Conversion of pyrroles into bi-1,2,5-thiadiazoles: a new route to biheterocycles

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Trithiazyl trichloride 1 converts 1,2,5-triphenylpyrrole 5 into its 3,4-dichloro derivative together with the isothiazole imine 6 and the imine hydrolysis product, the ketone 3. The best yield of the isothiazole 6 is obtained in the presence of 4 Å molecular sieves (Table 1). Conversion of the pyrrole 5 into the isothiazole 6 is exactly analogous to the reaction of 1 with 2,5-diphenyl-furan and -thiophene. Other *N*-aryl and the related 2,5-diphenylpyrroles 8 give similar results (Table 2). However, 1-methyl-2,5-diphenylpyrrole 11 reacts with 1 in an entirely different way to give 4,4′-diphenyl-3,3′-bi-1,2,5-thiadiazole 12, in which two thiadiazole rings have been fused onto the pyrrole and the CH_3N unit has been excised as HCN. The same product 12 is formed, in similar yields, by reaction of 1 with 1,4-diphenylbuta-1, 3-diyne and 1,4-diphenylbut-1-en-3-yne. Other *N*-alkyl 2,5-diphenylpyrroles 16 react similarly (Table 3), giving the best yield (70%) of bi-thiadiazole 12 in the presence of 4 Å molecular sieves (Table 4). 1-Methyl- and 1-ethyl-3,4-dibromo-2,5-diphenylpyrrole also give 12, together with 3-(benzoyldichloromethyl)-4-phenyl-1,2,5-thiadiazole 21 in high combined yield. The formation of bi-1,2,5-thiadiazole 12 from *N*-alkylpyrroles represents a new dissection of the pyrrole ring and a new and very short route to an aromatic biheterocyclic system. Mechanisms which rationalise the different pathways observed are proposed for all of these reactions.

We have already described the reactions of trithiazyl trichloride **1** with pyrroles bearing hydrogen, chlorine or bromine in the 2- and 3- positions; these result in the fusion of an N–S–N unit across the 2,3- bond to give a fused pyrrolo-1,2,5-thiadiazole, often in high yield.[1] This reaction would appear to be highly unlikely with 2,5-diphenylpyrroles, for example, and we have already shown that 2,5-diphenylfuran **2** reacts with trithiazyl trichloride **1** under the same conditions in an entirely different manner to give 5-benzoyl-3-phenylisothiazole **3** in high yield (>80%).[2] This new route to isothiazoles is regiospecific, giving none of the 3-benzoyl-5-phenyl isomer of **3**. It is thought to involve the highly reactive monomer N≡S–Cl (formed by thermal dissociation of its trimer **1**) reacting initially with the furan either by Diels–Alder cycloaddition or by electrophilic introduction of the thiazyl group, -SN, at the β-position.[2] 2,5-Diphenylthiophene gave the same product **3** with the trimer **1**, in lower yield, presumably *via* the 5-thiobenzoyl analogue **4** which is oxidised by the trimer **1** to give the benzoyl compound on work-up.[2] For comparison with the furan and thiophene, we wished to extend the trimer reaction to 2,5-diphenylpyrroles, where the heterocyclic ring is now expected to be more reactive to electrophilic attack and less reactive to cycloaddition.

1-Aryl-2,5-diphenylpyrroles and $(NSCl)_3$

We first studied 1,2,5-tripenylpyrrole **5** with an inert *N*-substituent. Treatment of this with the trimer **1** (0.33 equiv.) in refluxing tetrachloromethane for 12 h gave the starting pyrrole (40%) together with its 3,4-dichloro derivative **7** (17%, 28% conversion) and the isothiazole *N*-phenylimine **6** (32%, 54% conversion). The structure of **6** was based on spectroscopic and analytical data and on its ready hydrolysis to the ketone **3**. Formation of the chlorinated product **7** is in accord with the high reactivity of pyrroles towards halogenation; only the dichlorinated compound was observed, though the trimer does monochlorinate indoles normally.[1] Formation of the *N*-phenylimine **6** is entirely analogous to the furan and thiophene reactions and probably, though not necessarily, occurs by the same mechanism.[2] The reaction conditions were varied in an attempt to increase the product yields (Table 1). Higher reaction temperatures and an excess of $(NSCl)_3$ increased the yield of the dichlorinated compound **7**. At room temperature the reaction was slow though the ratio of isothiazole formation (both products) to dichlorination was relatively high; isolation of the benzoyl compound **3** indicated that the *N*-phenyl imine **6** was readily hydrolysed. Addition of an excess of pyridine, to neutralise the HCl liberated, had very little effect upon the reaction. The best yield of **6** (48%) was obtained in the presence of 4 Å molecular sieves, which absorb HCl; these are often beneficial in trimer reactions and much more effective than the addition of traditional bases such as pyridine.

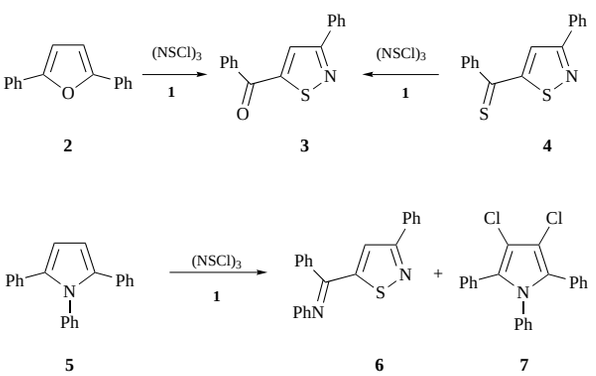
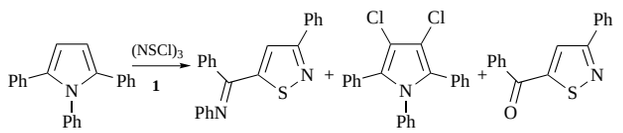


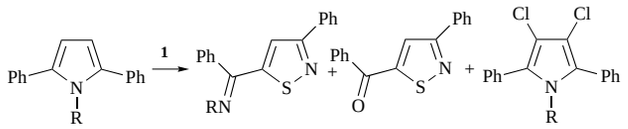
Table 1 Reaction of the pyrrole **5** with $(NSCl)_3$ **1**



Equiv. of $(NSCl)_3$ **1**	Reaction conditions	Yields (%) **6**	**7**	**3**
0.33	CCl_4, reflux, 12 h [a]	32	17	
2	CCl_4, reflux, 12 h	Trace	75	
0.33	CCl_4, pyridine, reflux, 12 h [b]	30	16	
0.67	PhMe, reflux, 12 h	17	61	
1	CCl_4, room temp., 96 h	23	20	23
2	CCl_4, mol. sieves 4 Å, reflux, 12 h	48	41	

[a] Plus **5** (40%). [b] Plus **5** (36%).

Table 2 Reaction of the pyrroles **8** with $(NSCl)_3$ **1** (1 equiv.)



8 **9** **3** **10**

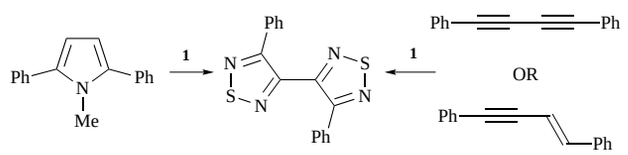
R		Reaction and conditions *			Yield (%)			
4-$MeOC_6H_4$	**8a**	A	**9a**[a]	10	**3**	36	**10a**	24
4-$MeOC_6H_4$	**8a**	B	**9a**[a]	16	**3**	Trace	**10a**	51
4-$O_2NC_6H_4$	**8b**	B	**9b**	5	**3**	42	**10b**	44
4-$O_2NC_6H_4$	**8b**	A[b]			**3**	18	**10b**	6
MeOCO	**8c**	C			**3**	78		
Bu^{t}OCONH	**8d**	C	**9d**[a]	61	**3**	Trace		

*A CCl_4, room temp., 96 h, 4 Å mol sieves; B CCl_4, reflux, 12 h; C CCl_4, room temp., 12 h. [a] ^{1}H NMR spectroscopy showed two isomers. [b] **8b** recovered (65%).

The reactions of $(NSCl)_3$ with a few other *N*-substituted 2,5-diphenylpyrroles **8a–d** were investigated and found to give broadly similar results (Table 2). Neither of the isothiazole *N*-arylimines **9a** and **9b** was very stable, both hydrolysing readily to give the 5-benzoyl compound **3**. However, they could be isolated and characterised by spectroscopy and mass spectrometry; the ^{1}H NMR of the *p*-methoxyphenyl imine **9a** showed two methoxy singlets at 3.74 and 3.79 ppm indicating the presence of two geometrical isomers. The *N*-methoxycarbonylpyrrole **8c** gave the ketone **3** directly, in high yield (78%), even at room temperature, the intermediate imine being completely hydrolysed on chromatographic work-up. The *N*-*tert*-butoxycarbonylamino compound **8d** reacted similarly to give the stable hydrazones **9d** (61%) as a mixture of the two geometrical isomers, with ^{1}H NMR singlets for the *tert*-butyl groups at 1.52 and 1.60 ppm.

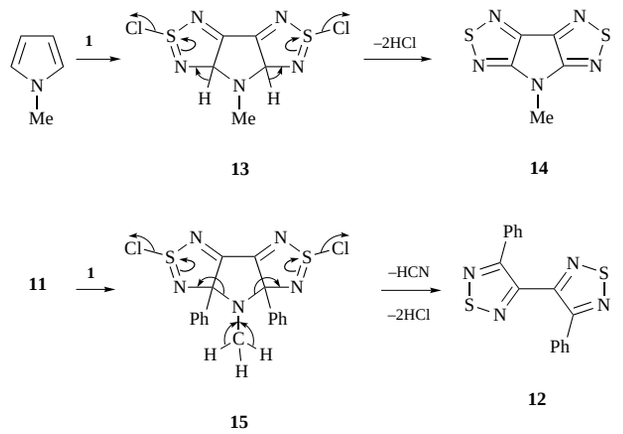
1-Methyl-2,5-diphenylpyrrole with $(NSCl)_3$

When the above *N*-substituents were replaced by a methyl group an entirely new and unexpected reaction was observed. Treatment of 1-methyl-2,5-diphenylpyrrole **11** with the trimer **1** (2 equiv.) in boiling tetrachloromethane gave only traces of 5-benzoyl-3-phenylisothiazole **3**, presumably formed by hydrolysis of its *N*-methyl imine; the major product (45%) was a colourless crystalline solid with one less carbon atom and with four nitrogen and two sulfur atoms in its molecular formula, $C_{16}H_{10}N_4S_2$. Assuming that the MeN unit has been lost and the remaining carbon connectivity retained, the bi-1,2,5-thiadiazole structure **12** seemed possible. Following the formation of 1,2,5-thiadiazoles from the trimer **1** and alkenes or alkynes,[3] we treated 1,4-diphenylbuta-1,3-diyne and (*E*)-1,4-diphenylbut-1-en-3-yne[4] with the trimer **1** under the same conditions, and in each case the identical product **12** was formed in almost the same yield (43–44%).



11, $C_{17}H_{15}N** **12**, $C_{16}H_{10}N_4S_2$

It is striking that 1,2,5-triphenylpyrrole **5** and 1-methyl-2,5-diphenylpyrrole **11** react so differently with the trimer **1**, and interesting to see if this arises reasonably from our proposed mechanisms. We have explained the formation of 1,2,5-thiadiazoles from alkenes and alkynes by effective 1,3-cycloaddition of an N–S–N unit of the trimer followed by fragmentation of the remaining S–N–S unit as $[ClSNSCl]^+$ Cl^- or $[SNS]^+$ Cl^-.[3] This overall mechanism is directly applicable to α,β-unsubstituted pyrroles to give the observed bicyclic pyrrolothiadiazole.[1] With *N*-methylpyrrole, for example, the process can occur twice *via* an intermediate such as **13** which would rapidly aromatise by elimination of HCl to give the observed bithiadiazolopyrrole **14** (Scheme 1). Nitrile imides have been shown to undergo double cycloaddition to *N*-methylpyrrole to give somewhat similar, but stable, tricyclic species in which the pyrrole ring is fully saturated.[5] The analogous intermediate **15** from 1-methyl-2,5-diphenylpyrrole **11** cannot aromatise similarly, but it can do so by the loss of two hydrogens from the *N*-methyl group which has to be accompanied by cleavage of the N–C_α pyrrole bonds (see arrows in **15**) to give the very stable bi-thiadiazole **12** and HCN, which was shown to be a product of this reaction (Scheme 1). (In **13** and **15** the sulfur–chlorine bonds are shown as covalent but these would be ionised to some extent to the thiadiazolium chlorides). The intermediate analogous to **15** for the *N*-phenyl and related compounds (Tables 1 and 2) cannot aromatise by any such elimination and, if formed at all, would probably be in equilibrium with its precursors; the main reaction therefore takes the different pathway described above. Thus the dominant role of the *N*-substituent and the extensive rearrangement involved in the conversion of **11** into **12**, whilst initially puzzling, appear rational on mechanistic grounds.



13 **14** **11** **15** **12**

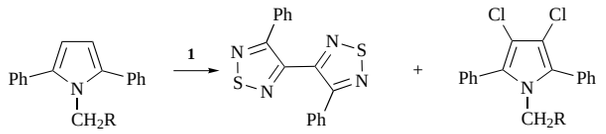
Scheme 1

In support of the mechanism in Scheme 1 we sought, and found, evidence for HCN as a gaseous product of the reaction. Of the many methods available for HCN detection we finally chose the Kitagawa length-of-stain detector tube method (see Experimental section) since this was sensitive and semi-quantitative. Blank experiments showed that the method was not sensitive to the hydrogen chloride formed in the reaction but that the monomer, NSCl, did interfere with the test. However, by the use of a double walled water condenser all of the NSCl could be condensed out, and a detector tube at the top of the condenser above a refluxing solution of $(NSCl)_3$ in boiling tetrachloromethane gave no response. Addition of 1-methyl-2,5-diphenylpyrrole **11** to this solution resulted in the whole of the detector tube turning red. The procedure was then repeated but using 1-ethyl-2, 5-diphenylpyrrole **16a** which reacts analogously with the trimer **1** (see below) to give bi-thiadiazole **12** and acetonitrile (presumably, but certainly not HCN) and no colour change was observed in the detector tube. This detection of HCN in the reaction of **11** with the trimer strongly supports the overall correctness of the proposed mechanism, regardless of such fine details as the timing of the steps, which are as yet unknown.

Other *N*-alkyl-2,5-diphenylpyrroles 16 with $(NSCl)_3$

We have seen that the reactions of $(NSCl)_3$ with 2,5-diphenyl-

Table 3 Reaction of *N*-alkyl-2,5-diphenylpyrroles with $(NSCl)_3$ **1** (2 equiv.) in refluxing tetrachloromethane for 12 h



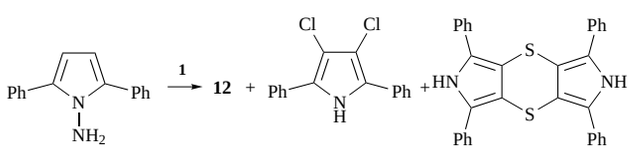
16 **12** **17**

R		Yield of **12** (%)	Yield of **17** (%)	
Me	**16a**	12	**17a**	63
Ph	**16b**	6	**17b**	57
4-$MeOC_6H_4$	**16c**	12	**17c**	44
4-$O_2NC_6H_4$	**16d**	12	**17d**	60
EtOCO	**16e**	23	**17e**	52

pyrroles are sensitive to the nature of the *N*-substituent. Substituents which are inert under the reaction conditions, such as aryl or ester groups, lead to the formation of isothiazoles such as **3**, **6** and **9**, but an *N*-methyl group is lost as HCN and the bi-thiadiazole **12** results. It therefore seemed likely that CH_2R substituents on the pyrrole nitrogen would also favour the latter reaction to give the same bi-thiadiazole **12**, but with loss of RCN. In order to test this, selected *N*-alkyl-2,5-diphenylpyrroles **16** were prepared and treated with $(NSCl)_3$ under standard conditions and the results are shown in Table 3.

The bi-thiadiazole **12** was isolated from each reaction but the yields were lower than from the *N*-methyl compound **11** because of the formation of major amounts of the 3,4-dichlorinated pyrroles **17**. These dichloro products were inert towards $(NSCl)_3$; no reaction was observed when **17a** and **17b** were heated under reflux with an excess of $(NSCl)_3$ in either tetrachloromethane or toluene for 24 h. A simple way to improve the yields of bi-thiadiazole **12** is described below.

It was hoped that *N*-amino-2,5-diphenylpyrrole **18** with $(NSCl)_3$ would give a higher yield of **12** by elimination of N_2 in place of the HCN shown in **15**; however the reaction was disappointingly complex, probably because the *N*-amino group reacted preferentially with the electrophilic reagent **1**. The thiadiazole **12** was isolated (21%) together with two other compounds: the chlorinated and deaminated product, 3,4-dichloro-2,5-diphenylpyrrole (4%) and a new yellow crystalline solid, mp 235–237 °C. This was assigned the dipyrrolo-1,4-dithiin structure **19** on the basis of its spectroscopic and mass spectrometric properties. The mode of formation of **19** is unknown though it may well involve the 3,4-dichloro compound.



18 **19**

Optimising the formation of bi-1,2,5-thiadiazole 12

Elimination of HCl is necessary for the formation of the bi-thiadiazole **12** in the above reactions, but addition of pyridine was found to be inefficient and stronger bases such as triethylamine and diisopropylethylamine, which themselves react with the trimer **1**, gave intractable tars. The beneficial effect of molecular sieves in trimer reactions was referred to above and we repeated some of these trimer–pyrrole reactions in the presence of 4 Å molecular sieves under the standard conditions. This caused a marked improvement in the yield of **12** compared with the reactions without molecular sieves, as shown in Table 4.

In all cases the yield of **12** was increased, sometimes substantially, and the yield of the 3,4-dichloro-2,5-diphenylpyrrole **17** was usually reduced, but only substantially so with the *N*-ethyl compound **16a**. Reaction of the *N*-methyl derivative **11** or the *N*-ethyl derivative **16a** with trimer provides a good synthesis of the bi-thiadiazole **12** (70 and 60% yield respectively) in one step from readily available pyrroles.

Since the outcome of the trimer reaction with **16a** was sensitive to the presence of molecular sieves, we repeated this reaction but with the sieves replaced by alumina and by silica gel, to see if these solids influenced the reaction. The results are included in Table 4 where it is seen that both have a significant effect, with the yield of bi-thiadiazole **12** being increased at the expense of the dichloropyrrole **17a**, though to a smaller extent than with the molecular sieves.

We have shown earlier[1] that some brominated pyrroles and chlorinated indoles react with $(NSCl)_3$ faster than the unhalogenated compounds to give higher yields of the fused 1,2,5-thiadiazoles; we have also shown above that 3,4-dichloro-2,5-diphenylpyrroles **17** do not react with $(NSCl)_3$. To see if 3,4-dibromo-2,5-diphenylpyrroles would react with the trimer, the analogous 3,4-dibromo-2,5-diphenylpyrroles **20** substituted on nitrogen by methyl, ethyl, benzyl, *p*-methoxybenzyl, *p*-nitrobenzyl and ethoxycarbonylmethyl were prepared in uniformly high yield (84–97%) by bromination with *N*-bromosuccinimide in THF.[6] These compounds were treated with $(NSCl)_3$ (2 equiv.) in boiling tetrachloromethane in the presence of an excess of 4 Å molecular sieves (see Table 5). The *N*-methyl and *N*-ethyl compounds did indeed give the bi-thiadiazole **12** in reasonable yield, and from both reactions another substantial product was isolated. This was shown to be 3-(benzoyldichloromethyl)-4-phenyl-1,2,5-thiadiazole **21** by X-ray diffraction analysis,[7] and a mechanism for its formation (Scheme 2) is suggested below.

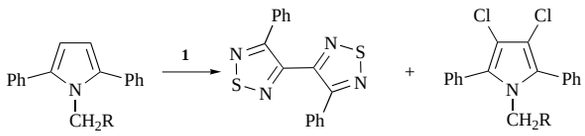
The reactions of $(NSCl)_3$ with the three *N*-benzylated compounds **20b**, **c** and **d** surprisingly gave very high yields of the 3,4-dichloropyrroles **17b**, **c** and **d** in which bromine has been replaced by chlorine. The reason for this dominating process, with these particular substrates, is not known though it does appear to provide another example of the trimer **1** acting as an effective chlorinating agent.

The formation of bi-thiadiazole **12** and the dichloro ketone **21** in high combined yield from 1-methyl- and 1-ethyl-3,4-dibromo-2,5-diphenylpyrrole can be readily rationalised (Scheme 2, shown for the *N*-methyl compound) by the same basic mechanism as shown earlier in Scheme 1. The overall cycloaddition of the intact trimer **1** across the 2,3-pyrrole positions could lead to **22** which, with the 3-bromine present, can undergo elimination as shown to give $[ClSNSCl]^+$ Br^- and the key intermediate **23**. This intermediate can react again in exactly the same way by cycloaddition of **1** across the 4,5-pyrrole bond, and elimination, to give the tricyclic species **15** which, as before (Scheme 1), leads to the observed bi-thiadiazole **12**. However, the intermediate **23** can also achieve aromatic stability more directly by rearrangement to a monocyclic thiadiazole **24** (Scheme 2).† The actual product isolated, after work-up, was the dichlorinated ketone **21** in which the bromine has been exchanged for chlorine, probably by $(NSCl)_3$, and the *N*-methyl- and *N*-ethyl-imines have been hydrolysed. Thus, although the formation of **21** was initially surprising it can be rationalised by a reasonable reaction sequence. Whilst all of these trimer reaction mechanisms are speculative, their cumulative success in explaining the formation of the novel products isolated adds to their credibility.

The one-step formation of the bi-1,2,5-thiadiazole **12** from the trimer reactions with 1-methyl- and 1-ethyl-2,5-diphenylpyrrole and their 3,4-dibromo derivatives (Tables 4 and 5) is as useful as it was unexpected. There has been a very marked increase in interest in biheterocyclic compounds in recent years[8]

† We thank a referee for the interesting suggestion that ring opening of **23** on the way to **21** could be by extended elimination of HCl exactly as proposed for the conversion of **15** into **12** in Scheme 1.

Table 4 Reaction of the pyrroles **16** with $(NSCl)_3$ **1** (2 equiv.) in refluxing tetrachloromethane in the presence of 4 Å molecular sieves (MS), alumina and silica gel

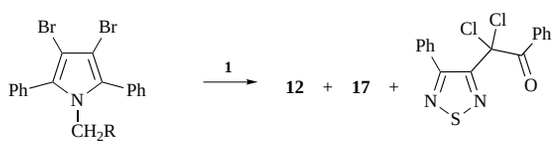


16 **12** **17**

R		Yield (%) of **12** with MS	Yield (%) of **12** without MS	Yield (%) of **17** with MS		Yield (%) of **17** without MS
H	**11**	70	45		—	—
Me	**16a**	66	12	**17a**	14	63
Ph	**16b**	18	6	**17b**	55	57
4-$MeOC_6H_4$	**16c**	25	12	**17c**	40	44
4-$O_2NC_6H_4$	**16d**	30	12	**17d**	61	60
Me[a]	**16a**	32	12	**17a**	30	63
Me[b]	**16a**	48	12	**17a**	20	63

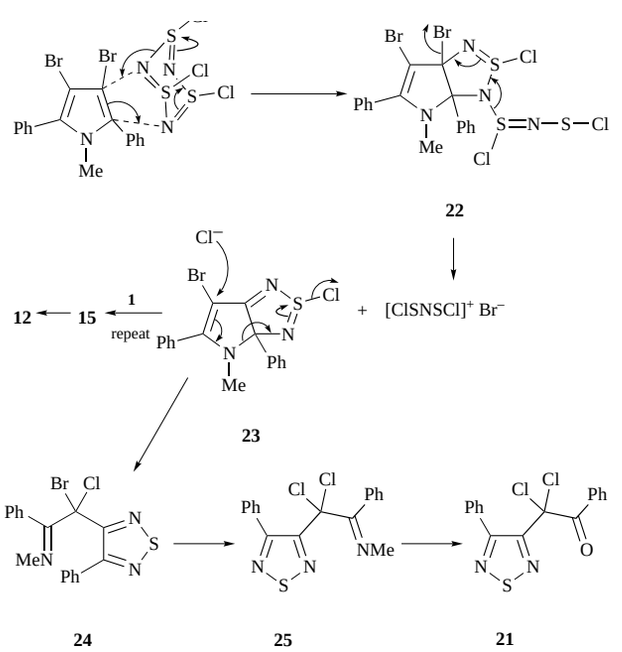
[a] With alumina replacing the molecular sieves. [b] With silica gel replacing the molecular sieves.

Table 5 Reaction of the pyrroles **20** with $(NSCl)_3$ **1** (2 equiv.) in refluxing tetrachloromethane in the presence of 4 Å molecular sieves for 12 h



20 **21**

20 R		Yield (%) **12**	Yield (%) **17**		Yield (%) **21**
H		64		—	31
Me	**20a**	41		—	33
Ph	**20b**	10	**17b**	84	—
4-$MeOC_6H_4$	**20c**	4	**17c**	91	—
4-$O_2NC_6H_4$	**20d**	—	**17d**	97	—
EtOCO	**20e**	32	**17e**	45	—



22 **23** **24** **25** **21**

Scheme 2

since they appear as structural subunits in many natural products and in conducting polymers like polypyrroles and polythiophenes, and they have provided a wide range of finely tuned chelating ligands in coordination and organometallic chemistry. The large numbers of different biheterocycles reported[8] have been prepared by the application of standard coupling, cyclisation and cycloaddition reactions, together with a few reactions involving the extrusion of sulfur or dinitrogen. The present method appears to be an entirely new and unusually short route, forming bi-1,2,5-thiadiazoles which are very rare[9] and, hitherto, were not readily available.

Experimental

For general details see earlier papers in this series.[1,2,3]

1,2,5-Triphenylpyrrole 5

The procedure was adapted from the literature.[10] A mixture of 1,2-dibenzoylethane (1 g), aniline (0.4 g), and acetic acid (10 ml) was refluxed for 2 h during which time solid material began to separate from the reaction mixture. The crystals which separated on cooling were filtered off, washed with water and dried to give the product (1.19 g, 97%) a needless, mp 231–233 °C (lit.,[10] 229 °C).

2,5-Diphenylpyrrole

The above procedure was adapted. A mixture of 1,2-dibenzoylethane (1 g), ammonium acetate (2 g), and acetic acid (10 ml) was refluxed for 20 h. After cooling, the reaction mixture was poured into ice–water (100 ml), and the solid which separated was filtered off, washed with water and dried to give the product (0.9 g, 98%) as fine needles, mp 142–143 °C (lit.,[11] 143 °C).

1-Methyl-2,5-diphenylpyrrole 11

30% Aqueous methylamine (80 ml) was added slowly to a mixture of 1,2-dibenzoylethane (10 g), benzene (150 ml) and acetic acid (50 ml), and the mixture was refluxed for 24 h, water being removed in a Dean–Stark apparatus. The yellow crystals (8 g, 85%), mp 205 °C (lit.,[11] 204 °C), were filtered off after the mixture had cooled.

The following 2,5-diphenylpyrroles were prepared by a similar condensation of 1,2-dibenzoylethane with the relevant amine in refluxing acetic acid, and were purified by recrystallisation.

1-Ethyl-2,5-diphenylpyrrole 16a. Pale brown crystalline solid, mp 90–92 °C (lit.,[11] 88–89 °C).

1-(4-Methoxyphenyl)-2,5-diphenylpyrrole 8a. Crystalline solid, mp 232–233 °C (lit.,[12] 229 °C).

1-(4-Nitrophenyl)-2,5-diphenylpyrrole 8b. Yellow crystalline solid, mp 252–254 °C (lit.,[12] 252 °C).

1-Benzyl-2,5-diphenylpyrrole 16b. Crystalline solid, mp 143–144 °C (lit.,[12] 144 °C).

1-(4-Methoxybenzyl)-2,5-diphenylpyrrole 16c. Crystalline solid, mp 109–110 °C (Found: M^+, 339.1623. $C_{24}H_{21}NO$ requires M^+, 339.1623); $\nu_{max}(CHCl_3)/cm^{-1}$ 3024, 3014, 1666, 1604, 1512, 1485, 1466, 1305, 1250, 1243, 1232, 1216, 1203, 1194, 1176, 1042, 1037 and 917; δ_H(270 MHz, $CDCl_3$) 3.80 (3H, s, OMe), 5.17 (2H, s, CH_2), 6.34 (2H, s, pyrrole), 6.57–6.66 (2H, d, *p*-$MeOC_6H_4$), 6.85–6.88 (2H, d, *p*-$MeOC_6H_4$), 7.27–7.38 (10H, m, Ph); *m/z* 339 (M^+, 1.3%), 218 ($M^+ - p$-$MeOC_6H_4CH_2$, 3), 179 (22), 121 (*p*-$MeOC_6H_4CH_2^+$, 100) and 77 (Ph^+, 22).

1-(4-Nitrobenzyl)-2,5-diphenylpyrrole 16d. Yellow crystalline solid, mp 102–103 °C (Found: M^+, 354.1367. $C_{23}H_{18}N_2O_2$ requires M^+, 354.1368); $\nu_{max}(CHCl_3)/cm^{-1}$ 3037, 3005, 1604, 1518, 1486, 1466, 1452, 1388, 1345, 1321, 1266, 1246, 1236, 1215, 1111, 1075, 1043, 917 and 860; δ_H(270 MHz, $CDCl_3$) 5.31 (2H, s, CH_2), 6.38 (2H, s, pyrrole), 6.69–6.72 (2H, d, *p*-$NO_2C_6H_4$), 7.27–7.34 (10H, m, Ph), 7.93–7.96 (2H, d, *p*-$NO_2C_6H_4$); *m/z* 354 (M^+, 51%), 218 ($M^+ - p$-$NO_2C_6H_4CH_2$, 100), 191 (5), 149 (6), 115 (8), 106 (20), 89 (9) and 77 (3).

1-*tert*-Butyloxycarbonylamino-2,5-diphenylpyrrole 8d. Crystalline solid, mp 184–185 °C (lit.,[13] 183–184.5 °C).

1-Ethoxycarbonylmethyl-2,5-diphenylpyrrole 16e. Crystalline solid, mp 98–99 °C (Found: M^+, 305.1414. $C_{20}H_{19}NO_2$ requires M^+, 305.1416); $\nu_{max}(CHCl_3)/cm^{-1}$ 3036, 3002, 1746 (C=O), 1605, 1485, 1467, 1451, 1377, 1250, 1245, 1243, 1215, 1211, 1189, 1033, 922 and 874; δ_H(270 MHz, $CDCl_3$) 1.10–1.14 (3H, t, CH_3), 4.06–4.14 (2H, q, CH_2), 4.57 (2H, s, NCH_2), 6.33 (2H, s, ArH) and 7.32–7.44 (10H, m, Ph); *m/z* 305 (M^+, 100%), 277 ($M^+ - Et$, 15), 232 ($M^+ - CO_2Et$, 93), 218 (6), 202 (9), 154 (8), 128 (18), 115 (10), 102 (7) and 77 (14).

Methyl 2,5-diphenylpyrrole-1-carboxylate 8c

In a 250 ml three-neck flask fitted with a gas inlet tube, reflux condenser with drying tube and a magnetic stirrer were placed 2,5-diphenylpyrrole (5.0 g) and dry light petroleum (bp 60–80 °C) (50 ml). The light petroleum was warmed to dissolve the pyrrole after which potassium (1 g) was added to the solution. After the mixture had been stirred and refluxed for 3 h under dry nitrogen, methyl chloroformate (2.5 g) was added to it and refluxing was continued for 0.5 h. After this the mixture was cooled and acetic acid (5 ml) was added to it with rapid stirring to react with any remaining potassium. The reaction mixture was then poured into water (200 ml) and ether (100 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 × 20 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated at reduced pressure to leave a pale brown oil which subsequently solidified. Recrystallization of this from hexane gave the product **8c** (4.0 g, 62%) as pale yellow cubic crystals, mp 99–100 °C (lit.,[14] 100 °C).

1-Amino-2,5-diphenylpyrrole 18

A mixture of 1-*tert*-butyloxycarbonylamino-2,5-diphenylpyrrole **8d** (2.2 g) and methanol (30 ml) was heated to reflux and hydrogen chloride gas was passed through the solution for 0.5 h. A pink solid separated. The mixture was allowed to stand at room temperature for 2 h after which the solid was filtered off and washed with methanol. The crude solid was recrystallized from dimethylformamide to give the product **18** (1.23 g, 80%) as cream coloured flakes, mp 218–219 °C (lit.,[13] 218–220 °C).

The following 3,4-dibromo-2,5-diphenylpyrroles were prepared by brominating the corresponding 2,5-diphenylpyrroles with *N*-bromosuccinimide (NBS) (2 equiv.) in dry tetrahydrofuran at 4 °C.[6] These brominated pyrroles were purified by recrystallization. The physical data for the compounds prepared are as follows.

3,4-Dibromo-1-methyl-2,5-diphenylpyrrole. Crystals, mp 128–130 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3036, 3008, 1604, 1482, 1471, 1432, 1324, 1242, 1216, 1214, 1195, 1160, 1030, 975 and 920; δ_H(270 MHz, $CDCl_3$) 3.37 (3H, s, Me), 7.42–7.47 (10H, m, Ph); *m/z* 393 ($M^+ + 4$, 50%), 391 ($M^+ + 2$, 100), 389 (M^+, 51), 310 ($M^+ - Br$, 3), 297 ($M^+ - Me - Br$, 3), 230 ($M^+ - Br_2$, 13), 216 ($M^+ - Br_2 - Me$, 9), 202 (5), 195 (5), 189 (5), 128 (7), 118 (17), 113 (12) and 77 (Ph^+, 18).

3,4-Dibromo-1-ethyl-2,5-diphenylpyrrole 20a. Crystals, mp 118–120 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3036, 3008, 1432, 1345, 1291, 1248, 1244, 1216, 1214, 1183, 1045, 902 and 848; δ_H(270 MHz, $CDCl_3$) 0.75–0.80 (3H, t, CH_3), 3.82–3.88 (2H, q, CH_2) and 7.40–7.50 (10H, m, Ph); *m/z* 407 ($M^+ + 4$, 20%), 405 ($M^+ + 2$, 40), 403 (M^+, 20), 376 ($M^+ - Et$, 5), 216 ($M^+ - Et - Br_2$, 10), 113 (100) and 77 (Ph^+, 45).

1-Benzyl-3,4-dibromo-2,5-diphenylpyrrole 20b. Needles, mp 177–178 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3033, 3017, 1605, 1497, 1483, 1453, 1318, 1241, 1232, 1216, 1213, 1197, 1045, 1030, 974 and 817; δ_H(270 MHz, $CDCl_3$) 5.02 (2H, s, $PhCH_2$), 6.52–6.55 (2H, m, Ph), 7.08–7.10 (3H, m, Ph) and 7.30–7.39 (10H, m, Ph); *m/z* 469 ($M^+ + 4$, 10%), 467 ($M^+ + 2$, 17) 465 (M^+, 10), 388 ($M^+ - Ph$, 6), 386 ($M^+ - Br$, 5), 376 ($M^+ - PhCH_2$, 17), 307 (7), 295 ($M^+ - PhCH_2 - Br$, 5), 216 ($M^+ - PhCH_2 - Br_2$, 13) 204 (7), 113 (20) and 91 ($PhCH_2^+$, 100).

3,4-Dibromo-1-(4-methoxybenzyl)-2,5-diphenylpyrrole 20c. Needles, mp 127–128 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3038, 3024, 3017, 1613, 1514, 1483, 1467, 1306, 1253, 1244, 1216, 1196, 1177, 1046, 1037, 1030, 813 and 769; δ_H(270 MHz, $CDCl_3$) 3.71 (3H, s, OMe), 4.95 (2H, s, CH_2), 6.40–6.43 (2H, d, 4-$MeOC_6H_4$), 6.59–6.62 (2H, d, 4-$MeOC_6H_4$) and 7.31–7.42 (10H, m, Ph); *m/z* 499 ($M^+ + 4$, 4%), 497 ($M^+ + 2$, 8), 495 (M^+, 4), 376 ($M^+ - p$-methoxybenzyl, 1.4), 295 ($M^+ - p$-methoxybenzyl−Br, 1.2), 216 ($M^+ - p$-methoxybenzyl−Br_2, 5), 121 (*p*-$MeOC_6H_4CH_2$, 100), 113 (11) and 77 (Ph^+, 11).

3,4-Dibromo-1-(4-nitrobenzyl)-2,5-diphenylpyrrole 20d. Crystals, mp 166–167 °C; $\nu_{max}(CHCl_3/cm^{-1}$ 3033, 3017, 1603, 1525, 1484, 1346, 1315, 1244, 1232, 1216, 1213, 1196 and 861; δ_H(270 MHz, $CDCl_3$) 5.14 (2H, s, CH_2), 6.67–6.71 (2H, d, 4-$NO_2C_6H_4$), 7.27–7.45 (10H, m, Ph) and 7.93–7.97 (2H, d, 4-$NO_2C_6H_4$); *m/z* 516 ($M^+ + 4$, 1.2%), 514 ($M^+ + 2$, 19), 512 (M^+, 37), 496 ($M^+ - O$, 7), 376 ($M^+ - NO_2 - C_6H_4CH_2$, 100), 297 ($M^+ - NO_2C_6H_4CH_2 - Br$, 25), 296 (25), 216 ($M^+ - NO_2C_6H_4CH_2 - Br_2$, 51) 113 (55), 90 (32) and 77 (Ph^+, 12).

3,4-Dibromo-1-ethoxycarbonylmethyl-2,5-diphenylpyrrole 20e. Needles, mp 142–143 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3029, 3024, 3014, 1748 (C=O), 1605, 1484, 1446, 1417, 1376, 1322, 1254, 1244, 1241, 1232, 1216, 1213, 1194, 1191, 1046, 1028, 974, 812, 794 and 770; δ_H(270 MHz, $CDCl_3$) 1.07–1.12 (3H, t, CH_3), 4.02–4.07 (2H, q, CH_2), 4.37 (2H, s, NCH_2), 7.39–7.45 (10H, m, Ph) *m/z* 465 ($M^+ + 4$, 5%), 463 ($M^+ + 2$, 100), 461 (M^+, 55), 390 ($M^+ - CO_2Et$, 26), 309 ($M^+ - CO_2Et - Br$, 42), 230 ($M^+ - CO_2Et - Br_2$, 45), 202 (27), 127 (19), 113 (12), 105 (20) and 77 (Ph^+, 24).

Reactions of trithiazyl trichloride $(NSCl)_3$

With 1,2,5-triphenylpyrrole 5: typical procedures. (*a*) To tetrachloromethane (20 ml) was added 1,2,5-triphenylpyrrole (295 mg, 1 mmol) and the mixture was warmed with stirring to give a clear solution. To this stirred solution was added trithiazyl trichloride (82 mg. 0.33 mmol) after which the mixture was heated at reflux for 12 h under nitrogen. The tetrachloromethane was removed from the mixture by evaporation *in vacuo* and the residue was purified by column chromatography on silica gel. Elution with dichloromethane (20%) in light petroleum gave 3,4-*dichloro*-1,2,5-*triphenylpyrrole* **7** (60 mg, 17%) as colourless needles, mp 214–215 °C (Found: M^+, 363.0582. $C_{22}H_{15}NCl_2$ requires M^+, 363.0582); $\nu_{max}(CHCl_3)/cm^{-1}$ 3019, 1604, 1500, 1489, 1444, 1350, 788, 773 and 763; δ_H(270 MHz, $CDCl_3$) 6.8–7.3 (15H, m, Ph); δ_C(67.5 MHz, $CDCl_3$) 137.70, 130.45, 129.75, 129.71, 128.67, 127.88–127.59 (3 singlets?), 127.51 and 111.14; *m/z* 367 ($M^+ + 4$, 12%), 365 ($M^+ + 2$, 66), 363 M^+, 100), 328 (5), 293 (16), 227 (7), 225 (21), 145 (12) and 77 (Ph^+, 16). Elution with dichloromethane (30%) in light petroleum gave

1,2,5-triphenylpyrrole **5** (120 mg, 40%). Elution with dichloromethane (60%) in light petroleum gave N-[3-*phenyl*-1,2-*thiazol*-5-*yl*(*phenyl*)*methylidene*]*aniline* **6** as pale yellow crystals (110 mg, 32%), mp 107–108 °C (Found: C, 77.5; H, 4.8; N, 8.2%. $C_{22}H_{16}N_2S$ requires C, 77.6; H, 4.7; N, 8.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3068, 3007, 1610, 1592, 1492, 1484, 1445, 1394, 1272, 1028, 870 and 699; δ_H(270 MHz, $CDCl_3$) 6.75–7.92 (16H, m, ArH); *m*/*z* 340 (M^+, 100%), 263 ($M^+ - Ph$, 38), 236 (34), 180 (36), 103 ($PhCN^+$, 6) and 77 (Ph^+, 73).

(*b*) The procedure described in (a) was followed using the **5** (295 mg, 1 mmol) and trithiazyl trichloride (488 mg, 2 mmol) to give the pyrrole **7** (265 mg, 75%), mp 214–215 °C, identical with that described under (a) and a trace of the imine **6** (TLC).

(*c*) The procedure described in (a) was followed with the addition of pyridine, the mole ratio of reactants being 1,2,5-triphenylpyrrole : trithiazyl trichloride : pyridine = 1 : 3 : 12, to give the pyrrole **7** (56 mg, 16%), mp 214–215 °C, the pyrrole **5** (106 mg, 36%) and the imine **6** (103 mg, 30%), mp 107–108 °C.

(*d*) To a solution of the pyrrole **5** (295 mg, 1 mmol) in toluene (20 ml) was added thrithiazyl trichloride (163 mg, 0.67 mmol). The solution was heated at reflux under nitrogen for 12 h, after which the work-up procedure described in (a) was followed to give the pyrrole **7** (214 mg, 61%), mp 214–215 °C and the imine **6** (58 mg, 17%), mp 107–108 °C.

(*e*) To a solution of the pyrrole **5** (295 mg, 1 mmol) in tetrachloromethane (30 ml) was added trithiazyl trichloride (244 mg, 1 mmol). The solution was stirred at ambient temperature under nitrogen for 96 h, after which the work-up procedure described in (a) was followed to give the pyrrole **7** (70 mg, 20%), the imine **6** (78 mg, 23%) and 5-benzoyl-3-phenyl-1,2-thiazole **3** (61 mg, 23%) as a clear oil which was identical with an authentic sample.[2]

(*f*) To a solution of the pyrrole **5** (295 mg, 1 mmol) in tetrachloromethane (30 ml) was added trithiazyl trichloride (498 mg, 2 mmol) and dried 4 Å molecular sieves (2 g). The mixture was heated at reflux with stirring under nitrogen for 12 h. The molecular sieves were filtered off and washed with dichloromethane. The work-up procedure described in (a) was followed to give the pyrrole **7** (143 mg, 41%), mp 214–215 °C, and the imine **6** (163 mg, 48%), mp 107–108 °C.

With 1-(4-methoxyphenyl)-2,5-diphenylpyrrole 8a. (*a*) To a solution of the pyrrole **8a** (326 mg, 1 mmol) in tetrachloromethane (20 ml) was added trithiazyl trichloride (122 mg, 0.5 mmol) and the mixture was heated at reflux for 4 h, after which more trithiazyl trichloride (122 mg) was added to it. The mixture was heated at reflux for a further 8 h, after which the general work-up procedure was followed to give 3,4-*dichloro*-1-(4-*methoxyphenyl*)-2,5-*diphenylpyrrole* **10a** (200 mg, 51%), mp 167–168 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3036, 3010, 1605, 1513, 1488, 1466, 1444, 1353, 1297, 1254, 1243, 1182, 1170, 1107, 1070, 1044, 1032, 839 and 819; *m*/*z* 397 ($M^+ + 4$, 10%), 395 ($M^+ + 2$, 51), 393 (M^+, 80), 361 (37), 359 ($M^+ - Cl$, 100), 324 ($M^+ - 2Cl$, 17), 280 (13), 255 (33), 221 (41), 178 (10), 145 (11), 139 (12) and 77 (16); the thiazole **3** (traces), and N-[3-*phenyl*-1,2-*thiazol*-5-*yl*(*phenyl*)*methylidene*]-4-*methoxyaniline*, **9a** (59 mg, 16%), mp 80–86 °C (unstable); δ_H(270 MHz, $CDCl_3$) 3.74, 3.79 (3H, s, OMe, two isomers in the ratio 3 : 10), 6.69–6.84 (4H, m, ArH), 7.27–7.50 (9H, m, ArH) and 7.81–7.91 (2H, m, ArH); *m*/*z* 370 (M^+, 100%), 355 (54), 103 (3.6) and 77 (44).

(*b*) A mixture of the pyrrole **8a** (326 mg, 1 mmol), trithiazyl trichloride (244 mg, 1 mmol), dry 4 Å molecular sieves (2 g) in tetrachloromethane (30 ml) was stirred at room temperature under nitrogen for 96 h. The above work-up procedure gave the pyrrole **10a** (94 mg, 24%), mp 167–168 °C the imine **9a** (37 mg, 10%) and the thiazole **3** (101 mg, 36%), all identical with authentic specimens.

With 1-(4-nitrophenyl)-2,5-diphenylpyrrole 8b. (*a*) To a stirred solution of the pyrrole **8b** (680 mg, 2 mmol) in tetrachloromethane (30 ml) was added trithiazyl trichloride (244 mg, 1 mmol) and the mixture was heated at reflux for 4 h; some starting material remained (TLC). Trithiazyl trichloride (244 mg, 1 mmol) was added to the reaction mixture which was then refluxed under nitrogen for a further 8 h. The general work-up procedure was followed to give 3,4-*dichloro*-1-(4-*nitrophenyl*)-2,5-*diphenylpyrrole* **10b** (180 mg, 44%), mp 192–193 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3043, 3020, 3011, 1597, 1521, 1498, 1470, 1446, 1391, 1351, 1292, 1243, 1111, 952, 861 and 821; δ_H(270 MHz, $CDCl_3$) 7.01–7.06 (4H, m, Ph), 7.10–7.14 (2H, m, Ph), 7.22–7.30 (6H, m, Ph) and 8.01–8.50 (2H, d, *p*-$NO_2C_6H_4$); *m*/*z* 410 ($M^+ + 2$, 11%), 408 (M^+, 16), 374 ($M^+ - Cl$, 100), 328 ($M^+ - Cl - NO_2$, 23), 291 ($M^+ - NO_2 - Cl_2$, 26), 189 (19) and 146 (21); 5-benzoyl-3-phenyl-1,2-thiazole **3** (223 mg, 42%), identical with an authentic sample, and N-[3-*phenyl*-1,2-*thiazol*-5-*yl*(*phenyl*)*methylidene*]-4-*nitroaniline* **9b** (39 mg, 5%), mp 127–135 °C (unstable); $\nu_{max}(CHCl_3)/cm^{-1}$ 3414, 3008, 1623, 1601, 1588, 1517, 1396, 1343, 1312, 1171, 1111, 910, 877, 860, 731 and 704; δ_H(270 MHz, $CDCl_3$) 6.85–6.88 (2H, d, *p*-nitro C_6H_4) 7.24–7.27 (1H, m, Ph), 7.35–7.50 (6H, m, Ph), 7.59 (1H, s, ArH), 7.85–7.92 (3H, m, Ph) and 8.04–8.07 (2H, d, *p*-nitro C_6H_4); *m*/*z* 385 (M^+, 100%), 355 ($M^+ - NO$, 31), 338 ($M^+ - NO_2$, 5), 308 (21), 281 (28), 263 (24), 235 (30), 225 (26), 179 (25) and 77 (43).

(*b*) The reaction described above was repeated, using the pyrrole **8b** (340 mg, 1 mmol) and trithiazyl trichloride (244 mg, 1 mmol). The reaction mixture was stirred at room temperature for 96 h under nitrogen to give unchanged **8b** (221 mg, 65%), the pyrrole **10b** (25 mg, 6%) and the thiazole **3** (96 mg, 18%).

With methyl 2,5-diphenylpyrrole-1-carboxylate 8c. A solution of the ester **8c** (180 mg, 0.65 mmol) and trithiazyl trichloride (318 mg, 1.30 mmol) in tetrachloromethane (40 ml) was stirred at room temperature under nitrogen for 12 h; by then all starting material had disappeared and one major product had been formed (TLC). The mixture was concentrated by evaporation of the tetrachloromethane *in vacuo* and the residue was separated on silica gel by dry flash column chromatography. Elution with dichloromethane (50%) in light petroleum gave the thiazole **3** (134 mg, 78%), identical with an authentic sample.

With 1-*tert*-butoxycarbonylamino-2,5-diphenylpyrrole 8d. A solution of the pyrrole **8d** (368 mg, 1.1 mmol) and trithiazyl trichloride (269 mg, 1.1 mmol) in tetrachloromethane (30 ml) was stirred at room temperature under nitrogen for 12 h; by then all the starting material had disappeared and traces of the thiazole **3** and one major product were present (TLC). The mixture was concentrated by evaporation of the *in vacuo* and the residue was separated on silica gel. Elution with dichloromethane (70%) in light petroleum gave 5-*benzoyl*-3-*phenyl*-1,2-*thiazole*-tert-*butoxycarbonylhydrazone* **9d** (127 mg, 61%), mp 151–153 °C (Found: M^+, 379.1354 $C_{21}H_{21}N_3O_2S$ requires M^+, 379.1354); $\nu_{max}(CHCl_3)/cm^{-1}$ 3353 (NH), 3030, 3009, 1736 (C=O), 1484, 1371, 1266, 1256, 1250, 1245, 1239, 1219, 1202, 1195, 1154, 1085, 1065, 1048, 1028 and 855; δ_H(270 MHz, $CDCl_3$) 1.52, 1.60 (9H, s, Bu′, two isomers, ratio 5 : 1), 7.30 (1H, s, ArH), 7.38–7.42 (4H, m, Ph), 7.61–7.63 (3H, m, Ph) and 7.84–7.87 (3H, m, Ph); *m*/*z* 379 (M^+, 0.5%), 323 ($M^+ - Bu'$, 1.3), 279 ($M^+ - Bu'CO_2$, 22), 264 (13), 219 (18), 176 (18), 161 (31), 103 ($PhCN^+$, 77), 77 (Ph^+, 44), 56 (52) and 44 (CO_2^+, 100).

With 1-methyl-2,5-diphenylpyrrole 11. (*a*) To a solution of the pyrrole **11** (233 mg, 1 mmol) in tetrachloromethane was added trithiazyl trichloride (488 mg, 2 mmol); the solution turned black and the mixture was heated at reflux under nitrogen for 12 h. After this starting material was still left and one major product had been formed (TLC). Base-line material was separated by filtering the reaction mixture through a pad of silica gel and washing this with dichloromethane. The filtrate was concentrated by solvent evaporation *in vacuo* and the residue was separated on silica gel. Elution with dichloromethane (60%) in light petroleum and recrystallization from hexane gave 4,4′-*diphenyl*-3,3′-*bi*-1,2,5-*thiadiazole* **12** (145 mg, 45%) as colourless crystals, mp 82–83 °C (Found: C, 59.4; H, 2.9; N, 17.2. $C_{16}H_{10}N_4S_2$ requires C, 59.6; H, 3.1; N, 17.4%); $\nu_{max}(CHCl_3)/$

cm^{-1} 3067, 3012, 1466, 1430, 1351, 1235, 1220, 1136, 1016, 941, 935 and 842; δ_H(270 MHz, $CDCl_3$) 7.13–7.22 (6H, m, Ph) and 7.23–7.34 (4H, m, Ph); δ_C(67.5 MHz, $CDCl_3$) 161.43 (thiadiazole), 152.69 (thiadiazole), 131.60 (Ph), 129.53 (Ph), 128.51 (Ph), 128.06 (Ph); *m/z* 322 (M^+, 100%), 275 (19), 245 ($M^+ - Ph$, 21), 219 ($M^+ - PhCN$, 54), 161 (13), 135 ($PhCNS^+$, 69), 103 ($PhCN^+$, 42) and 77 (Ph^+, 38).

(*b*) A mixture of the pyrrole **11** (233 mg, 1 mmol), 4 Å molecular sieves (2 g), trithiazyl trichloride (488 mg, 2 mmol) and tetrachloromethane (40 ml) was heated at reflux under nitrogen for 12 h. The work-up procedure described in (a) the bithiadiazole **12** (226 mg, 70%), identical with an authentic sample.

With 1,4-diphenylbuta-1,3-diyne. (*a*) A mixture of 1,4-diphenylbutadiyne (202 mg, 1 mmol), trithiazyl trichloride (488 mg, 2 mmol) and tetrachloromethane (40 ml) was heated at reflux under nitrogen for 12 h. The general work-up procedure gave the bithiadiazole **12** (142 mg, 44%), identical with an authentic sample.

(*b*) The last reaction was repeated, but in the presence of 4 Å molecular sieves (2 g), to give bithiadiazole **12** (226 mg, 70%), identical with an authentic sample.

With (*E*)-1,4-diphenylbut-1-en-3-yne[4]. The general procedure was followed, using the enyne (204 mg, 1 mmol) and trithiazyl trichloride (488 mg, 2 mmol) to give the bithiadiazole **12** (138 mg, 43%), identical with an authentic sample.

With 1-ethyl-2,5-diphenylpyrrole 16a. (*a*) The general procedure was followed, with the pyrrole **16a** (247 mg, 1 mmol) and triathiazyl trichloride (488 mg, 2 mmol) to give 3,4-*dichloro*-1-*ethyl*-2,5-*diphenylpyrrole* **17a** (198 mg, 63%), mp 100–101 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3077, 3026, 3014, 1606, 1578, 1485, 1468, 1445, 1380, 1331, 1243, 1196, 1193, 1084, 1075, 1033, 1016 and 921; δ_H(270 MHz, $CDCl_3$) 0.77–0.82 (3H, t, CH_3), 3.85–3.93 (2H, q, CH_2) and 7.40–7.52 (10H, m, Ph); *m/z* 319 ($M^+ + 4$, 11%), 317 ($M^+ + 2$, 62), 315 (M^+, 100), 300 ($M^+ - Me$, 10), 286 ($M^+ - Et$, 20), 279 ($M^+ - Cl$, 5), 265 ($M^+ - Me - Cl$, 8), 251 ($M^+ - Et - Cl$, 10), 245 (5), 216 (6), 202 (4), 189 (5), 183 (5), 149 (8), 113 (10), 104 (10) and 77 (6); and the bithiadiazole **12** (39 mg, 12%), identical with an authentic sample.

(*b*) A mixture of the pyrrole **16a** (466 mg, 2 mmol), dry 4 Å molecular sieves (4 g), trithiazyl trichloride (976 mg, 4 mmol) and tetrachloromethane (50 ml) was heated at reflux under nitrogen for 12 h. The molecular sieves were filtered off and washed with dichloromethane. The general work-up procedure gave the pyrrole **17a** (88 mg, 14%) and the bithiadiazole **12** (425 mg, 66%).

(*c*) A mixture of the pyrrole **16a** (233 mg, 1 mmol), dry aluminium oxide (2 g), trithiazyl trichloride (488 mg, 2 mmol) and tetrachloromethane (30 ml) was heated at reflux under nitrogen for 12 h. The general work-up procedure gave the pyrrole **17a** (95 mg, 30%) and the bithiadiazole **12** (103 mg, 32%).

(*d*) A mixture of the pyrrole **16a** (233 mg, 1 mmol), dry silica gel (40–60 Å; 2 g), trithiazyl trichloride (488 mg, 2 mmol) and tetrachloromethane (30 ml) was heated at reflux under nitrogen for 12 h. The general work-up procedure gave the pyrrole **17a** (64 mg, 20%) and the bithiadiazole **12** (155 mg, 48%).

With 1-benzyl-2,5-diphenylpyrrole 16b. (*a*) The general procedure was followed, with the pyrrole **16b** (309 mg, 1 mmol) and trithiazyl trichloride (488 mg, 2 mmol) to give 1-*benzyl*-3,4-*dichloro*-2,5-*diphenylpyrrole* **17b** (215 mg, 57%), mp 124–125 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3026, 3012, 1606, 1578, 1496, 1487, 1453, 1329, 1252, 1243, 1195, 1155, 1076, 1044, 1033, 1012, 1000 and 920; δ_H(270 MHz, $CDCl_3$) 5.02, (2H, s, $PhCH_2$), 6.55–6.60 (2H, m, Ph), 7.08–7.10 (3H, m, Ph) and 7.32–7.38 (10H, m, Ph); *m/z* 381 ($M^+ + 4$, 0.2%), 379 ($M^+ + 2$, 1.3), 377 (M^+, 2.1), 343 ($M^+ - Cl$, 45%), 308 (9), 285 (3), 252 (79), 218 (23), 202 (2.3), 91 ($PhCH_2^+$, 100), 77 (3.1); and the bithiadiazole **12** (19 mg, 6%), identical with an authentic sample.

(*b*) The last reaction was repeated, but in the presence of 4 Å molecular sieves (2 g) to give the pyrrole **17b** (207 mg, 55%) and the bithiadiazole **12** (58 mg, 18%).

With 1-(4-methoxybenzyl)-2,5-diphenylpyrrole 16c. (*a*) The general procedure was followed, with the pyrrole **16c** (339 mg, 1 mmol) and trithiazyl trichloride (488 mg, 2 mmol) to give 3,4-*dichloro*-1-(4-*methoxybenzyl*)-2,5-*diphenylpyrrole* **17c** (179 mg, 44%), mp 95–97 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3061, 3018, 1612, 1513, 1486, 1466, 1328, 1306, 1256, 1243, 1188, 1178, 1076, 1045, 1035, 817, 800 and 781; δ_H(270 MHz, $CDCl_3$) 3.71 (3H, s, OMe), 4.95 (2H, s, CH_2), 6.40–6.43 (2H, d, *p*-$MeOC_6H_4$), 6.59–6.62 (2H, d, *p*-$MeOC_6H_4$) and 7.31–7.42 (10H, Ph); *m/z* 411 ($M^+ + 4$, 0.4%), 409 ($M^+ + 2$, 2.1), 407 (M^+, 3.5), 287 (0.5), 121 (*p*-$MeOC_6H_4CH_2^+$, 100), 77 (3) and the bithiadiazole **12** (39 mg, 12%).

(*b*) The last reaction was repeated but in the presence of 4 Å molecular sieves (2 g) to give the pyrrole **17c** (163 mg, 40%) and bithiadiazole **12** (81 mg, 25%).

With 1-(4-nitrobenzyl)-2,5-diphenylpyrrole 16d. (*a*) The general procedure was followed, with the pyrrole **16d** (354 mg, 1 mmol) and trithiazyl trichloride (488 mg, 2 mmol) to give 3,4-*dichloro*-1-(4-*nitrobenzyl*)-2,5-*diphenylpyrrole* **17d** (253 mg, 60%), mp 190–192 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3036, 3012, 1605, 1530, 1488, 1449, 1351, 1196, 1111, 1045, 1034, 861, 836 and 817; δ_H(270 MHz, $CDCl_3$) 5.12 (2H, s, CH_2), 6.65–6.68 (2H, d, *p*-$NO_2C_6H_4$), 7.93–7.97 (2H, d, *p*-$NO_2C_6H_4$) and 7.31–7.41 (10H, m, Ph); *m/z* 426 ($M^+ + 4$, 3.6%), 424 ($M^+ + 2$, 19), 422 (M^+, 29), 286 ($M^+ - p$-nitrobenzyl, 78), 251 ($M^+ - p$-nitrobenzyl − Cl, 18), 216 ($M^+ - p$-nitrobenzyl − 2Cl, 9), 113 (19), 106 (100), 77 (Ph^+, 13); and the bithiadiazole **12** (38 mg, 12%).

(*b*) The last reaction was repeated but in the presence of 4 Å molecular sieves (2 g) to give the pyrrole **17d** (257 mg, 61%) and bithiadiazole **12** (97 mg, 30%).

With 1-ethoxycarbonylmethyl-2,5-diphenylpyrrole 16e. The general procedure was followed, with the pyrrole **16e** (305 mg, 1 mmol) and trithiazyl trichloride (488 mg, 2 mmol) to give 3,4-*dichloro*-1-*ethoxycarbonylmethyl*-2,5-*diphenylpyrrole* **17e** (194 mg, 52%), mp 100–101 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3026, 3020, 3011, 1749 (C=O), 1607, 1488, 1447, 1420, 1395, 1376, 1346, 1262, 1250, 1247, 1243, 1193, 1190, 1026 and 818; δ_H(270 MHz, $CDCl_3$) 1.06–1.15 (3H, t, CH_3), 4.02–4.11 (2H, q, CH_2), 4.41 (2H, s, NCH_2) and 7.38–7.46 (10H, m, Ph); *m/z* 377 ($M^+ + 4$, 11%), 375 ($M^+ + 2$, 65), 373 (M^+, 100), 345 ($M^+ - Et$, 8), 300 ($M^+ - Et - CO_2$, 50), 265 ($M^+ - Et - CO_2 - Cl$, 65), 230 ($M^+ - EtCO_2 - 2Cl$, 25), 202 (23), 162 (19), 127 (14), 113 (12), 77 (Ph^+, 22); and bithiadiazole **12** (74 mg, 23%).

With 1-amino-2,5-diphenylpyrrole 18. (*a*) To a mixture of tetrachloromethane (20 ml) and tetrahydrofuran (10 ml) was added the pyrrole **18** (234 mg, 1 mmol); the mixture was warmed to dissolve the pyrrole after which trithiazyl trichloride (244 mg, 1 mmol) was added to the solution which turned black. The mixture was stirred at room temperature for 4 h, after which more trithiazyl trichloride (244 mg, 1 mmol) was added to it. After the mixture had been heated at reflux for 12 h it was evaporated *in vacuo* and the residue was separated on silica gel. Elution with dichloromethane (30%) in light petroleum gave 3,4-*dichloro*-2,5-*diphenylpyrrole* (40 mg, 14%) as a crystalline solid, mp 155–157 °C (Found: M^+, 287.0270. $C_{16}H_{11}Cl_2N$ requires M^+, 287.0269); δ_H(270 MHz, $CDCl_3$) 7.32–7.38 (2H, m, Ph), 7.44–7.49 (4H, m, Ph), 7.67–7.70 (4H, m, Ph) and 8.28 (1H, br, NH); *m/z* 289 ($M^+ + 2$, 63%), 287 (M^+, 100), 251 ($M^+ - Cl$, 6), 217 ($M^+ - 2Cl$, 10), 149 (30), 143 (12), 113 (16), 104 (11) and 77 (17). Elution with dichloromethane (50%) in light petroleum gave the bithiadiazole **12** (68 mg, 21%) and 1,3,5,7-*tetraphenyl*-2H,6H-*dipyrrolo*[3′,4′-e;3,4-b]1,4-*dithiin* **19** (20 mg, 8%) as bright yellow plates, mp 235–237 °C (Found: M^+, 498.1220. $C_{32}H_{22}N_2S_2$ requires M^+, 498.1220); $\nu_{max}(CHCl_3)/cm^{-1}$ 3690 (NH), 3031, 3014, 3011, 2927, 1721, 1603, 1487, 1464, 1380, 1281, 1252, 1248, 1242, 1234, 1195, 1044, 800, 795, 778 and 734; δ_H(270 MHz, $CDCl_3$)

7.39–7.51 (12H, m, Ph), 7.60–7.62 (8H, m, Ph) and 8.40 (2H, br, NH); *m/z* 498 (M^+, 18%), 466 ($M^+ - S$, 4), 434 ($M^+ - 2S$, 2), 394 (7), 313 (25), 279 (21), 251 (67), 249 (78), 219 (24), 145 (30), 104 (19), 102 (24), 77 (28) and 64 (100).

(*b*) To a mixture of the pyrrole **18** (234 mg, 1 mmol), tetrachloromethane (30 ml), tetrahydrofuran (15 ml) and 4 Å molecular sieves (2 g) was added trithiazyl trichloride (488 mg, 2 mmol). The reaction mixture was heated at reflux for 12 h, after which the molecular sieves were filtered off and washed with dichloromethane (20 ml). The work-up procedure described in (a) was followed to give 3,4-dichloro-2,5-diphenylpyrrole (36 mg, 13%), the bithiadiazole **12** (106 mg, 33%), and the dipyrroledithiin **19** (13 mg, 5%).

The reactions of the following 3,4-dibromo-2,5-diphenylpyrroles (1 mmol) with trithiazyl trichloride (2 mmol) were carried out in refluxing tetrachloromethane in the presence of 4 Å molecular sieves (2 g) for 12 h; the mixtures were evaporated *in vacuo* and the residues were separated on silica gel by column chromatography.

With 3,4-dibromo-1-methyl-2,5-diphenylpyrrole. This gave the bithiadiazole **12** (260 mg, 64%) and 3-(*benzoyldichloromethyl*)-4-*phenyl*-1,2,5-*thiadiazole* **21** (108 mg, 31%), mp 99–100 °C (Found: C, 54.8; H, 3.0; N, 8.05. $C_{16}H_{10}Cl_2N_2OS$ requires C, 55.0; H, 2.9; N, 8.0%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3067, 3013, 1714 (C=O), 1598, 1581, 1448, 1387, 1224, 1186, 1008, 904, 828, 803, 774, 770, 754 and 690; δ_H(270 MHz, $CDCl_3$) 7.23–7.25 (2H, m, Ph), 7.30–7.32 (6H, m, Ph) and 7.43–7.47 (2H, m, Ph).

With 3,4-dibromo-1-ethyl-2,5-diphenylpyrrole 20a. This gave the bithiadiazole **12** (132 mg, 41%) and the thiadiazole **21** (115 mg, 33%), mp 99–100 °C, identical with the compounds described above.

With 1-benzyl-3,4-dibromo-2,5-diphenylpyrrole 20b. This gave the pyrrole **17b** (317 mg, 84%), mp 124–125 °C, identical with that described earlier, and bithiadiazole **12** (32 mg, 10%).

With 3,4-dibromo-1-(4-methoxybenzyl)-2,5-diphenylpyrrole 20c. This gave the pyrrole **17c** (395 mg, 97%), mp 95–97 °C, identical with that described earlier, and traces of the bithiadiazole **12** (TLC).

With 3,4-dibromo-1-(4-nitrobenzyl)-2,5-diphenylpyrrole 20d. This gave the pyrrole **17d** (414 mg, 98%), mp 190–192 °C, identical with that described earlier, and traces of the bithiadiazole **12** (TLC).

With 3,4-dibromo-1-ethoxycarbonylmethyl-2,5-diphenylpyrrole 20e. This gave the pyrrole **17e** (168 mg, 45%), mp 100–101 °C, identical with that described earlier, and the bithiadiazole **12** (103 mg, 32%).

Detection of hydrogen cyanide

(*a*) To a 50 ml B-14 round-bottom flask, equipped with a normal B-14 water-cooled condenser, was added trithiazyl trichloride (244 mg, 1 mmol) and tetrachloromethane (30 ml); the mixture was heated to reflux with stirring. A Kitagawa HCN length-of-stain detector [15] tube was put at the top of the condenser, and gas (100 ml) was drawn through the tube by a calibrated syringe; one-fifth of the tube turned red. The solution was allowed to cool, after which 1-methyl-2,5-diphenylpyrrole **11** (117 mg, 0.5 mmol) was added to it in one portion, and the mixture was heated again to reflux. A new detector tube was immediately put at the top of the condenser, and the procedure repeated exactly; the whole of the tube turned red.

(*b*) To a 50 ml B-14 round-bottomed flask, equipped with a double-walled B-14 water-cooled condenser, was added trithiazyl trichloride (244 mg, 1 mmol) and tetrachloromethane (30 ml); the mixture was heated to reflux with stirring. When the same test procedure was followed, as above, no colour change of the tube was observed. The solution was allowed to cool, 1-methyl-2,5-diphenylpyrrole **11** (117 mg, 0.5 mmol) was added in one portion to the mixture which was then heated again to reflux. A new detector tube was immediately put at the top of the condenser, and the procedure repeated exactly; half of the tube turned red.

The same procedure was followed to test the reaction of 1-ethyl-2,5-diphenylpyrrole **16a** with trithiazyl trichloride. A double-walled condenser was used, and no colour change of the detector tube was observed when 1-ethyl-2,5-diphenylpyrrole was added to the mixture which was then heated to reflux.

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