wire and redistilled. Tetrasulphur tetranitride was prepared by the method of Jolly,[14] following the recommendations of Banister;[15] it is sensitive to heat and shock and was *handled with care*. Chromatography was carried out on Merck silica gel 60 H at medium pressure (hand bellows). I.r. spectra were recorded on a Perkin-Elmer 298 spectrophotometer and u.v. spectra were recorded on a Pye-Unicam SP800B recording spectrophotometer. ^{1}H N.m.r. spectra were recorded at 90 MHz on a Perkin-Elmer R32 instrument and ^{13}C n.m.r. were recorded on a Bruker WM250 instrument at 62.9 MHz. Mass spectra were recorded on a VG Micromass 7070B spectrometer operating at 70 eV using a direct insertion probe. Photochemical reactions were performed in a Rayonet photochemical reactor in quartz vessels under a stream of dry nitrogen. M.p.s. were determined on a Kofler hot stage apparatus and are uncorrected.

Reaction of Tetrasulphur Tetranitride with Dimethyl Acetylenedicarboxylate.—A solution of tetrasulphur tetranitride (0.46 g, 2.5 mmol) and DMAD (0.61 ml, 5.0 mmol) in toluene (20 ml) was heated at reflux for 6 h, after which time all the S_4N_4 had been consumed (t.l.c.). The solvent was evaporated and the residue chromatographed on silica gel (20 g). Elution with light petroleum gave sulphur; elution with light petroleum–chloroform (9:1) gave *methyl* 1,3$\lambda^4\delta^2$,5,2,4,6-*trithiatriazepine*-7-*carboxylate* (**8**) (0.073 g, 14%) as colourless crystals, m.p. 81—83 °C (from light petroleum) (lit.,[3] 82—83 °C); $\lambda_{max.}$(EtOH) 266 (log ε 4.09) and 332 nm (3.40); $\nu_{max.}$(KBr disc) 1 740, 1 698, 1 440, 1 290, 1 157, 1 050, 980, 895, 750, 380, and 305; δ_H(90 MHz; CCl_4) 3.85(s); δ_C(62.9 MHz; $CDCl_3$) 53.7, 151.3, and 161.9; *m/z* 209 (M^+), 124, 78, 59, and 46. Elution with light petroleum–chloroform (4:1) gave *dimethyl* 1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine*-6,7-*dicarboxylate* (**7**) (0.032 g, 5%) as colourless needles, m.p. 72—74 °C (from light petroleum) (lit.,[3] 73.5—74 °C); $\lambda_{max.}$ (EtOH) 274 (log ε 4.26) and 334 nm (3.56); $\nu_{max.}$(KBr disc) 2 980, 1 725, 1 710, 1 478, 1 430, 1 260—1 160, 1 065, 990, 890, 878, 750, 720, 670, 619, 600, 388, and 272; δ_H(90 MHz); $CDCl_3$) 3.98 (s); δ_C(62.9 MHz; $CDCl_3$) 54.1, 140.9, and 162.7; *m/z* 266 (M^+), 235, 220, 124, 103, 78, 59, and 46. Elution with light petroleum–chloroform (1:1) gave dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**) (0.68 g, 67%) as an oil, b.p. 86—88 °C at 0.15 mmHg (lit.,[3] b.p. 111 °C at 0.3 mmHg), and elution with light petroleum–chloroform (1:3) gave dimethyl 1,2,4-thiadiazole-3,5-dicarboxylate (**4**) (0.03 g, 3%) as needles, m.p. 89—90 °C (from light petroleum) (lit.,[3] 89—90 °C) both of which had spectroscopic properties in agreement with the literature.[3]

The reaction of S_4N_4 with DMAD was repeated under various conditions, in benzene, as well as in toluene, with varying initial ratios of the two reactions, and in the presence of aluminium trichloride; there were no major changes in the product yields.

Thermolyses.—The trithiadiazepine (**7**) and the trithiatriazepine (**8**) showed no decomposition (t.l.c.) on boiling in xylene under nitrogen for 24 h. On heating in boiling decalin under nitrogen for 6 h the trithiadiazepine (**7**) decomposed to (at least) three products (t.l.c.) one of which was dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**); under the same conditions the trithiatriazepine (**8**) had partially decomposed after 33 h, but some starting material remained (t.l.c.).

Photolyses.—Trithiadiazepine (**7**) (22 mg) in light petroleum (40 ml) was irradiated at 300 nm for 1.66 h. The solvent was removed and the oily residue was chromatographed (p.l.c., silica gel) to give sulphur (4.6 mg) and dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**) (8.5 mg, 50%). Trithiatriazepine (**8**) (21 mg) in light petroleum (40 ml) was similarly irradiated for 4.16 h. Similar work-up gave sulphur (5.4 mg) and tetrasulphur tetranitride (1.2 mg, 12%).

Reaction with triphenylphosphine.—Trithiadiazepine (**7**) (33 mg) and triphenylphosphine (38 mg) were heated at reflux in toluene under nitrogen for 3 h. Compound (**7**) remained but all the triphenylphosphine had been consumed (t.l.c.). More triphenylphosphine (68 mg) was added and the heating continued for a further 12 h. Only a trace of compound (**7**) remained and at least four new products were present (t.l.c.). Trithiatriazepine (**8**) (27 mg) and triphenylphosphine (36 mg) were similarly heated for 57 h; negligible change occurred (t.l.c.).

Acknowledgements

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