Organic Heterocyclothiazenes. Part 6.[1] Improved Synthesis of Trithiadiazepines from Tetrasulphur Tetranitride and Alkynes

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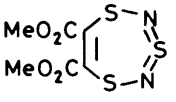
In the reaction of tetrasulphur tetranitride, S_4N_4, with alkynes to give 1,3,5,2,4-trithiadiazepines, 1,3,5,2,4,6-trithiatriazepines, and 1,2,4- and 1,2,5-thiadiazoles, the yields of trithiadiazepines are often greatly improved (up to 8-fold) by the presence of Lewis acids, particularly titanium(IV) chloride. Thus the yield of dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (**1**) from dimethyl acetylenedicarboxylate (DMAD) is increased from 5 to 40%, formation of the trithiatriazepine (**2**) being totally suppressed. Trithiadiazepine formation is also much enhanced (up to 5-fold) at higher reaction temperatures (150—160 °C) than previously used (80—110 °C), though it varies very little with solvent polarity.

We saw in Part 5[1] that alkynes with two strongly electron-withdrawing groups on the triple bond reacted with tetrasulphur tetranitride, S_4N_4, to give trithiadiazepines in good yield. Since relatively few such alkynes are readily available there is still a need to be able to divert the reaction of S_4N_4 with alkynes in general away from the formation of five- to the formation of seven-membered heterocyclic rings. One possible approach to this would be to disrupt the tight S_4N_4 cage structure to give more reactive species which could undergo different cycloaddition reactions with alkynes. This might be done by (i) conducting the reactions at higher temperatures where the S_4N_4 is extensively dissociated; (ii) replacing S_4N_4 by its cycloaddition adducts with strained alkenes like norbornadiene; or (iii) replacing S_4N_4 by its Lewis acid adducts.

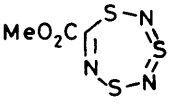
We have now explored all of these possibilities and found the first and third approaches to be successful.

Results and Discussion

Higher Temperature Reactions.—The usual conditions for S_4N_4–alkyne reactions involve heating at reflux in toluene (110 °C) for 6 h.[2,3] We have shown[3] that with dimethyl acetylenedicarboxylate (DMAD) the major products are compounds (**1**)—(**4**), formed in the yields shown in Table 1.



(**1**)



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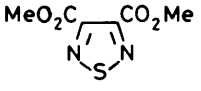

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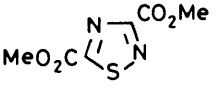
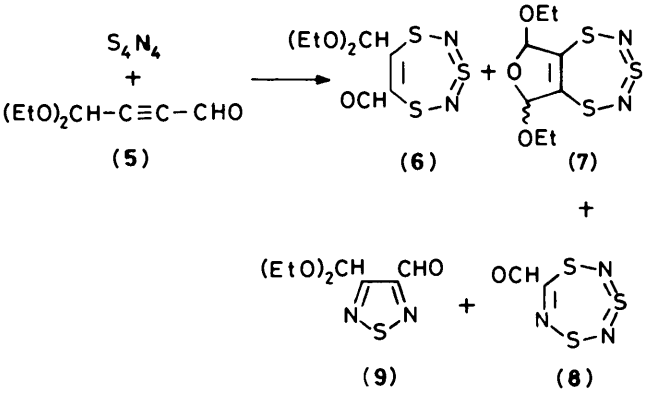


(**4**)

For higher temperature reactions we chose bromobenzene as solvent since at its boiling point (156 °C) S_4N_4 should, by comparison with gas phase data,[4a] be extensively dissociated, with all its fragmentation products, S_4N_2, S_3N_3, and S_2N_2, present; it is completely decomposed at about 185 °C. When DMAD was added to S_4N_4 in boiling bromobenzene the yield of dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (1) increased almost four-fold (Table 1, entry 2) at the expense of the other products. When S_4N_4 was added to DMAD in boiling bromobenzene the yield of compound (**1**) increased five-fold (Table 1, entry 3); this order of addition was usually better and became our standard procedure for thermally stable alkynes. For less stable alkynes, the two reactants were added synchronously to boiling bromobenzene. The 23% yield of compound (**1**) was much higher than previously observed[2,3] and now provides an acceptable source of the trithiadiazepine ring system.

A very similar improvement in trithiadiazepine yield at the higher temperature was observed in the reaction of S_4N_4 with 4,4-diethoxybut-2-ynal (**5**) (Table 2). In boiling toluene this reaction gave the trithiadiazepine (**6**), the trithiatriazepine (**8**),



(**5**) (**6**) (**7**)

(**9**) (**8**)

the 1,2,5-thiadiazole (**9**), and an isomer of (**9**), probably a 1,2,3-thiadiazole. The trithiatriazepine (**8**) was identical with a minor product of the reaction of S_4N_4 with ethyl 3-formylpropynoate.[1]

In boiling bromobenzene the same products were formed together with a 1:1 mixture of two other trithiadiazepines (**7**), the cyclic isomers of (**6**). Thus the combined yield of trithiadiazepines increased four-fold as the reaction temperature was raised from 110 to 156 °C (Table 2). The structures of the products were assigned by comparison of their spectroscopic properties (see Experimental section) with those of authentic trithiadiazepines, trithiatriazepines, and thiadiazoles,[1,3,5] and on the basis of their chemical transformations. The diethoxydihydrofurans (**7**) were probably formed from the formyl acetal (**6**) in the S_4N_4 reaction; attempted acidic hydrolysis of acetal (**6**) to the trithiadiazepine dialdehyde gave exclusively the isomers (**7**) in up to 95% yield. However, hydrolysis of the formyl acetal (**9**) with aqueous sulphuric acid on silica was normal to give 1,2,5-thiadiazole-3,4-dicarbaldehyde[1] (81%).

Table 1. Reaction of S_4N_4 with DMAD; percentage yield of products

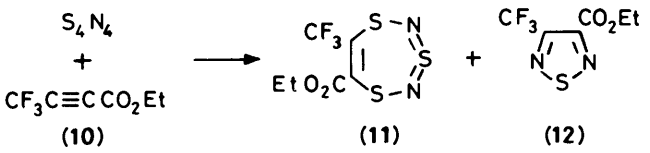
	Solvent	Temp (°C)	Time (h)	(1)	(2)	(3)	(4)
1	PhMe	110	6	5	14	60	8[b]
2	PhBr[a]	156	1	19	Trace	45	Trace[c]
3	PhBr[a]	156	1	23	5	47	3[c]

[a] See text for conditions. [b] Refs. 2 and 3. [c] This work.

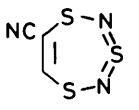
Table 2. Reaction of S_4N_4 with (5); percentage yield of products

Solvent	Temp. (°C)	Time (h)	(6)	(7)	(8)	(9)
PhMe	110	8	6	0	3	30
PhBr	156	2.5	18	6	3	25

The next alkyne investigated, ethyl 4,4,4-trifluorobut-2-ynoate (**10**), is very volatile (b.p. 96—98 °C) and the S_4N_4 reactions were conducted in sealed glass tubes in dichloromethane heated rapidly to 120 and to 150 °C. The reactions very cleanly gave the trithiadiazepine (**11**) and the 1,2,5-thiadiazole (**12**) only; the yields were, respectively, 4 and 55% at 120 °C, and 10 and 57% at 150 °C. Again the higher reaction temperature favoured trithiadiazepine formation though to a smaller but still significant extent, although there was no reduction in the thiadiazole yield.



(10) (11) (12)

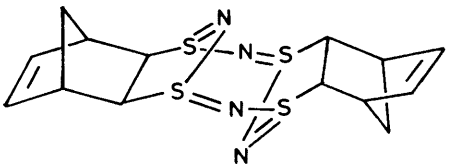


(13)

A similar improvement in trithiadiazepine formation was observed with monocyanoacetylene which gave 1,3,5,2,4-trithiadiazepine-6-carbonitrile (**13**). This alkyne is very susceptible to polymerisation, especially anionic,[6] and 8—10 equiv. were needed to consume all the S_4N_4. Concentrated solutions of the reactants (in toluene, sealed tubes) had to be heated rapidly to the desired temperature to prevent extensive polymerisation, and even then the reactions were complex and gave a large number of minor products from which only the trithiadiazepine (**13**) could be isolated pure. 1,2,5-Thiadiazole-3-carbonitrile was not detected, though this would be very volatile and easily lost during the necessary chromatographic separation. The yield of trithiadiazepine increased steadily with temperature, being 0, 5, and 10% at 100, 125, and 140 °C, respectively. These yields are in striking contrast with the high values obtained for dicyanoacetylene, with its two electron-withdrawing groups.[1] Bis(pentane-2,4-dionato)nickel(II), which has been shown to catalyse reactions of the cyano group in acyl cyanides, presumably by co-ordination with the nitrogen atom,[7] had no effect on the reaction between monocyanoacetylene and S_4N_4 at 140 °C.

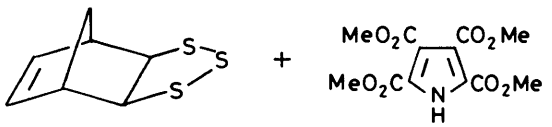
Since the yield of dimethyl trithiadiazepine-6,7-dicarboxylate (**1**) was much improved when the S_4N_4–DMAD reaction was run in boiling bromobenzene, it was hoped that the analogous di-t-butyl ester, which should then be more readily hydrolysed, could similarly be obtained in higher yield. The DMAD and di-t-butyl acetylenedicarboxylate reactions with S_4N_4 were very similar in boiling toluene.[5] However, with the t-butyl ester none of the corresponding trithiadiazepine (nor trithiatriazepine) were formed at 156 °C, and it seems likely that the starting ester is being cleaved under these conditions. It is known that this happens, thermally, at the slightly higher temperature of 165 °C.[8] In the absence of S_4N_4, di-t-butyl trithiadiazepine-6,7-dicarboxylate itself was stable for 2 h in boiling bromobenzene. These last three reactions underline the need for an alternative approach to the seven-membered heterocyclic rings with very volatile or thermally unstable alkynes, and led us to explore the possibility of activating S_4N_4 by chemical modification.

Reactions of S_4N_4*-Alkene Adducts.*—Our first approach was to replace S_4N_4 by its 1:2-cycloadducts [*e.g.* (**14**)] with the strained alkenes, norbornadiene and dicyclopentadiene.[9] In



(14)

DMAD



(15) (16)

+ (3)

these crystalline adducts, of known structure,[9] the S_4N_4 cage has been disrupted, as in (**14**). Furthermore these 1:2-adducts dissociate readily and reversibly on heating in solution into S_4N_4 and the alkene, presumably *via* the 1:1-adduct. We hoped that one of the adducts would react more rapidly with an alkyne to give higher yields of trithiadiazepine or trithiatriazepine. In the event, with DMAD, the formation of the azepines (**1**) and (**2**) was totally suppressed.

Treatment of the cycloadduct (**14**) with DMAD in boiling benzene gave a mixture of norbornadiene cyclic polysulphides (32% as $C_7H_8S_3$) from which the major product, trisulphide

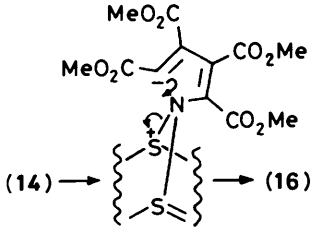
Table 3. Reaction of S_4N_4 with DMAD in the presence of titanium(IV) chloride; percentage yield of products

Solvent	Temp. (°C)	Time (h)	(1)	(2)	(3)	(4)
PhMe[a]	110	6	5	14	60	8
C_6H_6	80	3.5	40	Nil	41	Nil
MeCN	80	4	35	Nil	36	Nil
PhMe	110	1	38	Nil	37	Nil
PhBr	156	0.25	36	Nil	46	Nil
PhBr[b]	156	1.25	30	8	43	Nil

[a] No $TiCl_4$. [b] $AlCl_3$ in place of $TiCl_4$.

(**15**), was isolated and fully characterised, together with thiadiazole (**3**) (36%) and the pyrrole tetra-ester (**16**) (38%). At no point in this reaction was S_4N_4 observed (t.l.c.), suggesting that DMAD was indeed reacting with an adduct rather than with S_4N_4, and that this reaction does not result in trithiadi- and trithiatri-azepine formation; cycloaddition of DMAD across sulphur atoms, at least, is likely to be much suppressed in adduct (**14**) compared with S_4N_4 itself.

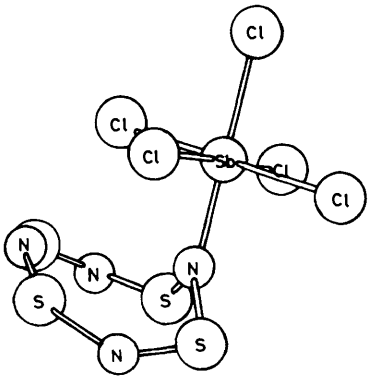
Control experiments in which the cycloadduct (**14**) was heated in benzene in the presence and absence of sulphur did not produce any norbornadiene polysulphides, indicating that DMAD is involved in their formation. The ^1H n.m.r. spectrum of the trisulphide (**15**) was very similar to that of adduct (**14**). The mass spectrum (ions at *m/z* 220, 252, and 284) indicated the presence of the hexasulphide, and the tetra and penta sulphides may also have been formed. The thiadiazole (**3**) was the same as that formed in the S_4N_4 reaction, but the pyrrole (**16**) was a new type of product. It may result from enhanced nucleophilicity of nitrogen, and reduced reactivity towards cycloaddition, in the adduct (**14**). This would favour Michael addition to DMAD, followed by addition to another DMAD[10] to give an intermediate [partial structure (**17**)] which could cyclise and undergo N–S bond cleavage to give the observed product (**16**).



(**17**)

A similar reaction between DMAD and the bis(dicyclopentadiene)–S_4N_4 cycloadduct[9] analogous to (**14**) gave very similar results. The same thiadiazole (**3**) and pyrrole (**16**) were formed, together with dicyclopentadienyl polysulphides (28% as $C_{10}H_{12}S_3$). So although the use of these S_4N_4 cycloadducts did modify the alkyne reaction markedly, formation of the seven-membered heterocyclic compounds was not favoured and a different method of activating S_4N_4 was required.

Lewis Acid Catalysis.—We therefore considered Lewis acid catalysis since many S_4N_4–Lewis acid adducts have been reported.[4b] These appear to have broadly similar structures, of which S_4N_4·$SbCl_5$ (**18**) is typical.[11] The S_4N_4 cage structure is opened up to give an approximately planar S_4N_3 unit with the remaining nitrogen atom, co-ordinated to the Lewis acid, above the plane; bond lengths[4c] indicate that the valence electrons in the ring are somewhat more localised in the complex than in S_4N_4. Thus, cycloaddition to the heterocyclic ring could be favoured both electronically and sterically.



(**18**)

We started with our standard reaction of S_4N_4 with DMAD (2 equiv.) in toluene. Addition of aluminium(III) chloride (1 equiv.) resulted in only a very modest increase in the yield of trithiadiazepine (**1**), but the yield of trithiatriazepine (**2**) was greatly reduced, and so some selectivity had resulted. However, addition of titanium(IV) chloride, the most successful of the Lewis acids investigated, gave a dramatic increase in the yield of trithiadiazepine, to 38%, with the total suppression of trithiatriazepine formation. The eight-fold increase in trithiadiazepine yield was significantly greater than that observed for the high temperature reaction.

In both aluminium and titanium chloride reactions the yield of 1,2,5-thiadiazole (**3**) was reduced and the ratio of trithiadiazepine to thiadiazole was greatly increased, as desired. The rate of the S_4N_4 reaction was also increased, about six-fold with titanium chloride (Table 3). The yields of the two products were remarkably constant in different solvents, at temperatures in the range 80—156 °C; there was no appreciable reaction at 60 °C. The trithiadiazepine yield in the boiling bromobenzene reaction increased from 23% in the absence of aluminium chloride to 30% in its presence.

The titanium chloride was acting catalytically since 0.1 equiv. was as effective as 1 or 2 equiv., and the order of mixing the three reactants did not affect the outcome. When an equimolar mixture of S_4N_4 and titanium chloride was heated in toluene, in the absence of DMAD, the complex and the S_4N_4 were completely destroyed within 1 h.

In a preliminary experiment tin(IV) chloride was as effective as titanium(IV) chloride. Boron trifluoride–diethyl ether and iron(III) chloride affected the reaction by suppressing the formation of trithiatriazepine (**2**) but there was no substantial increase in the yield of trithiadiazepine (**1**). Zinc(II) chloride and iodide, which gave no red colourization characteristic of complex formation with S_4N_4, had no effect on the reaction.

The effect of titanium chloride on the reaction of S_4N_4 with di-t-butyl acetylenedicarboxylate was then investigated since here the higher temperature conditions were not applicable. The reaction closely paralleled that of DMAD. With 0.2 equiv. of

Table 4. Effect of solvent on the reaction of S_4N_4 and DMAD (2 equiv.); yields of products

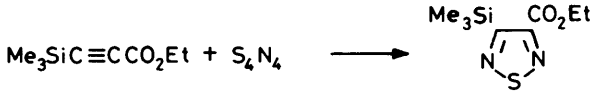
Solvent	Dielectric constant	Temp. (°C)	Time[a] (h)	(1)	(2)	(3)	(4)
Dioxane	2.2	101	24	8.1	0.4	64	11
C_6H_6	2.3	80	96	7.0	15	60	11
PhMe	2.4	110	6	7.5	11	59	10
PhMe + TFA[b]	—	110	6	7.6	11	61	12
EtOAc	6.0	77	96	5.4	1.4	60	17
$ClCH_2CH_2Cl$	10	83	56	10	5.6	59	12
MeCN	36	82	24	6.7	4.3	64	10
$MeNO_2$	39	101	24	7.2	2.8	59	[c]

[a] For complete reaction of S_4N_4. [b] Trifluoroacetic acid (2 equiv.). [c] Interference prevented determination.

catalyst in boiling toluene (1.5 h) the yield of di-t-butyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate was much increased, from 4[5] to 30%; the yield of t-butyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate was reduced, and a purple compound analogous to those observed before,[1] was also isolated.

Lewis acids had a similar influence on the reaction of S_4N_4 with ethyl 4,4,4-trifluorobut-2-ynoate (**10**) in dichloromethane. With titanium chloride at 120 °C the trithiadiazepine (**11**) yield was increased from 4 to 25% and the thiadiazole (**12**) yield was reduced from 55 to 14%; with aluminium chloride at 150 °C the trithiadiazepine yield increased to 15%. Again Lewis acids were more effective than high temperatures.

Titanium(IV) chloride did not invariably produce a satisfactory yield of trithiadiazepine however. Methyl prop-2-ynoate reacts with S_4N_4 in boiling toluene to give the corresponding trithiadiazepine (2%), trithiatriazepine (ester) (5%), and thiadiazole (7%);[2] with 1 equiv. of catalyst the yield of trithiadiazepine increased to 7%, the trithiatriazepine was absent, and the thiadiazole yield actually increased to 30%. S_4N_4 had also been shown to give low yielding reactions with other terminal alkynes,[2] and in view of our poor result with methyl propynoate we decided to replace the terminal acidic hydrogen with a trimethylsilyl group.



(**19**) (**20**)

Ethyl 3-trimethylsilylpropynoate (**19**), previously prepared by ethoxycarbonylation of trimethylsilylacetylene,[12] was here prepared more cheaply from ethyl propynoate with butyllithium and trimethylsilyl chloride. However, treatment of (**19**) with S_4N_4 (uncatalysed) in boiling toluene for 16 h gave only a low yield (26%) of the 1,2,5-thiadiazole (**20**). No trithiadiazepine was observed even under high temperature (PhBr, 156 °C) or titanium chloride-catalysed conditions. We have seen[1] that trithiadiazepine formation decreases with increasing electron density in the triple bond, and replacing the terminal hydrogen by trimethylsilyl apparently deactivates the alkyne further. Other relatively unreactive alkynes, $RC{\equiv}CR^1$ ($R = R^1 = Ph$; $R = R^1 = TMS$; and $R = Ph$, $R^1 = CO_2Me$) gave equally poor results in titanium(IV) catalysed reactions. These all gave very polar, 'baseline' products together with sulphur, though again the blood red $S_4N_4{\cdot}TiCl_4$ complex was formed and the rate of decomposition of S_4N_4 enhanced.

Effect of Solvent in the S_4N_4–DMAD Reaction.—Before we had found the beneficial effects of high reaction temperature and Lewis acid catalysis, we investigated the effect of solvent polarity on product yields. The results, obtained by h.p.l.c. analysis, are shown in Table 4. The solvents are arranged in order of increasing dielectric constant.

Some clear patterns of product yields emerge for this group of solvents, which has a relatively narrow boiling point range but a wide range of dielectric constants. The yields of trithiadiazepine (**1**) and the thiadiazoles (**3**) and (**4**) vary very little; yields of (**3**) are virtually constant and yields of (**1**) and (**4**) vary by less than a factor of two. The yields of trithiatriazepine (**2**) however do vary much more (nearly 40-fold). Apart from the results in dioxane and ethyl acetate the trithiatriazepine yields are inversely proportional to the dielectric constant of the solvent, but the very low yields in dioxane and, to a lesser extent, ethyl acetate are completely out of line with this trend. Addition of trifluoroacetic acid made no difference to all four product yields. Clearly variation of solvent polarity did not provide a way of enhancing the formation of the seven-membered heterocyclic rings and hence our investigation of reaction temperature and catalysis.

Experimental

For general points see references 1 and 3. Known reaction products were identified by direct comparison with authentic compounds (m.p. or b.p., R_F, i.r., n.m.r., and m.s.). H.p.l.c. analysis was on a Gilson instrument with a u.v. detector at 254 nm.

Reaction of S_4N_4 with DMAD in Bromobenzene.—Dimethyl acetylenedicarboxylate (DMAD) (0.62 ml, 5 mmol) was added to refluxing bromobenzene (150 ml) followed immediately by tetrasulphur tetranitride (S_4N_4) (0.460 g, 2.5 mmol) in warm bromobenzene (150 ml). The S_4N_4 solution was added over 0.25 h and heating continued for a further 0.5 h. The solvent was removed and the residue, pre-adsorbed onto silica, was separated by column chromatography. Elution with light petroleum gave sulphur followed by methyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate (**2**)[3] (0.025 g, 5%); dichloromethane–light petroleum (1:50) gave dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (**1**) (0.150 g, 23%) of purity >99% by h.p.l.c.; dichloromethane–light petroleum (1:4) gave dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**)[2,3] (0.474 g, 47%); chloroform–light petroleum (1:1) gave dimethyl 1,2,4-thiadiazole-3,5-dicarboxylate (**4**)[2,3] (0.030 g, 3%). A similar experiment but with the order of addition of DMAD and S_4N_4 reversed gave the yields shown in Table 1.

Reaction of S_4N_4 with 4,4-Diethoxybut-2-ynal (**5**).—(*a*) *In bromobenzene.* The alkyne (**5**)[13] (0.780 g, 5 mmol) in bromobenzene (50 ml) and S_4N_4 (0.460 g, 2.5 mmol) in warm bromobenzene (50 ml) were added dropwise and synchronously to refluxing bromobenzene (70 ml) over 1 h, followed by heating for a further 1.5 h. The reaction mixture was separated as above.

Light petroleum eluted sulphur, followed by 1,3,5,2,4,6-trithiatriazepine-7-carbaldehyde (**8**)[1] (0.012 g, 3%), followed by a 1:1 mixture of *cis* and *trans* isomers of 6,8-*diethoxy*-6,8-*dihydrofurano*[3,4-f][1,3,5,2,4]*trithiadiazepine* (**7**) (0.040 g, 6%) as a low melting solid; $\lambda_{max.}$(EtOH) 223 (log ε 4.17), 270 (3.51), and 329 nm (3.79); $\nu_{max.}$(melt) 2 970m, 2 920m, 2 880m, 1 440w, 1 370w, 1 325m, 1 290w, 1 160m, 1 110s, 1 030s, 940m, and 660m cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.28 (6 H, t, *J* 6.8 Hz, 2 × Me), 1.29 (6 H, t, *J* 6.8 Hz, 2 × Me), 3.79 [8 H, (2 × 16 line ABX_3 spin systems, 26 lines visible) 2 × (2 × CH_2)], 6.27 (2 H, s, 2 × CH), 6.52 (2 H, s, 2 × CH); δ_C (62.9 MHz, $CDCl_3$) 15.1 (br, 4 × Me), 62.9 (2 × CH_2), 63.3 (2 × CH_2), 105.7 (2 × CH), 106.0 (2 × CH), 140.1 (2 × ArC), and 140.2 (2 × ArC); *m/z* (170 °C) 282 (M^+ + 2, 11%), 280 (M^+, 73), 235 (M^+ − OEt, 56), 207 (66), 161 (36), 160 (37), 132 (56), 116 (54), 78 (43), 61 (54), 57 (31), 46 (32), 45 (37), and 29 (100); dichloromethane–light petroleum (1:20) eluted 7-*diethoxymethyl*-1,3,5,2,4-*trithiadiazepine*-6-*carbaldehyde* (**6**) (0.125 g, 18%) as needles, m.p. 99—100 °C (light petroleum) (Found: C, 34.5; H, 4.25; N, 9.95; S, 34.6. $C_8H_{12}N_2O_3S_3$ requires C, 34.3; H, 4.3; N, 10.0; S, 34.3%); $\lambda_{max.}$(EtOH) 273 (log ε 4.11) and 315 nm (3.67); $\nu_{max.}$(CCl_4) 2 990m, 2 940m, 1 670s (CO), 1 170m, 1 100s, 1 060s, and 1 025m cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.30 (6 H, t, 2 × Me); 3.8 [4 H, (16 line ABX_3 spin system), 2 × CH_2], 5.62 (1 H, s, CH), and 10.70 (1 H, s, CHO); δ_C (62.9 MHz, $CDCl_3$) 14.9 (Me), 64.4 (CH_2), 101.0 (CH), 144.0 and 152.4 (ArC), and 188.5 (CHO); *m/z* (100 °C) 282 (M^+ + 2, 1.6%), 280 (M^+, 10), 235 (M^+ − OEt, 7), 234 (M^+ − NS, 20), 207 (13) 103 (EtO–$\overset{+}{C}$H–OEt, 72), 78 (NS_2, 14), 75 (EtO–$\overset{+}{C}$H–OH, 79), 47 (HO–$\overset{+}{C}$H–OH, 100), 46 (NS, 11), and 29 (CHO, 36); dichloromethane–light petroleum (1:9) eluted an oil (0.85 g, 8%) tentatively assigned the structure 4(or 5)-diethoxymethyl-1,2,3-thiadiazole-5(or 4)-carbaldehyde, b.p. 75—80 °C, 0.5 mmHg (Found: N, 13.2; S, 15.0. $C_8H_{12}N_2O_3S$ requires N, 13.0; S, 14.8%); $\nu_{max.}$(CCl_4) 2 980m, 2 925w, 1 710s (CO), 1 170w, 1 105m, 1 060s, and 1 000m cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.22 (6 H, t, *J* 6.9 Hz, 2 × Me), 3.70 [4 H, m(ABX_3 spin system, 11 lines visible), 2 × CH_2], 6.30 (1 H, s, CH), and 10.60 (1 H, s, CHO); δ_C (62.9 MHz, $CDCl_3$) 15.0 (Me), 63.7 (CH_2), 96.1 (CH), 155.8 and 162.6 (ArC), and 184.2 (CHO); *m/z* (100 °C) 217 (MH^+, 1.7%), 171 (M^+ − OEt, 64), 168(28), 140(62), 103 (EtO–$\overset{+}{C}$H–OEt, 100), 75 (EtO–$\overset{+}{C}$H–OH, 65), 47 (HO–$\overset{+}{C}$H–OH, 100), and 29 (CHO, 100); dichloromethane–light petroleum (1:3) eluted 4-*diethoxymethyl*-1,2,5-*thiadiazole*-3-*carbaldehyde* (**9**) (0.270 g, 25%), b.p. 170 °C, 5 mmHg (Found: C, 44.1; H, 5.8; S, 15.0. $C_{18}H_{12}N_2O_3S$ requires C, 44.4; H, 5.6; S, 14.8%); $\lambda_{max.}$(EtOH) 257 (log ε 3.84) and 305 nm (3.03); $\nu_{max.}$ 2 990s, 2 940m, 2 900m, 1 710s (CO), 1 670w, 1 560w, 1 450w, 1 375w, 1 330m, 1 295w, 1 170m, and 1 060s cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.28 (6 H, t, 2 × Me), 3.82 [4 H, (16 line ABX_3 spin system) 2 × CH_2], 6.16 (1 H, s, CH), and 10.34 (1 H, s, CHO); δ_C (62.9 MHz, $CDCl_3$) 15.0 (Me), 63.2 (CH_2), 97.6 (CH), 156.2 and 162.4 (ArC), and 183.5 (CHO); *m/z* (100 °C) 216 (M^+, 30%), 188 (23), 187 (32), 172 (26), 171 (M^+ − OEt, 66), 159 (22), 143 (M^+ − OEt − CO, 100), 142 (23), 141 (46), 103 (EtO–C–$\overset{+}{H}$–OEt, 23), 75 (EtO–$\overset{+}{C}$H–OH, 19), 47 (HO–$\overset{+}{C}$H–OH, 37), and 29 (CHO, 60).

(*b*) *In toluene.* S_4N_4 (0.400 g, 2.17 mmol), the alkyne (0.700 g, 4.49 mmol), and toluene (50 ml) were heated at reflux for 15 h. Separation as before gave 1,3,5,2,4,6-trithiatriazepine-7-carbaldehyde (0.010 g, 3%), 6-diethoxymethyl-1,3,5,2,4-trithiadiazepine-7-carbaldehyde (0.035 g, 6%), the compound tentatively assigned structure 4(or 5)-diethoxymethyl-1,2,3-thiadiazole-5(or 4)-carbaldehyde (0.042 g, 4%), and 4-diethoxymethyl-1,2,5-thiadiazole-3-carbaldehyde (0.280 g, 30%) identical with the compounds described above.

6,8-*Diethoxy*-6,8-*dihydrofurano*[3,4-f][1,3,5,2,4]*trithiadiazepine* (**7**).—7-Diethoxymethyl-1,3,5,2,4-trithiadiazepine-6-carbaldehyde (**6**) (0.100 g, 0.36 mmol) in chloroform (10 ml) was stirred vigorously with aqueous sulphuric acid (4M; 10 ml) for 5 days at room temperature. The aqueous layer was extracted with chloroform and the combined chloroform layers were washed once with water, dried (Na_2SO_4), and evaporated to give a 1:1 mixture of *cis* and *trans* isomers of the title compound (**7**) (0.095 g, 95%) identical with that described above. Attempted hydrolysis of the acetal (**6**) with 50% aqueous trifluoroacetic acid,[14] with 50% aqueous formic acid,[15] and with 15% aqueous sulphuric acid on silica,[16] all gave isomers of (**7**) only in 45, 65, and 75% yields, respectively.

Hydrolysis of 4-*Diethoxymethyl*-1,2,5-*thiadiazole*-3-*carbaldehyde* (**9**).—4-Diethoxymethyl-1,2,5-thiadiazole-3-carbaldehyde (0.080 g, 0.37 mmol) in dichloromethane (5 ml) was added to a slurry made by shaking silica (3 g), dichloromethane (15 ml), and aqueous sulphuric acid (15%, 20 drops), and stirred vigorously for 7 days. The silica was filtered off and washed with a little dichloromethane and the combined organic portions were evaporated to give 1,2,5-thiadiazole-3,4-dicarbaldehyde (0.043 g, 81%).[1]

Reaction of S_4N_4 *with Ethyl* 4,4,4-*Trifluorobut*-2-*ynoate* (**10**).—The alkyne (**10**)[17] (0.950 g, 5.7 mmol) was collected in a receiver cooled with solid carbon dioxide and alcohol. It was transferred in dichloromethane (30 ml) to a tube containing S_4N_4 (0.368 g, 2 mmol) and dichloromethane (10 ml). The tube was sealed and heated at 150 °C for 6 h. The reaction mixture was evaporated and the residue separated by dry flash chromatography on silica (50 g) with gradient elution. Dichloromethane (5—25%) in light petroleum eluted sulphur. Dichloromethane (45—50%) in light petroleum eluted *ethyl* 7-*trifluoromethyl*-1,3,5,2,4-*trithiadiazepine*-6-*carboxylate* (**11**) (0.056 g, 10%), b.p. 130 °C/0.2 mmHg (Found: C, 25.6; H, 1.8; N, 9.4; S, 33.35. $C_6H_5F_3N_2O_2S_3$ requires C, 24.8; H, 1.7; N, 9.65; S, 33.1%); $\lambda_{max.}$(EtOH) 250 (log ε 3.90) and 329 nm (3.46); $\nu_{max.}$($CHCl_3$) 2 940w, 1 730s (CO), 1 370w, 1 170s, 1 150s, 1 005m, and 855w cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.43 (3 H, t, Me) and 4.50 (2 H, q, CH_2); δ_F (84.6 MHz, $CDCl_3$, standard $CFCl_3$) + 50.2 (s, CF_3); δ_C (62.9 MHz, $CDCl_3$); 13.7 (s, Me), 64.1 (s, CH_2), 121.8 (q, *J* 280 Hz, CF_3), 135.1 (q, *J* 29 Hz, C-7), 142.5 (s, C-6), and 161 (s, ester CO); *m/z* (130 °C) 292 (M^+ + 2, 13%), 290 (M^+, 95), 245 (M^+ − OEt, 23), 244 (M^+ − NS, 11), 172 (19), 149 (13), 124 (N_2S_3, 62), 78 (NS_2, 69), 46 (NS, 53), and 29 (CHO, 100). Dichloromethane (65—85%) in light petroleum eluted *ethyl* 4-*trifluoromethyl*-1,2,5-*thiadiazole*-3-*carboxylate* (**12**) (0.510 g, 57%), b.p. 100 °C, 25 mmHg (Found: C, 31.9; H, 2.3; N, 12.3; S, 13.9. $C_6H_5F_3N_2O_2S$ requires C, 31.9; H, 2.2; N, 12.4; S, 14.2%); $\lambda_{max.}$(EtOH) 266 nm (log ε 3.88); $\nu_{max.}$(neat) 2 985m, 1 745s (CO), 1 480m, 1 440m, 1 430m, 1 390w, 1 365w, 1 290br, s, 1 180br, s, 1 100w, 1 040s, 1 010w, 865w, and 850w cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.50 (3 H, t, Me) and 4.60 (2 H, q, CH_2); δ_F (84.6 MHz, $CDCl_3$, standard $CFCl_3$) +62.3 (s, CF_3); δ_C (62.9 MHz, $CDCl_3$) 13.2 (s, Me), 62.6 (s, CH_2), 118.9 (q, *J* 273 Hz, CF_3), 150.6 (q, *J* 40 Hz, C-4), 151.1 and 158.1 (2 × s, ester CO and C-3); *m/z* (170 °C) 226 (M^+, 11%), 199 (22), 182 (21), 181 (M^+ − OEt, 90), 154 (25), 86 (13), 69 (27), 45 (20), and 29 (100).

A similar reaction at 120 °C gave the same products, (**11**) (4%) and (**12**) (55%).

Reaction of S_4N_4 *with Monocyanoacetylene.*—S_4N_4 (184 mg, 1 mmol), monocyanoacetylene[18] (460 mg, 9 mmol), and toluene (25 ml) were sealed in a glass tube and immediately heated to 125 °C, in a preheated oven, for 10 h. The complex mixture of products was submitted to preparative t.l.c. on Merck 60 GF_{254}

silica to give 1,3,5,2,4-*trithiadiazepine*-6-*carbonitrile* (**13**) (8 mg, 5%), m.p. 71 °C (Found: C, 20.8; H, 0.6; N, 23.5. $C_3HN_3S_3$ requires C, 20.6; H, 0.6; N, 24.0%); $\lambda_{max.}$(EtOH) 248 (log ε 3.96), 332 nm (3.43); $\nu_{max.}$($CHCl_3$) 2 920m, 2 855m, 2 220s, 1 600w, 1 455w, 1 160m, and 1 110sh cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.35 (1 H, s); *m/z* (100 °C) 177 (M^+ + 2, 15%), 175 (M^+, 100), 149 (M^+ − CN, 50), 129 (M^+ − NS, 20), 124 (N_2S_3, 33), 78 (NS_2, 71), and 46 (NS, 81). A repeat of this experiment at 140 °C, in the absence and presence of bis(pentane-2,4-dionato) nickel(II), gave compound (**13**) (10%).

Reaction of Bis(norbornadiene)–Tetrasulphur Tetranitride Adduct (**14**) *with DMAD.*—Tetrasulphur tetranitride bis(norbornadiene) (**14**) (0.920 g, 2.5 mmol) and DMAD (0.61 ml, 5 mmol) were refluxed in benzene (50 ml) for 6 h. The reaction products were separated by chromatography on silica (20 g). Light petroleum eluted a yellow oil (0.15 g, 32% as $C_7H_8S_3$) which was probably a mixture of norbornadiene tri-(**15**), tetra-, penta-, and hexa-sulphide (Found: C, 36.95; H, 3.8. $C_7H_8S_3$ requires C, 44.6; H, 4.3. $C_7H_8S_4$ requires C, 38.2; H, 3.7. $C_7H_8S_5$ requires C, 33.3; H, 3.2. $C_7H_8S_6$ requires C, 30.0; H, 2.8%); $\nu_{max.}$($CHCl_3$) 2 940s, 2 865m, 1 570m, 1 450s, 1 320s, 1 270s, 1 230m, br, 1 150m, 1 020m, 980m, 910m, 870w, and 645m cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.74 and 2.52 (1 H, and 1 H, 2 × d, *J* 10 Hz, CH_2), 2.92 (2 H, s, CH_2CH), 4.08 (2 H, d, *J* 2 Hz, CHS), and 6.43 (2 H, s, =CH); *m/z* (120 °C) 284 (3%), 252 (18), 220 (5), 188 (82), and 122 (100). Rechromatography and crystallisation from light petroleum, b.p. 40—60 °C, gave 3,4,5-*trithiatricyclo*-[5.2.1.$0^{2,6}$]*dec*-8-*ene* (**15**) (0.040 g, 9%) as yellow needles, m.p. 25—31 °C (Found: C, 44.4; H, 4.2%); $\lambda_{max.}$(hexane) 285 nm (log ε = 3.49); $\nu_{max.}$($CHCl_3$) 2 940s, 2 865m, 1 570m, 1 450s, 1 320s, 1 270s, 1 230m, br, 1 150m, and 1 020m, 980m, 910m, 900m, 870w, and 645m cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.73 (1 H, dt, *J* 3 and 10 Hz, CH_2), 2.48 (1 H, d, *J* 10 Hz, CH_2), 2.91 (2 H, s, CH_2–CH), 4.08 (2 H, d, *J* 2 Hz, CHS), and 6.43 (2 H, s, =CH); *m/z* (90 °C) 190 (M^+ + 2, 5.4%), 188 (M^+, 38), and 122 (100). Dichloromethane–light petroleum (1:9) eluted dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**) (0.360 g, 36%). Dichloromethane–methanol (100:1) eluted crude tetramethyl pyrrole-2,3,4,5-tetracarboxylate (**16**) (0.380 g) purified by dry flash chromatography. Ether–light petroleum (7:3) eluted the pure pyrrole (**16**) (0.282 g, 38%), m.p. 120—123 °C (methanol) (lit.,[19] 124—125 °C) (Found: C, 48.3; H, 4.3; N, 4.7. Calc. for $C_{12}H_{13}NO_8$: C, 48.2; H, 4.4; N, 4.7%), $\nu_{max.}$($CHCl_3$) 3 140m, 2 960w, 2 845w, 1 745sh (CO), 1 730s (CO), 1 565m, 1 455m, 1 310sh, 1 260s, and 1 230sh cm^{-1}; δ_H (250 MHz, $CDCl_3$) 3.83 (6 H, s, 2 × Me), 3.86 (6 H, s, 2 × Me), and 10.12 [1 H, s br, NH]; δ_C (62.9 MHz, $CDCl_3$) 52.5, 52.7, 121.8, 123.3, 159.1, and 163.1; *m/z* 299 (M^+, 45%), 268 (52), and 236 (100).

Reaction of the Bis(dicyclopentadiene)–Tetrasulphur Tetranitride Adduct with DMAD.—Bis(dicyclopentadiene)–tetrasulphur tetranitride adduct (0.560 g, 1.25 mmol) and DMAD (0.31 ml, 2.5 mmol) were refluxed in dichloromethane for 3 h. The reaction products were separated by chromatography on silica (15 g). Light petroleum eluted a yellow oil (0.081 g, 28% as $C_{10}H_{12}S_3$) which was probably a mixture of dicyclopentadiene polysulphides similar to that in the last experiment. Dichloromethane–light petroleum (1:4) eluted dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**) (0.078 g, 15%). Dichloromethane–methanol (50:1) eluted tetramethyl pyrrole-2,3,4,5-tetracarboxylate (0.058 g, 16%) identical with that in the last experiment.

Reaction of S_4N_4 *with DMAD and Titanium*(IV) *Chloride.*—S_4N_4 (0.460 g, 2.5 mmol), DMAD (0.62 ml, 5 mmol), and toluene (50 ml) were pre-mixed, under nitrogen, and titanium(IV) chloride (0.475 g, 2.5 mmol) added and the mixture refluxed for 1 h. The solvent was evaporated off and dichloromethane added. The black inorganic solid was filtered off and washed thoroughly with dichloromethane. The dichloromethane soluble fraction was pre-adsorbed onto silica and separated by dry flash column chromatography on silica (60 g) using gradient elution. Dichloromethane (70—80%) in light petroleum gave dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (**1**) (0.252 g, 38%) and dichloromethane (90%) in light petroleum–methanol (20%) in dichloromethane gave dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3**) (0.372 g, 37%). Similar reactions in other solvents gave the results summarized in Table 3.

Reaction of S_4N_4 *with DMAD and Aluminium*(III) *Chloride.*—S_4N_4 (0.460 g, 2.5 mmol) in warm bromobenzene (100 ml) was added dropwise to a solution of DMAD (0.62 ml, 5 mmol) and aluminium chloride (0.050 g) in bromobenzene (100 ml) which was being heated at reflux over a period of 1 h and heating was then continued for a further 0.25 h. The bromobenzene was evaporated off and the residue, in dichloromethane, was pre-adsorbed onto silica and separated by dry flash chromatography on silica (60 g) with gradient elution. Dichloromethane (0—25%) in light petroleum eluted sulphur; dichloromethane (60—65%) in light petroleum eluted methyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate (**2**) (0.041 g, 8%); dichloromethane (70%) in light petroleum eluted dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (**1**) (0.196 g, 30%); dichloromethane (75—85%) in light petroleum eluted a mixture of products including a deep purple compound, and dichloromethane (90%) in light petroleum–methanol (20%) in dichloromethane eluted dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (0.430 g, 43%).

Reaction of S_4N_4 *with Di-t-butyl Acetylenedicarboxylate and Titanium*(IV) *Chloride.*—S_4N_4 (2.00 g, 10.9 mmol), di-t-butyl acetylenedicarboxylate (5.00 g, 22.1 mmol), titanium(IV) chloride (0.22 ml, 2.0 mmol), and toluene (150 ml) were heated at reflux for 1.5 h under nitrogen. The mixture was filtered and the filtrate stirred with water (50 ml) for 3 h. The residue from the filtration was shaken with water (50 ml) for 1 h after which the two aqueous portions were combined and extracted with dichloromethane (large volume to break the emulsion). The toluene layer was evaporated off and the residue dissolved in dichloromethane. The dichloromethane fractions were combined, pre-adsorbed onto silica, and separated by dry flash chromatography on silica (60 g) with gradient elution; complete separation was achieved with two such columns. Dichloromethane (0—20%) in light petroleum eluted sulphur; dichloromethane (40%) in light petroleum eluted t-butyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate[5] (0.060 g, 2%). Dichloromethane (45—50%) in light petroleum eluted di-t-butyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate[5] (1.150 g, 30%); dichloromethane (55—60%) in light petroleum eluted a purple compound (0.063 g); dichloromethane (65—100%) in light petroleum eluted *di-t-butyl* 1,2,5-*thiadiazole*-3,4-*dicarboxylate* (1.745 g, 28%), b.p. 130 °C, 0.1 mmHg (Found: C, 50.0; H, 6.3; N, 9.65; S, 11.5. $C_{12}H_{18}N_2O_4S$ requires C, 50.3; H, 6.3; N, 9.8; S, 11.2%); $\lambda_{max.}$(EtOH) 263 nm (log ε 4.03); $\nu_{max.}$(CCl_4) 2 980m, 2 930w, 1 740s, 1 720s, 1 470w, 1 450w, 1 420w, 1 390w, 1 370s, 1 300m, 1 255w, 1 225s, 1 160s, 1 075s, and 1 030w cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.66 (s); δ_C (62.9 MHz, $CDCl_3$) 27.7 (s, 6 × Me), 83.9 [s, 2 × CMe_3], 154.1 and 159.1 (2 × s, 2 × ArC and 2 × CO); *m/z* (120 °C) 287 (MH^+, 0.1%), 231 (MH^+ − C_4H_8, 0.5), 215 (1), 175 (MH^+ − 2 × C_4H_8, 19), 157 (2), 115 (4), 59 (20), 57 (100), and 56 (10).

Reaction of S_4N_4 *with Ethyl* 4,4,4-*Trifluorobut*-2-*ynoate* (**10**) *and Titanium*(IV) *Chloride.*—S_4N_4 (0.070 g, 0.38 mmol), ethyl 4,4,4-trifluorobut-2-ynoate (0.190 g, 1.14 mmol), titanium(IV) chloride (1 drop), and dichloromethane (20 ml) were heated at

120 °C in a sealed tube for 6 h. On cooling, water (10 ml) was added and the mixture shaken for 1 h. The organic layer was separated and the aqueous layer extracted with dichloromethane (2 × 10 ml). The combined organic layers were dried (Na_2SO_4), pre-adsorbed onto silica, and separated by dry flash column chromatography on silica (10 g) using gradient elution. Dichloromethane (40—50%) in light petroleum eluted ethyl 7-trifluoromethyl-1,3,5,2,4-trithiadiazepine-6-carboxylate (**11**) (0.028 g, 25%) identical with that described above; dichloromethane (55—60%) in light petroleum eluted an unidentified oil; dichloromethane (65—75%) in light petroleum eluted ethyl 4-trifluoromethyl-1,2,5-thiadiazole-3-carboxylate (**12**) (0.024 g, 14%) identical with that described above.

Reaction of S_4N_4 *with Methyl Propynoate and Titanium*(IV) *Chloride.*—S_4N_4 (0.368 g, 2 mmol), methyl propynoate (0.36 ml, 4 mmol), titanium(IV) chloride (0.22 ml, 2 mmol), and toluene (140 ml) were heated under reflux for 1 h. The mixture was filtered and the filtrate stirred with water (25 ml) for 6 h. The residue was shaken with water (25 ml) for 1 h after which the two aqueous portions were combined and extracted with dichloromethane (large volume to break the emulsion). The toluene layer was evaporated and the residue dissolved in dichloromethane. The dichloromethane fractions were combined, pre-adsorbed onto silica, and separated by dry flash chromatography. Dichloromethane (5—20%) in light petroleum eluted sulphur; dichloromethane (45—55%) in light petroleum eluted a mixture of methyl 1,3,5,2,4-trithiadiazepine-6-carboxylate and an unknown volatile compound which was removed at 25 °C and 5 mmHg. Sublimation at 80 °C and 1 mmHg gave pure *methyl* 1,3,5,2,4-*trithiadiazepine*-6-*carboxylate*, m.p. 111 °C (0.028 g, 7%) (Found: C, 23.3; H, 1.9; N, 13.3. $C_4H_4N_2O_2S_3$ requires C, 23.1; H, 2.0; N, 13.45%); $\lambda_{max.}$(EtOH) 262 (log ε 3.82) and 334 nm (3.30); $\nu_{max.}$($CHCl_3$) 2 950w, 2 920w, 2 850w, 1 710s (CO), 1 495w, 1 430w, 1 260m, 1 160m, 1 003w, 961m, and 908w cm^{-1}; δ_H (90 MHz, $CDCl_3$) 4.03 (3 H, s, CO_2Me) and 8.90 (1 H, s, ArH); δ_H (62.9 MHz, $CDCl_3$) 53.1 (Me), 134.7 and 135.9 (ArC), and 163.5 (ester CO); *m/z* (140 °C) 210 (M^+ + 2, 8%), 208 (M^+, 64), 177 (M^+ − MeO, 4), 162 (M^+ − NS, 45), 124 (N_2S_3, 9), 78 (N_2S, 78), 59 (CO_2Me, 33), 57 (27), 46 (NS, 57), and 45 (33). Dichloromethane (85—100%) in light petroleum eluted methyl 1,2,5-thiadiazole-3-carboxylate[2] (0.174 g, 30%).

Ethyl 3-(*Trimethylsilyl*)*propynoate* (**19**).—Ethyl propynoate (0.51 ml, 5 mmol) in ether (10 ml) was cooled to −78 °C. Butyllithium (1.5M; 3.25 ml, 5 mmol) was added over 10 min and the mixture stirred at −78 °C for 30 min. Freshly distilled chlorotrimethylsilane (0.63 ml, 5 mmol) was added and the mixture allowed to warm up to 25 °C over 4 h. The mixture was poured into aqueous ammonium chloride solution (10%; 20 ml), extracted with ether, and the ether layer was washed with water, dried ($MgSO_4$), evaporated and the residue distilled to give the title compound,[12] b.p. 130 °C at 30 mmHg (0.45 g, 52%); δ_H (60 MHz, $CDCl_3$) 0.23 (9 H, s, $SiMe_3$), 1.28 (3 H, t, Me), and 4.12 (2 H, q, CH_2).

Reaction of S_4N_4 *with Ethyl* 3-(*Trimethylsilyl*)*propynoate.*—S_4N_4 (0.368 g, 2 mmol), ethyl 3-(trimethylsilyl)propynoate (0.6 g, 4 mmol), and toluene (25 ml) were heated under reflux for 16 h. The solvent was evaporated off, and the residue pre-adsorbed onto silica and separated by dry flash column chromatography on silica (60 g) using gradient elution. Dichloromethane (0—20%) in light petroleum eluted sulphur; dichloromethane (45%) in light petroleum eluted heptasulphur imide (13 mg, 5%), m.p. 112—114 °C (lit.,[20] 113.5 °C); dichloromethane (65—80%) in light petroleum eluted *ethyl* 4-*trimethylsilyl*-1,2,5-*thiadiazole*-3-*carboxylate* (**20**) (0.237 g, 26%), b.p. 120 °C, 2 mmHg (Found: C, 42.2; H, 6.25; N, 11.9; S, 13.7. $C_8H_{14}N_2O_2SSi$ requires C, 41.7; H, 6.1; N, 12.2; S, 13.9%); $\nu_{max.}$(CCl_4) 2 980w, 2 960w, 2 900w, 1 725s (CO), 1 425m, 1 380m, 1 350m, 1 250m, 1 200s, 1 160m, and 845s cm^{-1}; δ_H (250 MHz, $CDCl_3$) 0.41 (9 H, s, Me_3Si), 1.44 (3 H, t, Me), and 4.47 (2 H, q, CH_2); δ_C (62.0 MHz, $CDCl_3$) −1.4 (s, Me_3Si), 14.1 (s, Me), 62.0 (s, CH_2), 158.2, 161.0, and 173.0 (3 × ArC and CO); *m/z* (120 °C) 230 (M^+, 4%), 215 (M^+ − Me, 84), 202 (13), 187 (100), 128 (11), 116 (31), 86 (15), 84 (13), 75 (15), 73 (42), and 43 (24).

Reaction of S_4N_4 *with DMAD in Various Solvents.*—S_4N_4 (0.023 g, 0.125 mmol), DMAD (0.03 ml, 0.25 mmol), and the solvent (10 ml) were heated at reflux for the times shown in Table 4. The solvent was evaporated off and the residue was pre-adsorbed onto silica and flushed through an 8 mm pad of silica with chloroform (200 ml). The chloroform was evaporated off and the residue dissolved in methanol (50 ml) and subjected to h.p.l.c. analysis on a Microsorb C18 (reverse phase) column using methanol–water (7:3) as eluant with a flow rate of 1 ml min^{-1}. The product concentrations were determined by comparing their peak areas, by triangulation, with those of standard solutions of concentration *ca.* 0.01 mg ml^{-1}. Identification of the trithiadiazepine (1) and trithiatriazepine (2) was confirmed by 'spiking' the reaction mixtures with the reference solutions and re-running the analysis. Typical retention times were 3.5 min (**2**), 4.0 min (1), 12.5 min (**3**), and 16.5 min (**4**).

Acknowledgements

We thank the S.E.R.C. for a studentship (P. J. D.).

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Received 10*th September* 1986; *Paper* 6/1808