Reaction of trithiazyl trichloride with alkenes and alkynes

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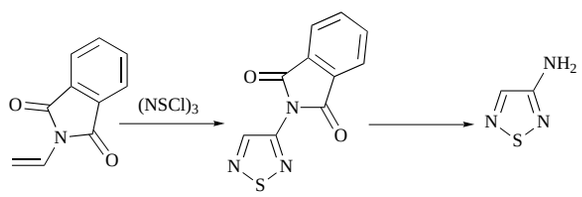
Alkenes and alkynes react readily with trithiazyl trichloride 1 to give 1,2,5-thiadiazoles 2 in one step. Thus 3-amino-1,2,5-thiadiazole 5 is now readily available from *N*-vinylphthalimide and 1 in two steps. Cyclic alkenes react similarly to give fused thiadiazoles (7, 12) and phenanthrene gives the phenanthrothiadiazole 16. Tetra-substituted alkenes such as 13 appear to give the analogous 3,4-dihydrothiadiazoles (*e.g.* 14) which spontaneously ring open to give readily hydrolysed bis(methyleneamino) sulfides (*e.g.* 15). A simple set of mechanisms is proposed for all of these reactions.

One of the simplest and most useful reactions of trithiazyl trichloride, $(NSCl)_3$, **1**[1,2] is with alkenes and alkynes to give 1,2,5-thiadiazoles **2** (Table 1). Early examples of this reaction with *trans*-stilbene and acenaphthylene in boiling chloroform to give 3,4-diphenyl-1,2,5-thiadiazole and the corresponding fused thiadiazole in low to moderate yields were reported by Barton and Bubb.[3] We found that the yield of 3,4-diphenyl-1,2,5-thiadiazole (14%) was increased to 28% upon reaction in boiling toluene, and we have extended the range of alkenes, alkynes and related compounds converted into 1,2,5-thiadiazoles, under mild conditions. Initially the reactants were stirred in benzene at room temperature and if necessary the solution was then heated under reflux to complete the reaction (TLC). The yields of thiadiazoles are shown in Table 1.

The 4-methoxy-4′-nitro derivative of *trans*-stilbene gave a much higher yield than stilbene, indicative of activation by a 'push–pull' effect. Terminal alkynes tended to give low yields of the monosubstituted thiadiazole, apparently because of competing polymerisation of the alkyne, together with minor amounts of the 3-substituted 4-chlorothiadiazole. Dimethyl maleate gave a reasonable yield of the heterocycle but dimethyl fumarate and fumaronitrile did not react with the trimer **1**.

We applied this one-pot alkene–trimer reaction to the synthesis of 3-amino-1,2,5-thiadiazole **5** which would be a useful intermediate in thiadiazole chemistry if it were more readily available (Scheme 1). It has been prepared[4] from aminoacetamidine and S_2Cl_2, but the synthesis of the amidine



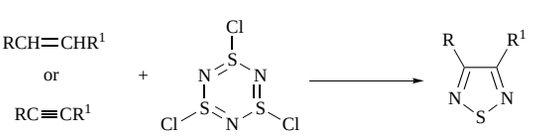
3 **4** **5**

Scheme 1

requires four steps and the S_2Cl_2 reaction can give problems. Treatment of commercially available *N*-vinylphthalimide **3** with trimer **1** in refluxing toluene in the presence of 4 Å molecular sieves gave 3-phthalimido-1,2,5-thiadiazole **4**, but only in 17% yield. HRMS and microanalysis indicated the formula $C_{10}H_5N_3O_2S$. Ready loss of HCN from the molecular ion, and the ^1H and ^{13}C NMR spectra, further supported the 4-unsubstituted thiadiazole structure **4**. The yield of **4** was higher in dioxane (35%) and in THF (38%), both with 4 Å molecular sieves. We have found that trimer **1** reactions are often improved by the presence of molecular sieves; we assume that these remove traces of water from the solvent, and thus minimise hydrolysis of the reagent, and also serve to adsorb the hydrogen chloride formed in the reactions.

The phthalimide group was rapidly removed with methylhydrazine in benzene at room temperature to give the amine

Table 1 Reaction of alkenes and alkynes with $(NSCl)_3$ in benzene



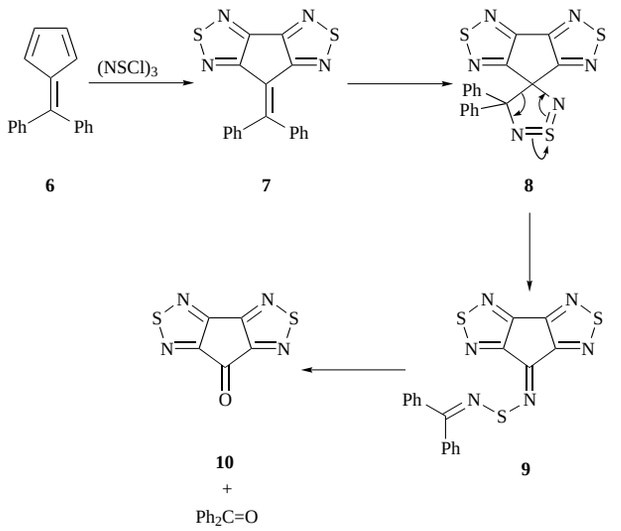
1 **2**

Alkene or alkynes	**2**	R	R^1	Yield (%)
(*E*)-Ph–CH=CH–Ph	**a**			28[a]
(*E*)-4-$O_2NC_6H_4$CH=CH–C_6H_4-4-OMe	**b**	4-$MeOC_6H_4$	4-$O_2NC_6H_4$	69
(*E*)-PhCO–CH=CH–COPh	**c**	PhCO	PhCO	42
(*Z*)-MeO_2C–CH=CH–CO_2Me	**d**	CO_2Me	CO_2Me	52
Ph–C≡C–Ph	**e**	Ph	Ph	32
Ph–C≡C–H	**f**	Ph	H	62
MeO_2C–C≡C–CO_2Me	**d**	CO_2Me	CO_2Me	84
4-$O_2NC_6H_4$C≡C–H	**g**	4-$O_2NC_6H_4$	H	62
4-$MeOC_6H_4$C≡C–H	**h**	4-$MeOC_6H_4$	H	14
3,4-$(MeO)_2C_6H_3$C≡C–H	**i**	3,4-$(MeO)_2C_6H_3$	H	14

[a] In toluene.

5 as a light yellow oil in 90% yield. The overall yield of **5** (34%) over two steps compares favourably with the literature method.[4]

In view of the ease with which trimer **1** converts monoenes into 1,2,5-thiadiazoles, we decided to extend the reaction to polyenes. 6,6-Diphenylfulvene **6** was treated with the reagent (2 equiv.) in refluxing tetrachloromethane overnight; the analogous bis-thiadiazole **7** was isolated (26%) as a brown–yellow crystalline solid, mp 209–210 °C (Scheme 2).



6 **7** **8** **9** **10** + $Ph_2C{=}O$

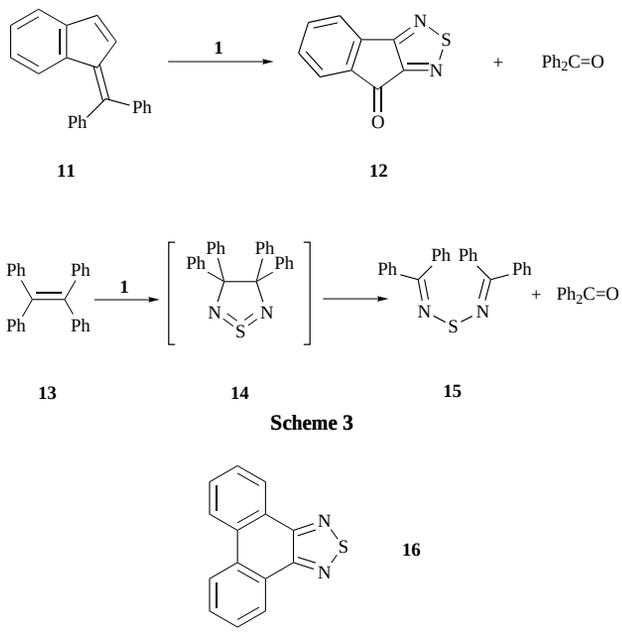
Scheme 2

The mass spectrum and microanalysis of the product showed it to be $C_{18}H_{10}N_4S_2$ and the spectroscopic data supported its highly symmetrical structure. The mono-thiadiazole, a presumed intermediate on the way to **7**, was not observed. The remaining carbon–carbon double bond in **7** is tetrasubstituted and cannot give an aromatic 1,2,5-thiadiazole with trimer **1**, but it was interesting to see if **1** would react with this double bond. The diphenylfulvene **6** was treated with 3 equiv. of **1** under more vigorous conditions, in refluxing toluene. After chromatography we isolated the bis-thiadiazole **7** (16%), the ketone **10** (21%) and benzophenone (18%). Formation of the two ketones suggested hydrolytic cleavage of an intermediate, possibly the bis(methyleneamino) sulfide **9**, which could have been formed from the fulvene–trimer cycloadduct **8** (see Scheme 2). This could readily undergo ring opening, as shown, driven in part by the covalency change of sulfur from 4 to 2. The ketone **10** is a heterocyclic analogue of fluorenone; it showed a strong carbonyl absorption at ν_{max} 1767 cm^{-1} in the IR spectrum, a strong fragment peak at *m*/*z* 168 (100%) corresponding to the loss of CO, and ^{13}C NMR signals at 171, 167 and 162 ppm, all consistent with the proposed structure.

The benzo derivative **11** of fulvene **6** was treated with trimer **1** (1.5 equiv.) in boiling tetrachloromethane and two major products were obtained. One was benzophenone (23%) and the other was 8*H*-indeno[1,2-*c*][1,2,5]thiadiazol-8-one **12** (66%) as a yellow crystalline solid which was identical with the product of the reaction of indan-1-one with S_4N_4 in boiling toluene (10%).[5] Thus the reagent has apparently attacked the exocyclic, as well as the endocyclic double bond, followed by hydrolysis on work-up, exactly as for the conversion of **7** into **10** above.

To test this proposed pathway, tetraphenylethene **13** was treated with $(NSCl)_3$ under the same conditions as **11** (Scheme 3). It reacted in the same way *via* **14**, though more slowly, but now the acyclic N–S–N intermediate, bis(diphenylmethyleneamino) sulfide **15**,[6] was stable enough to be isolated (13%). Its hydrolysis product, benzophenone, was also obtained (16%) together with unreacted **13** (30%).

Finally the reaction between $(NSCl)_3$, and the aromatic compound phenanthrene was investigated. The expected product,



11 **12**

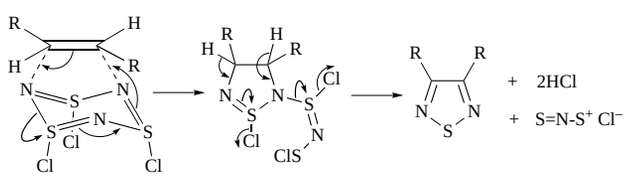
13 **14** **15**

Scheme 3

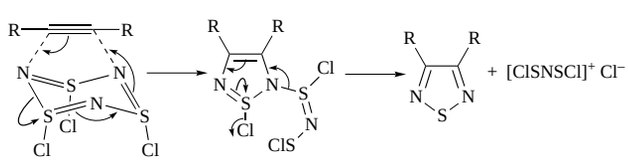
16

phenanthro[9,10-*c*][1,2,5]thiadiazole **16** has been prepared in low yield (*ca.* 10%) by heating 9,10-dihydrophenanthrene with S_4N_4 in xylene[7] and 10-diazophenanthren-9-one with S_4N_4 in toluene.[8] The reaction between trimer (3 equiv.) and phenanthrene was slow in boiling tetrachloromethane; after 2 days 54% of the hydrocarbon was recovered but 32% of thiadiazole **16** could be isolated.

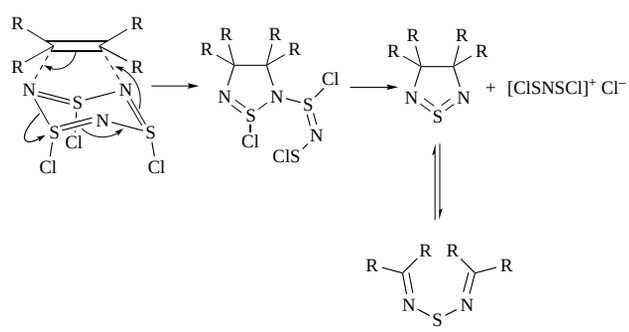
It is possible to propose a simple set of mechanisms for these $(NSCl)_3$ reactions based upon its electrophilic attack on, or cycloaddition to, the carbon–carbon double or triple bond. Since an N–S–N unit is transferred in each case we assume that the reacting species is the intact trimer **1**. The conversion of an alkene and an alkyne into 1,2,5-thiadiazoles are shown in Schemes 4 and 5, respectively. The cations $[SNS]^+$ and $[ClSNSCl]^+$, liberated from the initial adducts in the aromatis-



Scheme 4



Scheme 5



Scheme 6

ation reactions, are known species.[9] A slight variant on these mechanisms is shown in Scheme 6 for the reaction of a tetrasubstituted alkene to give a 3,4-dihydro-1,2,5-thiadiazole as observed in the reactions of **7**, **11** and **13**.

Experimental

For general details see earlier parts in this series.[2]

3-Phenyl-1,2,5-thiadiazole 2f

To a stirred solution of trithiazyl trichloride (244 mg, 1 mmol) in benzene (4 ml), phenylacetylene (102 mg, 109 μl, 1 mmol) in benzene (1 ml) was added at 6–7 °C by syringe, under nitrogen. The mixture turned green during the addition. The mixture was stirred at ambient temperature under nitrogen for 87 h. The resulting red solution was evaporated and the residue was separated on silica gel by chromatography. Elution with dichloromethane (45%) in light petroleum gave a minor product as an oil. Its structure was tentatively assigned as 3-chloro-4-phenyl-1,2,5-thiadiazole; δ_H(270 MHz, $CDCl_3$) 7.52 (3H, m, ArH), 8.05 (2H, m, ArH); *m*/*z* 198 (M^+, 37%), 196 (M^+, 100), 135 ($PhCNS^+$, 91), 103 ($PhCN^+$, 17), 93 (26), 77 (Ph^+, 16). Elution with dichloromethane (50–53%) in light petroleum gave 3-phenyl-1,2,5-thiadiazole **2f** (101 mg, 62%); mp 43 °C, identical with an authentic specimen.

3-(4-Nitrophenyl)-1,2,5-thiadiazole 2g

To a stirred solution of trithiazyl trichloride (244 mg, 1 mmol) in benzene (4 ml), 4-nitrophenylacetylene (147 mg, 1 mmol) in benzene (4 ml) was added under nitrogen at 5.5–7 °C. The mixture turned green during the addition. The mixture was stirred overnight (16 h) to give a red solution. It was then heated at reflux for 2 h. The solvent was evaporated and the residue was separated by flash chromatography on silica gel with gradient elution. Elution with dichloromethane (47–50%) in light petroleum gave a minor product which was tentatively assigned as 3-chloro-4-(4-nitrophenyl)-1,2,5-thiadiazole; δ_H(270 MHz, $CDCl_3$) 8.20–8.25 (2H, m, ArH), 8.35–8.45 (2H, m, ArH); *m*/*z* 243 (M^+, 36%), 241 (M^+, 100), 211 (21), 197 (10), 195 (29), 150 (16), 133 (11), 122 (13), 108 (10), 93 (16). Dichloromethane (53–62%), in light petroleum eluted 3-(4-*nitrophenyl*)-1,2,5-*thiadiazole* **2g** (128 mg, 62%); mp 177–179 °C (Found: M^+, 207.0102. $C_8H_5N_3O_2S$ requires *M*, 207.0102); ν_{max}(Nujol)/cm^{-1} 3094, 2926, 2855, 1603, 1519, 1466 (NO_2), 1421, 1347, 1327, 1284, 1110, 1082, 931, 888, 856; δ_H(270 MHz, $CDCl_3$) 8.15–8.25 (2H, m, ArH), 8.35–8.45 (2H, m, ArH), 9.00 (1H, s, 4-H); *m*/*z* 207 (M^+, 100%), 180 ($M^+ - HCN$, 6), 177 ($M^+ - NO$, 23), 161 ($M^+ - NO_2$, 22), 149 ($M^+ - HCNS$, 10), 134 ($M^+ - HCN - NO_2$, 32), 122 (9), 107 (6), 90 (13), 75 (10).

3-(4-Methoxyphenyl)-1,2,5-thiadiazole 2h

To a stirred solution of trithiazyl trichloride (244 mg, 1 mmol) in benzene (3 ml), 4-methoxyphenylacetylene (132 mg, 1 mmol) in benzene (1 ml) was added at 6–7 °C under nitrogen. After stirring at room temperature for 5 min, the mixture turned red and after stirring at room temperature for 78 h under nitrogen, a red precipitate was formed. The solution was filtered, evaporated and the residue was separated by chromatography on silica gel. Elution with dichloromethane (40%) in light petroleum gave a minor product which was tentatively assigned as 3-chloro-(4-methoxyphenyl)-1,2,5-thiadiazole; δ_H(270 MHz, $CDCl_3$) 3.85–3.90 (3H, s, OCH_3), 6.95–7.05 (2H, d, ArH), 7.90–7.95 (2H, d, ArH); *m*/*z* 228 ($M,^+$, 37%), 226 (M^+, 100), 165 (34), 150 (10), 135 ($PhCNS^+$, 15), 133 (29), 122 (12), 103 ($PhCN^+$, 6), 90 (10), 77 (Ph^+, 5). Elution with dichloromethane (50%) in light petroleum gave 3-(4-*methoxyphenyl*)-1,2,5-*thiadiazole* **2h** as colourless needles (27 mg, 14%); mp 94–96 °C (Found: C, 56.1; H, 4.1; N, 14.4. $C_9H_8N_2OS$ requires C, 56.2; H, 4.2; N, 14.6%); ν_{max}(neat)/cm^{-1} 3077 (Ar-H), 2931, 2850, 1609 (Ar, C=C), 1526, 1475, 1430, 1347, 1308, 1287, 1254, 1224, 1180, 1112, 1024, 929, 893, 836, 785; δ_H(270 MHz, $CDCl_3$) 3.85–3.92 (3H, s, OCH_3), 6.95–7.05 (2H, m, ArH), 7.90–8.00 (2H, m, ArH), 8.45 (1H, s, 4-H); *m*/*z* 192 (M^+, 100%), 177 ($M^+ - CH_3$, 7), 165 ($M^+ - HCN$, 29), 150 ($M^+ - HCN - CH_3$), 133 ($M^+ - HCNS$, 26), 122 (9), 90 (8), 63 ($HCNS^+$, 4).

3-(3,4-Dimethoxyphenyl)-1,2,5-thiadiazole 2i

3,4-Dimethoxyphenylacetylene (162 mg, 1 mmol) in benzene (1 ml) was added to a stirred solution of trithiazyl trichloride (244 mg, 1 mmol) in benzene (4 ml) under nitrogen at 10–12 °C. During the addition the mixture turned brown. After stirring at room temperature for 20 min the mixture turned an intense red and after stirring at room temperature for 17 h under nitrogen, a red precipitate was formed. The reaction mixture was filtered and evaporated and the residue was separated by chromatography on silica gel. Elution with dichloromethane gave 3-(3,4-*dimethoxyphenyl*)-1,2,5-*thiadiazole* **2i** as pale yellow needles (31.8 mg, 14%); mp 92–93 °C (Found: M^+, 222.0463. $C_{10}H_{10}N_2O_2S$ requires *M*, 222.0463); ν_{max}(neat)/cm^{-1} 3077 (Ar-H), 2931, 2850, 1609 (Ar, C=C), 1526, 1475, 1430, 1347, 1308, 1287, 1254, 1224, 1180, 1112, 1024, 929, 893, 836, 785; δ_H(270 MHz, $CDCl_3$) 3.90 (3H, s, OCH_3), 4.08 (3H, s, OCH_3), 6.90 (1H, d, ArH), 7.50 (1H, d, ArH), 7.60 (1H, s, ArH), 8.90 (1H, s, 4-H); *m*/*z* 222 (M^+, 83%), 207 ($M^+ - CH_3$, 16), 179 (11), 163 ($M^+ - HCNS$, 5), 149 ($M^+ - HCN_2S$, 36), 120 (11).

Dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate 2d

(i) Dimethyl acetylenedicarboxylate (142 mg, 1 mmol) in benzene (0.7 ml) was added dropwise to a stirred solution of trithiazyl trichloride (244 mg, 1 mmol) in benzene (4 ml) at room temperature under nitrogen. During the addition no significant colour and temperature changes were observed. After stirring at ambient temperature for 1 h, the mixture turned green, was then stirred for 17 h and was then heated at reflux for 3 h. The resulting red solution was evaporated and the residue was separated on silica gel. Elution with dichloromethane (60%) in light petroleum gave dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate **2d** as a colourless oil (169.5 mg, 84%) identical with an authentic specimen; ν_{max}(neat)/cm^{-1} 2958, 1747, (C=O), 1456, 1412, 1289, 1224, 1178, 1073, 967, 848, 823, 804, 791, 750; δ_H(270 MHz, $CDCl_3$) 4.05 (6H, s, OCH_3); *m*/*z* 202 (M^+, 11%), 172 (21), 171 ($M^+ - OCH_3$, 100), 144 (8), 141 (15), 86 (10), 59 (11).

(ii) To a stirred solution of trithiazyl trichloride (136 mg, 0.56 mmol) in benzene (4 ml), dimethyl maleate (80 mg, 0.56 mmol) in benzene (2 ml) was added dropwise. The mixture was stirred at room temperature overnight and then heated at reflux for 4 h. The solvent was evaporated and the residue was separated on silica gel. Elution with dichloromethane gave dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate **2d** as a colourless oil (58 mg, 52%), identical with that reported in (i).

3,4-Diphenyl-1,2,5-thiadiazole 2e

(i) Diphenylacetylene (135 mg, 0.76 mmol) in benzene (0.7 ml) was added dropwise under nitrogen to a stirred solution of trithiazyl trichloride (185 mg, 0.76 mmol) in benzene (3 ml) at room temperature with water bath cooling. During the addition the temperature change was within 0.5 °C. After stirring at room temperature for 0.5 h, the mixture turned an intense green; after another hour, it turned orange and cloudy. It was then stirred under nitrogen at room temperature for 17 h. The mixture was then filtered to give an orange solid (76 mg) which was found (IR spectroscopy) to be S_4N_3Cl. The filtrate was concentrated and separated on silica gel by chromatography. Elution with dichloromethane (40%) in light petroleum gave a minor product which was assigned as a monochlorinated 3,4-diphenyl-1,2,5-thiadiazole; δ_H(270 MHz, $CDCl_3$) 7.30–7.55 (7H, m, ArH), 8.00–8.07 (1H, m, ArH), 8.35–8.45 (1H, m, ArH); *m*/*z* 274 (M^+, 12%), 272 (M^+, 32), 238 ($M^+ - Cl + H$,

57), 237 ($M^+ - Cl$, 14), 171 (18), 169 (22), 135 ($PhCNS^+$, 100), 103 ($PhCN^+$, 16), 77 (Ph^+, 18). Elution with dichloromethane (50%) in light petroleum gave 3,4-diphenyl-1,2,5-thiadiazole **2e** as colourless needles (58 mg, 32%), mp 84–86 °C (lit.,[10] 85–86 °C); δ_H(270 MHz, $CDCl_3$) 7.30–7.45 (6H, m, ArH), 7.46–7.56 (4H, m, ArH); *m*/*z* 238 (M^+, 86%), 135 ($PhCNS^+$, 100), 119 (5), 103 ($PhCN^+$, 20), 77 (Ph^+, 19).

(ii) To a refluxing solution of (*E*)-stilbene (360 mg, 2 mmol) in toluene (10 ml), trithiazyl trichloride (734 mg, 3 mmol) in toluene (15 ml) was added dropwise. The reaction mixture was heated under reflux for 16 h. The mixture was cooled to room temperature and filtered through a short pad of silica. The filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with dichloromethane–light petroleum (1:1) afforded the title compound (133 mg, 28%) as a pale yellow solid, mp 84–86 °C identical with that reported in (i).

3,4-Dibenzoyl-1,2,5-thiadiazole 2c

To a stirred solution of (*E*)-1,2-dibenzoylethene (118 mg, 0.5 mmol) in tetrachloromethane (2 ml), trithiazyl trichloride (122 mg, 0.5 mmol) in tetrachloromethane (5 ml) was added dropwise. The mixture was heated at reflux under nitrogen for 10 h and was filtered to give S_4N_3Cl (IR spectroscopy) as a yellow powder (64 mg). The filtrate was concentrated and separated on silica gel. Elution with dichloromethane (70%) in light petroleum gave 3,4-dibenzoyl-1,2,5-thiadiazole **2c** (62 mg, 42%); mp 128–129 °C (lit.,[11] 124 °C) (Found: C, 65.4; H, 3.5; N, 9.5. Calc. for $C_{16}H_{10}N_2O_2S$: C, 65.3; H, 3.4; N, 9.5%); ν_{max}(Nujol)/cm^{-1} 3069, 3058, 1666 (C=O), 1652, 1593, 1578, 1452, 1413, 1324, 1311, 1290, 1213, 1183, 1121, 1026, 1000, 947, 878, 846; δ_H(270 MHz, $CDCl_3$) 7.48–7.56 (4H, m, ArH), 7.63–7.70 (2H, m, ArH), 8.06–8.12 (4H, m, ArH); *m*/*z* 294 (M^+, 22%), 217 ($M^+ - Ph$, 2), 105 ($PhCO^+$, 100), 77 (Ph^+, 42).

3-(4-Methoxyphenyl)-4-(4-nitrophenyl)-1,2,5-thiadiazole 2b

To a stirred solution of trithiazyl trichloride (154 mg, 0.63 mmol) in benzene (7 ml), (*E*)-1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethene (161 mg, 0.63 mmol) in benzene (3 ml) was added dropwise. No significant temperature or colour change was observed. After stirring at room temperature for 20 h, the mixture was heated at reflux for 1.5 h. The solvent was evaporated and the residue was separated by chromatography on silica gel. Elution with dichloromethane (70%) in light petroleum gave 3-(4-*methoxyphenyl*)-4-(4-*nitrophenyl*)-1,2,5-*thiadiazole* **2b** as bright yellow needles (136 mg, 69%); mp 223–223.5 °C (Found: C, 57.6; H, 3.5; N, 13.3. $C_{15}H_{11}N_3O_3S$ requires C, 57.5; H, 3.5; N, 13.4%); ν_{max}(Nujol)/cm^{-1} 2924, 2854, 1611, 1524 (NO_2), 1461, 1378, 1352 (NO_2), 1312, 1258, 1181, 1116, 1029, 959, 836, 772, 714, 695; δ_H(270 MHz, $CDCl_3$) 3.92 (3H, s, OCH_3), 7.00–7.10 (2H, d), 7.95–8.05 (2H, d), 8.30–8.40 (2H, d), 8.50–8.60 (2H, d); *m*/*z* 313 (M^+, 57%), 283 ($M^+ - OCH_3 + H$, 58), 180 (O_2N-C_6H_4-CNS, 35), 165 (H_3CO-C_6H_4-CNS, 61), 150 ($165 - CH_3$, 100), 134 (15), 133 (18), 118 (42), 90 (15).

3-Phthalimido-1,2,5-thiadiazole 4

To a refluxing solution of *N*-vinylphthalimide **3** (173 mg, 1 mmol) in THF (10 ml) in the presence of 4 Å molecular sieves (5 g), trithiazyl trichloride (245 mg, 1 mmol) in THF (10 ml) was added dropwise. The mixture was heated under reflux for 10 min and a second portion of trithiazyl trichloride (245 mg, 1 mmol) in THF (10 ml) was added dropwise. A third portion of trithiazyl trichloride (245 mg, 1 mmol) was added similarly after 10 min and the mixture was then heated under reflux for 1 h. The reaction mixture was cooled to room temperature and filtered through a short pad of silica, and the filtrate was concentrated under reduced pressure. Column chromatography of the residue with dichloromethane afforded the *title compound* (87 mg, 38%) as a colourless solid; mp 162–164 °C (ethanol) (Found: C, 51.7; H, 2.3; N, 17.9. $C_{10}H_5N_3O_2S$ requires C, 51.9; H, 2.2; N, 18.2%); ν_{max}(Nujol)/cm^{-1} 1723vs (C=O), 1286m, 1070m; δ_H(500 MHz, $CDCl_3$) 8.98 (1H, s, thiadiazole 4-H), 8.03 (2H, dd, *J* 5.5, 3.0), 7.87 (2H, dd, *J* 5.5, 3.0); δ_C(126 MHz, $CDCl_3$) 164.92 (C=O), 147.07, 144.43, 135.22, 131.30, 124.46; *m*/*z* 231 (M^+, 100%), 204 (51, M − HCN), 158 (26), 104 (36), 76 (31).

Similar experiments carried out in refluxing toluene and dioxane afforded the title compound in 17 and 35% yield respectively.

3-Amino-1,2,5-thiadiazole 5

To a solution of 3-phthalimido-1,2,5-thiadiazole **4** (50 mg, 0.22 mmol) in benzene (10 ml), methylhydrazine (101 mg, 2.2 mmol) was added dropwise at room temperature. The mixture was stirred at room temperature for 10 min and then filtered through a short pad of silica. The filtrate was concentrated under reduced pressure. Column chromatography of the residue with dichloromethane–ethyl acetate (60:40) afforded the *title compound* (20 mg, 90%) as a light yellow oil (Found: M^+, 101.0041. Calc. for $C_2H_3N_3S$: *M*, 101.0048); ν_{max}(neat)/cm^{-1} 3338vs and 3216vs (NH_2), 1621s, 1538s, 1412s; δ_H(300 MHz, $CDCl_3$) 7.85 (1H, s, 4-H), 4.89 (2H, br, NH_2); δ_C(76 MHz, $CDCl_3$) 159.65 (C-3), 138.82 (C-4); *m*/*z* 101 (M^+, 60%), 74 (100, M − HCN), 59 (16, M − NH_2CN).

7-Diphenylmethylene-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis([1,2,5]-thiadiazole) 7

Diphenylfulvene **6** (460 mg, 2 mmol) and trithiazyl trichloride (976 mg, 4 mmol) in tetrachloromethane (50 ml) were heated to reflux under nitrogen overnight. The reaction mixture was cooled to room temperature, filtered through a pad of silica, which was washed with dichloromethane. The combined solutions were evaporated *in vacuo* and the residue was separated by column chromatography on silica gel to give the *title compound* **7** (180 mg, 26%); mp 209–210 °C (Found: C, 62.2; H, 2.7; N, 16.0. $C_{18}H_{10}N_4S_2$ requires C, 62.4; H, 2.9; N, 16.2%. Found: M^+, 346.0350. $C_{18}H_{10}N_4S_2$ requires *M*, 346.0350); ν_{max}($CHCl_3$)/cm^{-1} 3011, 1658, 1601, 1579, 1448, 1320, 1280, 943, 921, 703, 640; δ_H(270 MHz, $CDCl_3$) 7.43–7.48 (10H, m, Ph); δ_C(270 MHz, $CDCl_3$) 174.16, 169.79, 153.24, 145.87, 139.10, 130.73, 130.15, 128.14; *m*/*z* 346 (M^+, 66%), 313 (100), 269 (20), 229 (22), 203 (16), 165 (30), 77 (Ph^+, 19).

7*H*-Cyclopenta[1,2-*c*:3,4-*c*′]bis([1,2,5]thiadiazol)-7-one 10

To a refluxing solution of diphenylfulvene (460 mg, 2 mmol) in toluene (10 ml), trithiazyl trichloride (1.47 g, 6 mmol) in toluene was added dropwise. The mixture was heated under reflux for 3 h. The reaction mixture was cooled to room temperature and filtered through a short pad of silica. The filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with dichloromethane–light petroleum (60:40) afforded a mixture of the *title compound* **10**, compound **7** and benzophenone. Repeated chromatography on silica with dichloromethane–light petroleum (60:40) gave compound **7** (112 mg, 16%); mp 209–210 °C (ethanol) identical with that described above. Further elution afforded the *title compound* **10** (82 mg, 21%) as colourless plates; mp 140–142 °C (ethanol) (Found: M^+, 195.9511. $C_5N_4OS_2$ requires *M*, 195.9514); ν_{max}(Nujol)/cm^{-1} 1767vs (C=O), 1748vs, 1568m (C=N), 1137m, 1068m; δ_C(101 MHz, $CDCl_3$) 171.44, 167.09, 161.95; *m*/*z* 196 (M^+, 35%), 168 (100, M − CO), 138 (13, M − CNS), 116 (17, SNCCNS), 86 (20, O=C=C=NS), 58 (35, CNS). Further elution afforded benzophenone (66 mg, 18%).

8*H*-Indeno[1,2-*c*][1,2,5]thiadiazol-8-one 12

1-(Diphenylmethylene)indene **11** (560 mg, 2 mmol) and trithiazyl trichloride (732 mg, 3 mmol) were heated at reflux in tetrachloromethane (50 ml) under nitrogen overnight. The reaction mixture was cooled to room temperature and filtered through a pad of silica which was washed with dichloro-

methane. The combined solutions were evaporated and the residue chromatographed on silica gel to give benzophenone (84 mg, 23%) and the *title compound* (248 mg, 66%); mp 112–114 °C (lit.,[5] mp 113 °C).

Bis(diphenylmethyleneamino) sulfide 15

Tetraphenylethene **13** (664 mg, 2 mmol) and trithiazyl trichloride (732 mg, 3 mmol) were heated at reflux in tetrachloromethane (50 ml) exactly as in the last experiment to give unreacted **13** (199 mg, 30%), benzophenone (58 mg, 16%) and the *title compound* **15** (102 mg, 13%) as yellow crystals; mp 165–166 °C (lit.,[6] 164–165 °C) (Found: C, 79.4; H, 5.15; N, 7.2. Calc. for $C_{26}H_{20}N_2S$: C, 79.6; H, 5.1; N, 7.1%); *m*/*z* 392 (M^+, 35%), 212 (80), 180 (70), 103 (100), 77 (95), 51 (93).

Phenanthro[9,10-*c*][1,2,5]thiadiazole 16

Phenanthrene (178 mg, 1 mmol) and trithiazyl trichloride (732 mg, 3 mmol) were heated at reflux in tetrachloromethane (50 ml) for two days to give (as in the last experiment) unreacted phenanthrene (96 mg, 54%) and the *title compound* **16** (76 mg, 32%) as colourless needles; mp 169–170 °C (lit.,[7] 169–170 °C).

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