# Organic Heterocyclothiazenes. Part 5.[1] Cycloaddition Reactions of Tetrasulphur Tetranitride with Highly Electron Deficient Alkynes

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In contrast with previous, complex, $S_4N_4$-alkyne reactions, treatment of butynedinitrile and $S_4N_4$ is found to give 1,3,5,2,4-trithiadiazepine-6,7-dicarbonitrile (**8**) and 1,2,5-thiadiazole-3,4-dicarbonitrile (**9**) very cleanly and in high yield. Hexafluorobut-2-yne and 4,4,4-trifluorobutynonitrile (**4**) similarly give the trithiadiazepines (**10**) and (**12**), though more slowly and in slightly lower yields. Structures (**8**) and (**10**) correct literature assignments. The analogous reactions of ethyl 3-formylpropynoate (**6**), hex-3-yne-2,5-dione (**7**), and butynedial, like those of acetylenedicarboxylate esters, give complex mixtures from which trithiadiazepines, trithiatriazepines, and thiadiazoles are variously isolated. A mechanistic rationalization of these results is suggested. 1,2,5-Thiadiazole-3,4-dicarbaldehyde (**18b**) is prepared in high yield from $S_4N_4$ and 1,1,4,4-tetraethoxybutyne (**20**), followed by hydrolysis. This dialdehyde and other 3,4-dioxo-1,2,5-thiadiazoles are used to prepare 1,2,5-thiadiazolo[3,4-*d*]pyridazine and its derivatives (**22**) for the first time. Improved preparations for ethyl 3-formylpropynoate (**6**) and hex-3-yne-2,5-dione (**7**) are reported.

It was shown in earlier Parts of this series[2,3] that the minor products of reaction of tetrasulphur tetranitride, $S_4N_4$, with dimethyl and di-t-butyl acetylenedicarboxylate included trithiadiazepine diesters and trithiatriazepine monoesters, but the yields were too low to be practically useful. It was also shown[3] that the parent trithiadiazepine, and its dihydro and benzo derivatives, could be synthesised in practicable quantities by high dilution cyclisation of bis-sulphenyl chlorides with bis-(trimethylsilyl)sulphurdi-imide. This route is somewhat limited by the availability of the appropriate bis-sulphenyl chlorides, and it lacks the simplicity and potential versatility of the $S_4N_4$ reaction.

We now show that simple alkynes with two strongly electron-withdrawing groups react with $S_4N_4$ very readily to give the corresponding trithiadiazepines in much higher yield.

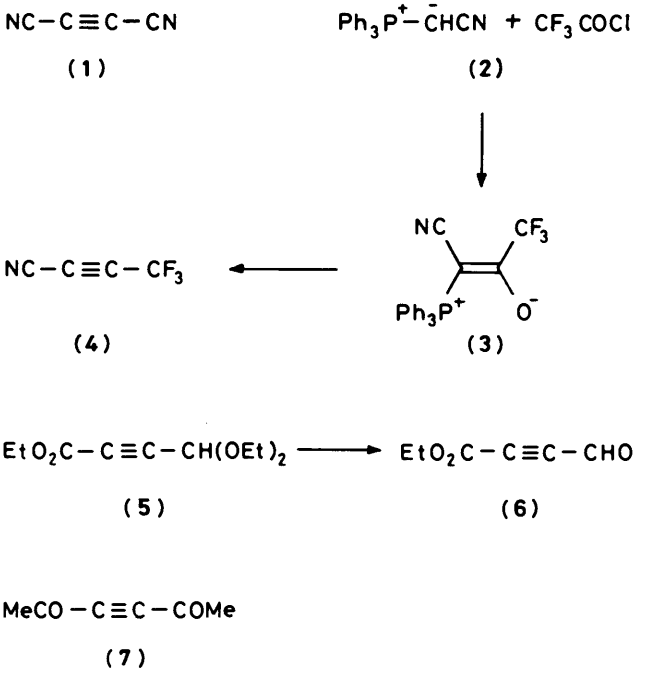
## Results and Discussion

*Preparation of the Alkynes.—Butynedinitrile* (**1**). Treatment of dimethyl acetylenedicarboxylate (DMAD) with concentrated aqueous ammonia at −10 °C gave the dicarboxamide in good yield. However, if the reaction temperature is allowed to rise above −10 °C or if the DMAD is added too rapidly, the yield of dicarboxamide falls sharply. Dehydration of acetylenedicarboxamide with phosphorus pentaoxide gave the dinitrile (**1**) smoothly and in reproducible yield (*ca.* 40%).[4]

4,4,4-*Trifluorobutynonitrile* (**4**). Trifluoroacetylation of the ylide (**2**)[5] gave the betaine (**3**) in high yield. Pyrolysis of the latter at 260 °C and 10 mmHg gave the alkyne (**4**) in somewhat variable yield (*ca.* 50%).[6] Although very volatile, boiling at *ca.* −10 °C, the alkyne could be handled satisfactorily in sealed vessels.

*Ethyl 3-formylprop-2-ynoate* (**6**). The first step in the literature preparation of this compound,[7] treatment of propynoic acid with ethyl orthoformate and zinc iodide, is found to give (**5**) in poor yield (10%). However, similar treatment of ethyl propynoate gave a higher yield (50%) of the acetal (**5**) which was converted into the aldehyde (**6**) with anhydrous formic acid.[7]

*Hex-3-yne-2,5-dione* (**7**). A satisfactory preparation of this compound has not been reported. Acheson *et al.*[8] showed that earlier methods were poor, and produced mixtures of the diketone (**7**) (up to 11%) and the corresponding keto alcohol (41%) in the oxidation of a mixture of hex-3-yne-2,5-diol and

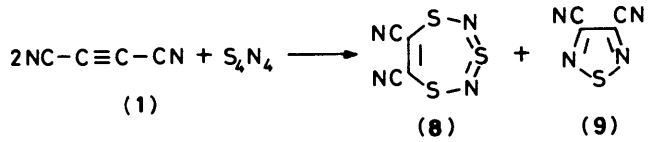



2-hydroxy-hex-3-yn-5-one with chromic acid at 0 °C. We find that if the oxidation of the diol is conducted at 40 °C the yield of diketone (**7**) is increased to 35% and the keto alcohol decreased to 15%; fractional distillation of the diketone is then practicable and it can be isolated in much improved yield (30%) and purity.

*Reaction of Alkynes with* $S_4N_4$.—In contrast to previous reactions of alkynes with $S_4N_4$,[2,9] butynedinitrile (**1**) reacted very cleanly to give 1,3,5,2,4-trithiadiazepine-6,7-dicarbonitrile (**8**) and 1,2,5-thiadiazole-3,4-dicarbonitrile (**9**) in high yield, with the stoicheiometry shown; strikingly almost no sulphur is formed and all the $S_4N_4$ is incorporated into the organic products. As seen in Table 1 the yields of the trithiadiazepine (**8**) are uniformly high at temperatures from 65—120 °C, and the conversions of $S_4N_4$ are also high in the presence of an excess of the acetylene. At the lower temperature $S_4N_4$ is undissociated and it is presumably the species reacting with the alkyne, rather

**Table 1.** Reaction of $S_4N_4$ with butynedinitrile (**1**) to give trithiadiazepine-6,7-dicarbonitrile (**8**)

| Butynedinitrile (Equiv.) | Temp. (°C) | Time (h) | Solvent (%) | Yield (%) | Conversion (%) |
|---|---|---|---|---|---|
| 4 + 2 | 65 | 10 + 6 | $C_6H_6$ | 70 | 60 |
| 3 | 80 | 6 | $C_6H_6$ | 70 | 35 |
| 4 + 2 | 80 | 6 + 6 | $C_6H_6$ | 75 | 75 |
| 2 | 120 | 12 | $C_6H_6$ | 90 | 50 |
| 3 | 120 | 6 | $CH_2Cl_2$ | 80 | 80 |





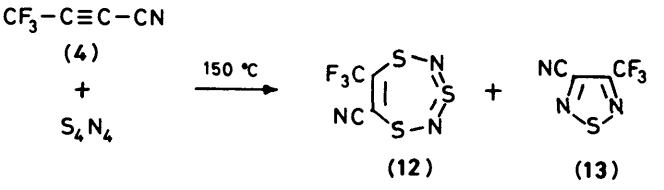
than one of its dissociation products, like $S_2N_2$. Aluminium trichloride does not catalyse this cycloaddition reaction at 20 °C or 40 °C which is striking since it catalyses the high yielding cycloaddition of butynedinitrile to benzene at 20 °C.[10]

The structure of the trithiadiazepine (**8**) was assigned by comparison of its spectral properties with those of other trithiadiazepines,[2,3] and confirmed by *X*-ray diffraction analysis.[11] Characteristically it exhibited long wavelength u.v. absorption at 325 nm (log ε 3.31) for the aromatic system, strong i.r. absorption at 1 180 $cm^{-1}$ for the N=S=N unit, and trithiadiazepine mass spectral fragmentation with loss of NS and the presence of NS, $NS_2$, and $N_2S_3$ fragments.

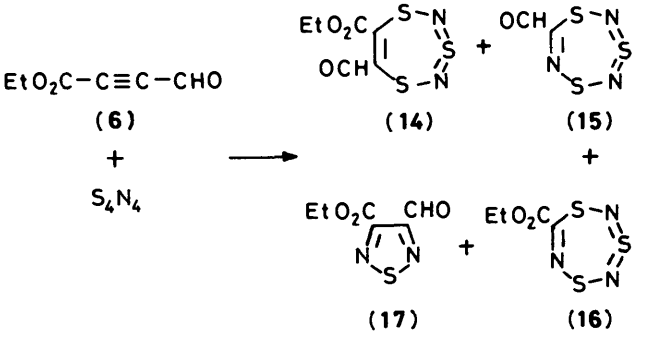
The reactions of $S_4N_4$ with dicyanoacetylene and with hexafluorobutyne (see below) were reported by Josey[12] in a preliminary account almost 20 years ago to give products assigned the bicyclic structures [(**11**) R = CN and $CF_3$ respectively]. However these structures are inconsistent with the thermal stability and spectroscopic properties of the products, which are now shown to be the aromatic trithiadiazepines (**8**) and (**10**).

Hexafluorobut-2-yne reacted very cleanly with $S_4N_4$, in dichloromethane at 125—140 °C, to give the bis(trifluoromethyl)trithiadiazepine (**10**) as the only organic product isolated; the corresponding thiadiazole was presumably formed as well, but this would be very volatile and readily lost. Trithiadiazepine (**10**) was isolated pure by direct distillation from the reaction mixture. Its yield increased with temperature, from 42% at 125 °C to 52% at 140 °C; it was not formed at 100 °C, hexafluorobutyne being much less reactive than butynedinitrile towards $S_4N_4$. Its structure was assigned by comparison of its spectroscopic properties [$\lambda_{max.}$ 329 nm (log ε 3.59), $\nu_{max.}$ 1 165s, and *m/z* for loss of NS, and for NS, $NS_2$, and $N_2S_3$ fragments] with those of the dicyanide (**8**).

The unsymmetrical trifluorobutynonitrile (**4**), intermediate between the above two alkynes, was studied next. With $S_4N_4$ at 150 °C in dichloromethane it gave the trithiadiazepine (**12**) in good yield (40%) together with the 1,2,5-thiadiazole (**13**) (30%). Again the reaction was clean though some sulphur was formed. The cyanide (**13**) was synthesised independently from the corresponding ethyl ester *via* the amide.

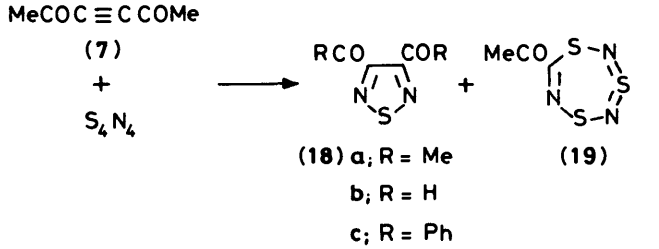



With the next alkyne, ethyl 3-formylprop-2-ynoate (**6**), bearing less strongly electron-withdrawing groups, the $S_4N_4$ reaction was considerably more complex. Several products, including (**14**)—(**17**), were formed, mostly in very low yields, reminiscent of the corresponding DMAD reaction.




In boiling toluene the expected trithiadiazepine (**14**) (14%) and thiadiazole (**17**) (33%) were formed, together with very minor amounts (*ca.* 1%) of the two possible trithiatriazepines (**15**) and (**16**) and an unidentified purple product. When the reaction temperature was raised to 156 °C (boiling bromobenzene) the yields of the seven-membered heterocycles were virtually unchanged, but much less thiadiazole (**17**) and more of the purple product were formed.

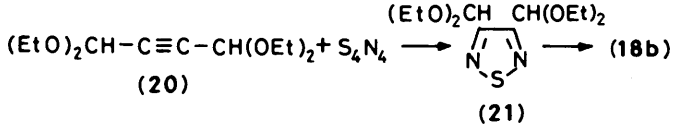
Thus a change of the alkyne substituents from cyano and trifluoromethyl to formyl and ethoxycarbonyl represents a cut-off in the simple reactions which gave high yields of trithiadiazepines. This trend is continued with diacetylacetylene (**7**) whose reaction with $S_4N_4$ gave no detectable amount of 6,7-diacetyl-1,3,5,2,4-trithiadiazepine, although the alkyne is distinctly more reactive than DMAD. Its reaction with $S_4N_4$ proceeds even at 60 °C, though very slowly, and is increasingly rapid in boiling benzene, toluene, and bromobenzene, being complete in about 1 h at the highest temperature. However the nature and yields of the products vary little over this temperature range.




The major product is 3,4-diacetyl-1,2,5-thiadiazole (**18a**) (30%), together with 7-acetyl-1,3,5,2,4,6-trithiatriazepine (**19**) (*ca.* 6%) and a very minor purple product analogous to that mentioned above. The complete absence of the trithiadiazepine is striking since, up to this point, all alkynes with electron-withdrawing groups had given some trithiadiazepine in their reactions with $S_4N_4$.

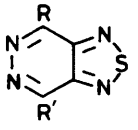
The reaction of butynedial and $S_4N_4$ was even more complex and only the 1,2,5-thiadiazole (**18b**) (*ca.* 20%) could be isolated.

The reaction was further complicated by the difficulty of isolating and purifying the highly reactive dialdehyde, generated from its bis(ethyl acetal) with formic acid;[7] the dialdehyde had to be used in formic acid as co-solvent, with dichloromethane or 1,2-dichloroethane, and this acid was shown to complicate the $S_4N_4$-DMAD reaction seriously. In boiling dichloromethane 8 mol equiv. of dialdehyde were needed to react with 1 mol equiv. of $S_4N_4$ and in dichloromethane 5 mol equiv. were required. The outcome was the same however, a low yield of thiadiazole dialdehyde (**18b**), a potentially useful intermediate for the synthesis of fused thiadiazoles. Earlier attempts at the preparation of this compound from 3,4-disubstituted thiadiazoles had failed.[13] We now find that an excellent route to the dialdehyde is afforded by the reaction of $S_4N_4$ with 1,1,4,4-tetraethoxybutyne (**20**) to give the thiadiazole (**21**) (86%) which is hydrolysed by a combination of aqueous sulphuric acid on silica followed by aqueous trifluoroacetic acid in 85% yield. The dialdehyde (**18b**) is a stable crystalline solid, readily oxidised on exposure to air; it gave the known diacid[14] on oxidation with potassium permanganate.




1,2,5-*Thiadiazolo*[3,4-d]*pyridazines*.—The above 3,4-dioxo-1,2,5-thiadiazoles (**17**) and (**18a**—**c**) should cyclise with hydrazine to form the corresponding thiadiazolopyridazines, and thus confirm the structures proposed for them. This is desirable since 1,2,3- and 1,2,4-thiadiazoles have also been reported, though usually as minor products, in $S_4N_4$-alkyne reactions.[9]

The diacetylthiadiazole (**18a**) was shown by its spectroscopic properties to be symmetrical and so the only other thiadiazole structure possible for it would be the 2,5-diacetyl-1,3,4 isomer which could not undergo this cyclisation reaction. Product (**18a**) and ethanolic hydrazine hydrate reacted rapidly and quantitatively to give 4,7-dimethyl-1,2,5-thiadiazolo[3,4-*d*]-pyridazine (**22a**). Similarly the formyl ester (**17**) gave the corresponding thiadiazolopyridazinone quantitatively. In DMSO this product appeared to exist largely in the phenolic form (**22b**), in view of the low field signal at 13 p.p.m. in its $^1H$ n.m.r. spectrum in this solvent. However in the solid state, strong carbonyl absorption (1 680 $cm^{-1}$) indicates predominance of the more usual oxo form.




(**22**) **a**; R = R′ = Me
**b**; R = H, R′ = OH
**c**; R = R′ = Ph
**d**; R = R′ = H

3,4-Dibenzoyl-1,2,5-thiadiazole (**18c**)[9] reacted quantitatively with hydrazine to give the diphenylthiadiazolopyridazine (**22c**). The analogous reaction of the thiadiazole dialdehyde (**18b**) gave the parent thiadiazolopyridazine (**22d**), though, in contrast with its derivatives which are stable high melting solids, this is a rather reactive low-melting solid which is sensitive to covalent hydration.[15] In this last respect it is similar to the isomeric 1,2,5-thiadiazolo[3,4-*b*]pyrazine.[16] 1,2,5-Thiadiazolo-[3,4-*d*]pyridazines have been very little investigated, the few previously reported derivatives having oxo, thio, or amino groups on the pyridazine ring.[17]

**Table 2.** Yield (%) of the 1,3,5,2,4-trithiadiazepine derivative in the reaction of the alkyne shown with $S_4N_4$

| | |
|---|---|
| NCC≡CCN | 80[a] |
| $CF_3C{\equiv}CCF_3$ | 52[a] |
| $CF_3C{\equiv}CCN$ | 40[a] |
| $EtO_2CC{\equiv}CCHO$ | 14[a] |
| $MeO_2CC{\equiv}CCO_2Me$ | 5[b] |
| $Bu^tO_2CC{\equiv}CCO_2Bu^t$ | 4[c] |
| $HC{\equiv}CCO_2Me$ | 2[d] |
| $PhC{\equiv}CCO_2Me$ | 2[d] |
| PhC≡CPh | 0[d] |

[a] This work. [b] Refs. 2 and 9. [c] Ref. 3. [d] Refs. 9 and 18.

*Formation of* 1,3,5,2,4-*Trithiadiazepines*.—The above results, taken with those in the literature,[2,9,18] show three categories of alkynes in these reactions with $S_4N_4$. Firstly, alkynes with two strongly electron-withdrawing groups (CN, $CF_3$) react cleanly with the stoicheiometry of equation (1) to give trithiadiazepines and thiadiazoles in high yield.*

$$S_4N_4 + 2\,YC{\equiv}CY \longrightarrow Y_2C_2N_2S_3 + Y_2C_2N_2S \quad (1)$$

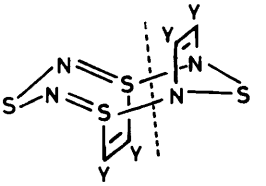
$$S_4N_4 + 2\,RC{\equiv}CR \longrightarrow 2R_2C_2N_2S + \tfrac{1}{4}S_8 \quad (2)$$

Secondly, alkynes with much less polar groups, such as phenyl, *p*-tolyl, diethoxymethyl, and benzoyl, react with the stoicheiometry of equation (2) to give 1,2,5-thiadiazoles in high yield. Thirdly, alkynes in between these two extremes, with one or two more weakly electron-withdrawing groups (*e.g.* $HC{\equiv}CCO_2Me$, $PhC{\equiv}CCO_2Me$, $OCHC{\equiv}CCO_2Et$, $MeO_2CC{\equiv}CCO_2Me$, and $MeCOC{\equiv}CCOMe$) give more complex reactions with a wide range of low yield products including the above, together with trithiatriazepines, and 1,2,4- and 1,2,3-thiadiazoles.

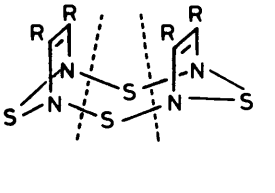
The resulting trend in trithiadiazepine formation is shown in Table 2. The best yield is obtained with butynedinitrile since this is so reactive that cycloaddition occurs at temperatures (65—120 °C) at which the $S_4N_4$ is thermally stable. The yields with the two fluoroalkynes are reduced by competing thermolysis of $S_4N_4$ at the temperatures (140—150 °C) needed for a reasonable cycloaddition rate.

For the first category the simplest mechanism leading to the formation of trithiadiazepine and 1,2,5-thiadiazole is 1,5-cycloaddition of the alkyne to S(1)–S(5) followed by 1,3-cycloaddition to N(2)–N(4), or *vice versa*, and dissociation of the 2:1-adduct (**23**) so formed.[2]

Similarly, for the second category 2 mol equiv. of thiadiazole would be formed by 1,3-cycloaddition to N(2)–N(4) and



(**23**)



(**24**)

* For these alkynes the yield of thiadiazole was calculated on the basis of equation (1); for all others the yield was based on equation (2).

N(6)–N(8) with cleavage of the 2:1-adduct (**24**) into the thiadiazole and sulphur. With the intermediate groups, where the energetics are more finely balanced (see below), both of these and other possible pathways, including 1,2-cycloaddition,[2] can complete with each other to complicate the picture.

Thus, the simplest overall mechanistic rationalisation would be initial 1,3-dipolar cycloaddition across nitrogen by the non-polar alkynes and initial 1,5-dipolar cycloaddition across sulphur by the electron deficient alkynes. There is also a third possibility, 1,3-dipolar cycloaddition across sulphur, which is observed in the reaction of $S_4N_4$ with strained alkenes like norbornadiene.[19]

The question of regioselectivity in these cycloadditions has been analysed by MO theory.[20] The calculations show that the highest occupied molecular orbitals ($3a_2$, $4b_1$, and $8b_2$) of $S_4N_4$ are almost degenerate, and group theory suggests that only two of these ($4b_1$ and $3a_2$) have the correct symmetry for overlap with the alkyne LUMO. Overlap with orbital $4b_1$ leads to 1,5-addition to sulphur whereas overlap with $3a_2$ leads to 1,3-addition to nitrogen. Hence both modes are possible, and almost equally favoured. The very high reactivity of butynedinitrile towards $S_4N_4$ is explained[20] by its LUMO being polarised away from the central triple bond towards the nitrogen atoms such that it overlaps very effectively with the $4b_1$ orbital on $S_4N_4$ leading to initial C–S bond formation, as suggested above.

## Experimental

For general points see reference 2. Distillations of small quantities of material were carried out in a Kugelrohr apparatus and boiling points refer to the oven temperature. All reactions of $S_4N_4$ were run under nitrogen.

*Preparation of Alkynes.*—(*a*) 4,4,4-*Trifluorobut*-2-*ynonitrile* (**4**). Cyanomethylene triphenylphosphorane (**2**)[5] (18 g, 60 mmol) and benzene (200 ml) were placed in a flask fitted with a solid carbon dioxide–alcohol condenser. Trifluoroacetyl chloride (4 g, 30 mmol) was passed into the reaction mixture which was stirred for 2 h under nitrogen and then heated to 80 °C for 1 h. The precipitate was filtered off, the solid washed with warm benzene (3 × 40 ml, 40 °C), and the benzene portions evaporated to give a yellow solid which was recrystallised from methanol to give the betaine (**3**) (**10** g, 84%), m.p. 192—195 °C (lit.,[6] 187—188 °C). Pyrolysis of the betaine (**3**) (1.79 g, 4.5 mmol) at 260 °C/10 mmHg for 0.75 h gave the title compound (**4**) (0.268 g, 50%) which was collected at −195 °C. This alkyne (**4**) is very volatile and subsequent reactions were performed in sealed glass tubes. The material was transferred in dichloromethane solution at −78 °C.

(*b*) *Ethyl* 3-*formylprop*-2-*ynoate* (**6**). Ethyl propynoate (25 g, 255 mmol), triethyl orthoformate (55 g, 37 mmol), and zinc iodide (1 g) in a fractional distillation apparatus (with a 25 $cm^3$ packed column) were carefully heated for 3 h to maintain the distillate temperature at 75—95 °C. The thick brown residue was poured into light petroleum (250 ml) and filtered. Evaporation of the filtrate followed by fractional distillation of the residue gave triethyl orthoformate (23.0 g), b.p. 40—50 °C/20 mmHg, followed by ethyl 4,4-diethoxybut-2-ynoate (**5**) (26.5 g, 51%), b.p. 117 °C/7 mmHg (lit.,[7] 77—78 °C/0.6 mmHg). Conversion into the formyl ester (**6**)[7] was carried out using anhydrous formic acid. This process was conveniently followed by $^1H$ n.m.r. spectroscopy.

(*c*) *Hex*-3-*yne*-2,5-*dione* (**7**). A solution of chromium(VI) oxide (63.4 g, 634 mmol) in water (320 ml) and concentrated sulphuric acid (56 ml) was added to hex-3-yne-2,5-diol (35.5 g, 31 mmol) in acetone (250 ml) at 40—45 °C over 1.5 h and stirred at this temperature for 1.25 h. The dark green solution was extracted with ether (4 ×) and the combined ether portions were washed with saturated aqueous sodium hydrogen carbonate water, and brine, dried ($MgSO_4$), and evaporated to give a yellow oil (17.5 g) shown by $^1H$ n.m.r. to be a mixture of the dione (**7**) and 2-hydroxy-hex-3-yn-5-one (7:3). Fractional distillation (receivers at −78 °C) gave hex-3-yne-2,5-dione (**7**) (10.3 g, 30%), b.p. 25—50 °C/0.2 mmHg (lit.,[21] 26—38 °C/0.1 mmHg); $\delta_H$ (90 MHz, $CDCl_3$) 2.45 (s, COMe); followed by 2-hydroxy-hex-3-yn-5-one (3.85 g, 11%), b.p. 50—75 °C/0.2 mmHg (lit.,[8] 50—75 °C/0.2 mmHg); $\delta_H$ (90 MHz, $CDCl_3$) 1.55 [3 H, d, C(OH)Me], 2.38 (3 H, s, COMe), 2.65 (1 H, br s, OH), and 4.72 (1 H, q, CH).

*Reactions of Tetrasulphur Tetranitride with Alkynes.*—(*a*) *With butynedinitrile.* $S_4N_4$ (0.644 g, 3.5 mmol), butynedinitrile (0.800 g, 10.5 mmol), and dichloromethane (30 ml) were heated in a sealed glass tube for 6 h at 120 °C. The dichloromethane was evaporated and the residue connected to a cold trap (−78 °C) and evacuated (2 mmHg) for 0.25 h. Unchanged butynedinitrile and dichloromethane collected in the cold trap. Sublimation at 45 °C/3 mmHg onto a carbon dioxide–alcohol cooled cold finger gave 1,2,5-thiadiazole-3,4-dicarbonitrile (**9**) (0.284 g, 60%) as plates, m.p. 50—51 °C (lit.,[22] 49.5—50.5 °C; $\nu_{max.}(CCl_4)$ 2 250w (CN), 1 390m, 1 285m, 1 140s, and 850s $cm^{-1}$; $\delta_C(CDCl_3)$, 136.8 (2 × ring carbon) and 108.9 (2 × CN); *m/z* (120 °C) 136 ($M^+$, 88%), 84 (100), and 57 (53). Spectroscopic properties were identical with those of an independently prepared sample.[22] The residue was separated by dry flash chromatography on silica (45 g) using gradient elution. Dichloromethane (5—10%) in light petroleum eluted sulphur (0.15 g, 3%); dichloromethane (60—80%) in light petroleum eluted a mixture of the thiadiazole (**9**) and the trithiadiazepine (**8**) (0.731 g). Recrystallisation from light petroleum gave 1,3,5,2,4-*trithiadiazepine*-6,7-*dicarbonitrile* (**8**) (0.565 g, 81%), m.p. 140 °C, as needles (Found: C, 23.8; N, 28.0; S, 47.7. $C_4N_4S_3$ requires C, 24.0; N, 28.0; S, 48.0%); $\lambda_{max.}$(EtOH) 268 (log ε 4.18), 275 (4.16), and 325 nm (3.31); $\nu_{max.}(CCl_4)$ 2 200m (CN), 1 460w, 1 180s (NSN), 1 055 m, and 675s $cm^{-1}$; $\delta_C$ (62.9 MHz, $CDCl_3$) 125.4 (2 × ArC) and 110.8 (2 × CN); *m/z* (160 °C) 202 ($M^+$ + 2, 14%), 200 ($M^+$, 100), 154 ($M^+$ − NS, 25), 124 ($N_2S_3$, 71), 78 ($NS_2$, 95), and 46 (NS, 80). Similar reactions at other temperatures gave results summarised in Table 1.

(*b*) *With hexafluorobut*-2-*yne.* $S_4N_4$ (0.368 g, 2 mmol), hexafluorobut-2-yne (0.67 g, 4.14 mmol) and dichloromethane (25 ml) were heated in a sealed glass tube at 140 °C for 12 h. The solvent was evaporated and the residue distilled to give 6,7-*bis*(*trifluoromethyl*)-1,3,5,2,4-*trithiadiazepine* (**10**) (0.295 g, 52%), b.p. 60—70 °C/50 mmHg (Found: C, 16.9; N, 10.1%; $M^+$, 285.9134. $C_4F_6N_2S_3$ requires C, 16.8; N, 9.8%; *M*, 285.9128); $\lambda_{max.}$(EtOH) 255 (log ε 4.13) and 329 nm (3.59); $\nu_{max.}$(neat) 1 460w, 1 235s, 1 165s, 1 035w, 1 005w, 865w, 715m, 680m, and 630m $cm^{-1}$; $\delta_F$ (84.6 MHz, $CDCl_3$, standard $CFCl_3$) +49.8 (s, 2 × $CF_3$); $\delta_C$ (62.9 MHz, $CDCl_3$) 121.5 (qq, *J* 287 and 7 Hz, 2 × $CF_3$) and 138.1 (m, 2 × ArC); *m/z* (130 °C) 288 ($M^+$ + 2, 9%), 286 ($M^+$, 63), 240 ($M^+$ − NS, 20), 124 ($N_2S_3$, 37), 113 (28), 78 ($NS_2$, 100), 69 ($CF_3$, 34), and 46 (NS, 74). Chromatography of the residue gave only sulphur.

Repeating the same procedure at 125 °C gave trithiadiazepine (**10**) (29%): $S_4N_4$ (30%) was recovered.

(*c*) *With* 4,4,4-*trifluorobut*-2-*ynonitrile* (**4**). The alkyne (**4**) (0.268 g, 2.25 mmol) was collected in a receiver cooled by liquid nitrogen. It was transferred in cold dichloromethane (20 ml, −78 °C) to a tube containing $S_4N_4$ (0.138 g, 0.75 mmol) and dichloromethane (20 ml). The tube was sealed and heated in an oven at 140—150 °C for 6 h. The solvent was evaporated and the flask containing the residue fitted to a one piece distillation apparatus with a receiver cooled to −78 °C. The apparatus was evacuated (2 mmHg) and 4-*trifluoromethyl*-1,2,5-*thiadiazole*-3-*carbonitrile* (**13**) (0.040 g, 30%), identical with independently synthesised material (see below), collected in the receiver as a

volatile yellow oil; $\nu_{max.}(CCl_4)$ 1 485m, 1 425m, 1 250s, 1 200s, 1 170s, and 1 050s $cm^{-1}$; $\delta_F$ (84.6 MHz, $CDCl_3$, standard $CFCl_3$) +62.2 (s, $CF_3$); *m/z* (40 °C) 179 ($M^+$, 100%), 160 ($M^+ - F$, 10), 127 [$M^+ - (CN)_2$, 37], 84 [$M^+ - (CN + CF_3)$, 42] and 69 ($CF_3$, 52). The residue was separated by dry flash chromatography on silica (25 g) using gradient elution. Dichloromethane (5—20%) in light petroleum eluted sulphur; dichloromethane (45—55%) in light petroleum eluted *7-trifluoromethyl-1,3,5,2,4-thiadiazepine-6-carbonitrile* (**12**) (0.073 g, 40%) as plates, m.p. 66—67 °C (light petroleum) (Found: $M^+$, 242.9200. $C_4F_3N_3S_3$ requires *M*, 242.9206); $\lambda_{max.}$(EtOH) 257 (log ε 4.23), 263sh (4.21), and 326 nm (3.46); $\nu_{max.}(CHCl_3)$ 2 220m (CN), 1 155s, 1 065w, and 960w $cm^{-1}$; $\delta_F$ (84.6 MHz, $CDCl_3$, standard $CFCl_3$) +54.0 (s, $CF_3$); $\delta_C$ (62.9 MHz, $CDCl_3$) 110.2 (s, CN), 117.8 (s, C-6), 121.1 (q, *J* 281 Hz, $CF_3$), and 143.7 (q, *J* 29 Hz, C-7); *m/z* (110 °C) 245 ($M^+ + 2$, 11%), 243 ($M^+$, 80), 197 ($M^+ - NS$, 20), 124 ($N_2S_3$, 68), 113 (12), 82 (12), 78 ($NS_2$, 100), 69 ($CF_3$, 30), and 46 (NS, 100).

(*d*) *With ethyl 3-formylprop-2-ynoate* (**6**). $S_4N_4$ (0.920 g, 5 mmol), the alkyne (**6**) (3.30 g, 26 mmol), and toluene (50 $cm^3$) were heated at reflux for 8 h. The solvent was evaporated off and the residue separated by *rapid* dry flash chromatography on silica (120 g) using gradient elution; the trithiadiazepine (**14**) is unstable to the chromatographic conditions. Dichloromethane (5—25%) in light petroleum eluted sulphur; dichloromethane (50%) in light petroleum eluted a mixture of compounds consisting mainly of *N*-formylheptasulphur imide (Found: $M^+$, 266.8098. $CHNOS_7$ requires *M*, 266.8103); $\nu_{max.}(CCl_4)$ 1 740s; *m/z* (100 °C) 269 ($M^+ + 2$, 14%), 267 ($M^+$, 44), 162 ($S_5 + 2$, 22), 160 ($S_5$, 100), 107 ($M^+ - S_5$, 18), 96 ($S_3$, 18), and 64 ($S_2$, 61). Dichloromethane (55—60%) in light petroleum eluted *1,3,5,2,4,6-trithiatriazepine-7-carbaldehyde* (**15**) (0.010 g, 1%), m.p. 56—58 °C (Found: $M^+$, 178.9276. $C_2NH_3OS_3$ requires *M*, 178.9282); $\lambda_{max.}$(EtOH) 268 and 334 nm; $\nu_{max.}(CCl_4)$ 1 690s, 1 150m, 1 120m, and 990w $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 9.90 (s, CHO); *m/z* (160 °C) 181 ($M^+ + 2$, 13%), 179 ($M^+$, 100), 149 (95), 78 ($NS_2$, 99), 57 (41), and 46 (NS, 57). Dichloromethane (65—70%) in light petroleum eluted *ethyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate* (**16**) (0.012 g, 1%) (Found: $M^+$, 222.9547. $C_4H_5N_3O_2S_3$ requires *M*, 222.9544); $\lambda_{max.}$(EtOH) 264 (log ε 4.26) and 325 nm (3.60); $\nu_{max.}(CCl_4)$ 2 980w, 1 750m, 1 705s (CO), 1 370w, 1 260s, 1 220m, 1 150w, 1 050w, and 665w $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 1.43 (3 H, t, Me) and 4.49 (2 H, q, $CH_2$); *m/z* (100 °C) 225 ($M^+ + 2$, 6%), 223 ($M^+$, 40), 124 ($N_2S_3$, 6), 78 ($NS_2$, 100), 46 (NS, 36), and 29 (CHO, 31). Dichloromethane (75—80%) in light petroleum eluted *ethyl 7-formyl-1,3,5,2,4-trithiadiazepine-6-carboxylate* (**14**) (0.171 g, 14%) as very pale yellow needles, m.p. 46—48 °C [after sublimation (100 °C/1 mmHg)]; (Found: $M^+$, 249.9533. $C_6H_6N_2O_3S_3$ requires *M*, 249.9541); $\lambda_{max.}$(EtOH) 257 (log ε 4.05) and 328 nm (3.51); $\nu_{max.}(CCl_4)$ 2 990w, 1 720s, (ester CO), 1 680s (aldehyde CO), 1 470w, 1 365w, 1 215s, 1 175m, 1 100m, 1 030w, and 1 010m $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 1.51 (3 H, t, Me), 4.57 (2 H, q, $CH_2$), and 10.17 (1 H, s, CHO); $\delta_C$ (62.9 MHz, $CDCl_3$) 14.1 (Me), 64.0 ($CH_2$), 143.0 and 149.7 (2 × ArC), 161.0 (ester CO), and 185.3 (CHO); *m/z* (140 °C) 252 ($M^+ + 2$, 7%), 250 ($M^+$, 46), 222 ($M^+ - CO$, 30), 205 ($M^+ - EtO$, 14), 204 ($M^+ - NS$), 176 [$M^+ - (NS + CO)$, 24], 148 (49), 124 ($N_2S_3$, 12), 104 (21), 78 ($NS_2$, 80), 46 (NS, 64), and 29 (CHO, 100). Dichloromethane (90%) in light petroleum to methanol (3%) in dichloromethane eluted a deep purple compound: methanol (4—10%) in dichloromethane eluted *ethyl 4-formyl-1,2,5-thiadiazole-3-carboxylate* (**17**) (1.5 g) as a black tar purified by bulb to bulb distillation to give a colourless liquid (0.613 g, 33%), b.p. 170 °C/1 mmHg; (Found: C, 38.4; H, 3.3. $C_6H_6N_2O_3S$ requires C, 38.7; H, 3.25%); $\lambda_{max.}$(EtOH) 275 nm (log ε 3.93); $\nu_{max.}(CCl_4)$ 2 980m, 1 750s, 1 725s, 1 710s, 1 450w, 1 420w, 1 380w, 1 300m, 1 230s, and 1 195s $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 1.47 (3 H, t, Me), 4.56 (4 H, q, $CH_2$), and 10.48 (1 H, s, CHO); $\delta_C$ (62.9 MHz, $CDCl_3$) 13.6 (Me), 62.65 ($CH_2$), 153.1, and 157.55, and 159.4 (2 × ArC and ester CO), and 182.2 (CHO); *m/z* (140 °C) 187 ($MH^+$, 12%), 185 ($M^+ - H$, 7), 158 (67), 141 (70), 130 (93), 112 (23), 86 (27), 85 (23), 84 (25), 59 (41), 58 (19), and 29 (100).

When bromobenzene solutions of $S_4N_4$ and the alkyne (**6**) (3 equiv.) were synchronously added to bromobenzene which was being heated at reflux (2 h), products (**15**) (1%), (**16**) (1%), (**14**) (16%), and (**17**) (10%) were isolated.

(*e*) *With hex-3-yne-2,5-dione* (**7**). $S_4N_4$ (0.368 g, 2 mmol), the alkyne (**7**) (0.77 g, 7 mmol), and toluene (50 ml) were heated at reflux for 6 h. Further alkyne (**7**) (0.41 g, 4 mmol) was added and heating at reflux continued for 7 h. The solvent was evaporated and the residue separated by dry flash chromatography on silica (30 g) using gradient elution. Dichloromethane (5—20%) in light petroleum eluted sulphur; dichloromethane (45—50%) in light petroleum eluted *7-acetyl-1,3,5,2,4,6-trithiatriazepine* (**19**) (0.026 g, 7%) as pale yellow plates, m.p. 52—53 °C (from light petroleum) (Found: C, 18.8; H, 1.6; N, 21.6. $C_3H_3N_3OS_3$ requires C, 18.65; H, 1.6; N, 21.7%); $\lambda_{max.}$(EtOH) 273 (log ε 4.10) and 340 nm (3.40); $\nu_{max.}(CCl_4)$ 2 930w, 1 690s, 1 415w, 1 355s, 1 220s, 1 150s, 990m, 925w, 880m, and 665s $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 2.79 (s, Me); $\delta_C$ (62.9 MHz, $CDCl_3$), 26.2 (Me), 160.2 (ArC), and 196.0 (CO); *m/z* (150 °C) 195 ($M^+ + 2$, 9%), 193 ($M^+$, 69), 124 ($N_2S_3$, 27), 78 ($NS_2$, 72), 46 (NS, 36), and 43 (MeCO, 100). Dichloromethane (62.5—65%) eluted a deep purple product; dichloromethane (67.5—85%) eluted *3,4-diacetyl-1,2,5-thiadiazole* (**18a**) (0.201 g, 29%) as needles, m.p. 30—32 °C, b.p. 90 °C/0.5 mmHg, (Found: C, 42.2; H, 3.6; N, 15.6; S, 18.8. $M^+$, 170.0146. $C_6H_6N_2O_2S$ requires C, 42.3; H, 3.85; N, 15.4; S, 18.8%. *M*, 170.0150); $\lambda_{max.}$(EtOH) 225 (log ε 3.67) and 266 nm (3.99); $\nu_{max.}(CCl_4)$ 1 720s, 1 710s, 1 405m, 1 360s, 1 250m, 1 140m, 950m, and 630m $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 2.72 (s, 2 × Me); $\delta_C$ (62.9 MHz, $CDCl_3$) 28.4 (2 × Me), 159.5 (2 × ArC), and 192.9 (2 × CO); *m/z* (120 °C) 170 ($M^+$, 27%), 155 ($M^+ - Me$), and 43 (MeCO, 100).

(*f*) *With butynedial.* $S_4N_4$ (0.115 g, 0.625 mmol) in dichloromethane (70 ml) was treated with a formic acid solution of butynedial, prepared from 1,1,4,4-tetraethoxybut-2-yne (0.575 g, 2.5 mmol) and formic acid (2.9 ml),[7] and heated at reflux for 4 h. The refluxing solution was then treated with further butynedial (2.5 mmol) in formic acid (2.9 ml) and heated at reflux for 3 h. The dichloromethane was evaporated off and the residual formic acid removed by co-evaporation with toluene. The residue was pre-adsorbed onto silica and separated by flash chromatography. Light petroleum eluted $S_4N_4$ (0.008 g, 7%). Dichloromethane eluted a mixture of products purified by further flash chromatography to give *1,2,5-thiadiazole-3,4-dicarbaldehyde* (**18b**) (0.032 g, 19%), m.p. 40—42 °C, b.p. 100 °C/5 mmHg; $\lambda_{max.}$(EtOH) 258 (log ε 4.04) and 335 nm (2.95); $\nu_{max.}(CHCl_3)$ 1 710s $cm^{-1}$ (CO); $\delta_H$ (90 MHz, $CDCl_3$) 10.45 (s, 2 × CHO); $\delta_C$ (62.9 MHz, $CDCl_3$) 158.2 (2 × ArC), and 183.0 (2 × CHO); *m/z* (80 °C) 142 ($M^+$, 5%), 141 ($M^+ - H$, 7), 114 ($M^+ - CO$, 100), 86 ($M^+ - 2CO$, 37), 59 (46), and 29 (CHO, 32).

The dialdehyde (**18b**) (0.060 g, 0.42 mmol) in acetone (10 ml) was treated with potassium permanganate (0.284 g, 1.8 mmol) in aqueous acetone (50 ml, 50%) over 18 h. The reaction was extracted with ether (6 ×) and the combined ether portions were washed once with a small volume of water which was back extracted with ether (2 ×). The combined ether portions were dried ($MgSO_4$) and evaporated to give 1,2,5-thiadiazole-3,4-dicarboxylic acid (0.046 g, 63%), m.p. 173 °C (sub.) (from water) (lit.,[14] 173 °C) (Found: C, 27.7; H, 1.1; N, 16.1. Calc. for $C_4H_2N_2O_4S$: C, 27.6; H, 1.2; N, 16.1%).

(*g*) *With 1,1,4,4-tetraethoxybut-2-yne* (**20**). $S_4N_4$ (0.460 g, 2.5 mmol), the alkyne (**20**)[7] (1.150 g, 5 mmol) and toluene (50 ml) were heated at reflux for 24 h. $S_4N_4$ (0.460 g, 2.5 mmol) was

added and the reaction heated at reflux for 48 h. The solvent was evaporated and the residue pre-adsorbed onto silica and separated by flash chromatography on silica (15 g). Light petroleum eluted sulphur. Dichloromethane–light petroleum (3:1) eluted 3,4-*bis*(*diethoxymethyl*)-1,2,5-*thiadiazole* (**21**) (1.249 g, 86%), b.p. 150 °C/0.25 mmHg (Found: C, 49.7; H, 7.7; N, 9.8; S, 10.9. $C_{12}H_{22}N_2O_4S$ requires C, 49.6; H, 7.6; N, 9.65; S, 11.0%); $\lambda_{max.}$(EtOH) 259 (log ε 3.75) and 337 nm (2.95); $\nu_{max.}$(neat) 2 980s, 2 930m, 2 890m, 1 640m, 1 440m, 1 370m, 1 330m, 1 170s, 1 060s (br), 830m, and 805m $cm^{-1}$; $\delta_H$ (250 MHz, $CDCl_3$) 1.23 (6 H, t, *J* 7.1 Hz, 4 × Me), 3.66 [8 H, 16 line $ABX_3$ spin system ($\delta_{Ha}$ 3.69, $\delta_{Hb}$ 3.62), $J_{ab}$ 9.5 Hz, $J_{ax}$ 7.1 Hz, $J_{bx}$ 7.1 Hz, 2 × (2 × $CH_2$)], and 5.91 (2 H, s, 2 × CH); $\delta_C$ (62.9 MHz, $CDCl_3$) 15.0 (4 × Me), 62.4 (4 × $CH_2$), 97.5 (2 × CH), and 159.3 (2 × ArC); *m/z* (110 °C) 290 ($M^+$, 0.2%), 289 (0.6), 246 (30), 245 ($M^+$ − EtO, 51), 244 (34), 215 (38), 201 (40), 187 (28), 171 (41), 159 (31), 157 (39), 143 (97), 141 (28), 127 (30), 115 (28), 113 (100), 103 (75), 75 (68), and 47 (92).

1,2,5-*Thiadiazolo*[3,4-d]*pyridazines*.—4,7-*Dimethyl*-1,2,5-*thiadiazolo*[3,4-d]*pyridazine* (**22a**). 3,4-Diacetyl-1,2,5-thiadiazole (**18a**) (0.067 g, 0.039 mmol), ethanol (10 ml) and hydrazine hydrate (0.038 g, 0.78 mmol) were stirred at 20 °C for 1.5 h and 40 °C for 1.5 h. Evaporation of the solvent gave the *pyridazine* (**22a**) (0.063 g, 96%) as a yellow powder, m.p. 144—146 °C (Found: C, 43.8; H, 3.6; N, 33.4 $C_6H_6N_4S$ requires C, 43.4; H, 3.6; N, 33.7%); $\lambda_{max.}$(EtOH) 284 nm (log ε 3.95); $\nu_{max.}$($CCl_4$) 1 460s, 1 385s, 1 370m, 1 160m, and 870s $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 3.10 (s, 2 × Me); $\delta_C$ (62.9 MHz, $CDCl_3$) 19.0 (2 × Me), 150.1, and 154.9; *m/z* (170 °C) 166 ($M^+$, 100%), 84 (13), and 73 (26).

1,2,5-*Thiadiazolo*[3,4-d]*pyridazin*-4-*one* (**22b**). The formyl ester (**17**) (0.216 g, 1.16 mmol), hydrazine hydrate (0.13 ml, 2.68 mmol), and ethanol (5 ml) were stirred at 25 °C for 4 h. The precipitate of the *pyridazone* (**22b**) (0.176 g, 98%) was collected as an off-white powder, m.p. 223—225 °C (Found: C, 31.3; H, 1.2; N, 33.6; S, 21.0. $C_4H_2N_4OS$ requires C, 31.2; H, 1.3; N, 33.35; S, 20.8%); $\lambda_{max.}$(EtOH) 241 (log ε 4.08), 260sh (3.67), and 326nm (3.67); $\nu_{max.}$(KBr) 3 320m, br, 3 060w, 2 980w, 1 680s, 1 490w, 1 410w, 1 370w, 1 270m, 1 140w, 910m, 830w, and 790w $cm^{-1}$; $\delta_H$ [250 MHz, $(CD_3)_2SO$] 8.68 (1 H, s, ArH) and 13.05 (1 H, s, OH); *m/z* (210 °C) 154 ($M^+$, 100%), 126 (5), 99 (11), 71 (23), and 45 (33).

4,7-*Diphenyl*-1,2,5-*thiadiazolo*[3,4-d]*pyridazine* (**22c**). 3,4-Dibenzoyl-1,2,5-thiadiazole[9] (**18c**) (0.125 g, 0.425 mmol), ethanol (25 ml), and hydrazine hydrate (0.042 g, 0.85 mmol) were stirred at 25 °C for 4 h. The solvent was evaporated off to give the *pyridazine* (**22c**) (0.120 g, 97%) as orange crystals, m.p. 208.5—209 °C (Found: C, 66.1; H, 3.4; N, 19.2; S, 11.2. $C_{16}H_{10}N_4S$ requires C, 66.2; H, 3.5; N, 19.3; S, 11.0%); $\lambda_{max.}$(EtOH) 256 (log ε 4.42), 290 (4.00), and 372 nm (4.11); $\nu_{max.}$($CHCl_3$) 3 050w, 2 980m, 1 600w, 1 450m, 1 410s, 1 360m, 1 350m, 880s, 860m, and 640s $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 7.5—7.7 (6 H, m,) and 8.5—8.8 (4 H, m); $\delta_C$(62.9 MHz, $CDCl_3$) 128.7, 130.1, 131.1, 134.3, 149.9, and 153.1.

1,2,5-*Thiadiazole*-3,4-*dicarbaldehyde* (**18b**). The bis(ethyl acetal) (**21**) (0.095 g, 0.33 mmol) in dichloromethane (2 ml) was added to a slurry made by adding sulphuric acid (15%; 1 ml) to silica (2 g) mixed with dichloromethane (20 ml) and shaking until the aqueous phase was all adsorbed. The mixture was stirred vigorously for 36 h after which the silica was filtered off and washed with a little dichloromethane the filtrate was then evaporated and the residue dissolved in chloroform (5 ml) and treated with aqueous trifluoroacetic acid (50%, 5 ml) at 25 °C for 12 h with vigorous stirring. Evaporation of the chloroform, trifluoroacetic acid, and water gave the dialdehyde (**18b**) (0.040 g, 85%) identical with that described above.

1,2,5-*Thiadiazolo*[3,4-d]*pyridazine* (**22d**). The dialdehyde (**18b**) (0.40 g, 0.28 mmol), hydrazine hydrate (0.028 g, 0.56 mmol), and ethanol (10 ml) were stirred at 20 °C for 4 h. Evaporation of the solvent gave the *pyridazine* (**22d**) (0.032 g, 83%) as a low-melting solid, b.p. 80 °C/5 mmHg; $\lambda_{max.}$(EtOH) 284 and 343 nm; $\nu_{max.}$($CHCl_3$) 1 560w, 1 340m, 1 105s, 905s, and 895s, $cm^{-1}$; $\delta_H$ (90 MHz, $CDCl_3$) 9.85 (s, 2 × ArH); *m/z* (120 °C) 140 ($M^+$ + 2, 5%), 138 ($M^+$, 100), and 84 (19).

4-*Trifluoromethyl*-1,2,5-*thiadiazole*-3-*carboxamide*. Ethyl 4-trifluoromethyl-1,2,5-thiadiazole-3-carboxylate[23] (0.200 g, 0.88 mmol) was stirred with saturated methanolic ammonia for 10 h at room temperature. Evaporation of the solvent gave the *title compound* (0.165 g, 95%) as needles, m.p. 108 °C (from dichloromethane) (Found: C, 24.5; H, 1.0; N, 21.2. $C_4H_2F_3N_3OS$ requires C, 24.4; H, 1.0; N, 21.3%); $\nu_{max.}$($CHCl_3$) 3 520m, 3 405m, 1 710s (CO), 1 580s, 1 475m, 1 345s, 1 310m, 1 165s, 1 020m, 850m, and 650w $cm^{-1}$; *m/z* (150 °C) 197 ($M^+$, 87%), 181 (73), 154 (100), 69 (25), and 44 (83).

4-*Trifluoromethyl*-1,2,5-*thiadiazole*-3-*carbonitrile* (**13**).—An intimate mixture of 4-trifluoromethyl-1,2,5-thiadiazole-3-carboxamide (0.600 g, 0.30 mmol) and phosphorus pentaoxide (1.5 g) was heated to 120 °C at 50 mmHg for 0.75 h. The title compound (**13**) (0.015 g, 28%) was collected at −78 °C; it was identical with the product from the $S_4N_4$–fluoroalkyne (**4**) reaction described above.

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## References

1 Part 4, J. L. Morris and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 217.
2 S. T. A. K. Daley and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 203.
3 J. L. Morris and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 211.
4 A. J. Saggiomo, *J. Org. Chem.*, 1957, **22**, 1171.
5 S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1959, 3874.
6 Yaeozeng Huang, Yanchang Shen, Weiyu Ding, and Jianhua Zheng, *Tetrahedron Lett.*, 1981, 5283.
7 A. Gorgues, A. Simon, A. LeCoq, A. Hercouet, and F. Corre, *Tetrahedron*, 1986, **42**, 351.
8 R. M. Acheson, M. G. Bite, and M. W. Cooper, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1908.
9 S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, **16**, 1009.
10 E. Ciganek, *Tetrahedron Lett.*, 1967, 3321.
11 R. Jones and D. J. Williams, Department of Chemistry, Imperial College, unpublished results.
12 A. D. Josey, Abstracts of the 155th National Meeting of the American Chemical Society, Division of Organic Chemistry, San Francisco, 1968, p. 14.
13 S. Mataka, M. Kurisu, K. Takahashi, and M. Tashiro, *J. Heterocycl. Chem.*, 1985, **22**, 325.
14 A. M. Khaletsky, V. G. Pesin, and Chzhou Tsin, *Proc. Acad. Sci. U.S.S.R., Chem. Sect.*, (*Engl. Transl.*), 1957, **114**, 593.
15 *cf.* A. Albert, *Adv. Heterocycl. Chem.*, 1976, **20**, 117.
16 A. P. Komin and M. Carmack, *J. Heterocycl. Chem.*, 1976, **13**, 13.
17 D. Pichler and R. N. Castle, *J. Heterocycl. Chem.*, 1971, **8**, 441.
18 S. T. A. K. Daley and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 207.
19 M. R. Brinkman and C. W. Allen, *J. Am. Chem. Soc.*, 1972, **94**, 1550; A. M. Griffin and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 895.
20 P. J. Dunn and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2.*, in the press.
21 S. Goldschmidt and A. Zoebelein, *Chem. Ber.*, 1961, **94**, 169.
22 J. D. Warren, V. J. Lee, and R. B. Angier, *J. Heterocycl. Chem.*, 1979, **16**, 1617.
23 P. J. Dunn and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, following paper.

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