Simultaneous 1,2-, 1,3- and 1,4-addition of trithiazyl trichloride to a conjugated diene

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1,4-Diphenylbuta-1,3-diene and trithiazyl trichloride 1 react to give a bi(thiadiazole) 2, an isothiazoloisothiazole 3, a dithiazolothiazine 4 and the thiazinodithiatriazepines 5 and 6, all of which could arise from initial addition of the trimer 1, or its monomer, to the conjugated diene by 1,2-,1,4- and, for the first time to an all-carbon diene, 1,3-('criss-cross') cycloaddition reactions.

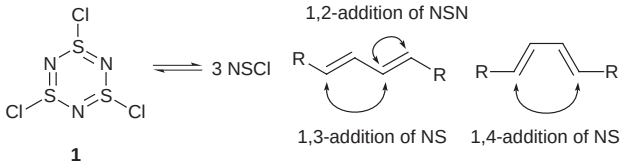
We have shown that trithiazyl trichloride $(NSCl)_3$ **1**, in thermal equilibrium with its monomer N≡SCl,[1] converts monoenes and monoynes directly into 1,2,5-thiadiazoles.[2] Furthermore, 1-alkyl-2,5-diphenylpyrroles are similarly converted into the bi(1,2,5-thiadiazole) **2**, thus reacting as masked 1,3-dienes.[3] It would be interesting therefore to explore the reaction of the reagent **1** with acyclic conjugated dienes where 1,3- and 1,4-cycloaddition, as well as 1,2-cycloaddition, can be envisaged, as shown in Scheme 1.

When (*E,E*)-1,4-diphenylbuta-1,3-diene was treated with a deficiency of **1** (1 mol) in refluxing CCl_4 for 30 min a rapid and complex reaction ensued, from which five crystalline organic compounds **2**–**6** were isolated in low yields† by careful chromatography and shown to be derivatives of five different, rare or new heterocyclic ring systems (Scheme 2). The same five products were obtained in higher yields,† shown in brackets in Scheme 2, when the diene was treated with **1** (1 mol) in refluxing toluene for 1 h. With more trimer (3 mol) in refluxing toluene for 16 h, the reaction was less complex and **2** was the major product (60%). In spite of their very different structures, the carbon connectivity of the starting diene is retained in all of these products.

The bi(1,2,5-thiadiazole) **2** was identical with that formed from *N*-alkyl-2,5-diphenylpyrroles.[3]

The isothiazolo[5,4-*d*]isothiazole structure **3** was suggested by its high stability and symmetry (^{1}H and ^{13}C NMR) and its mass spectrum, which gave fragments for PhCN and C_2S_2. This product was synthesised independently from the oxime of 5-benzoyl-3-phenylisothiazole[4] and disulfur dichloride in DMF at 100 °C, providing another approach to this rare ring system.

The new dithiazolo[4,5-*d*]thiazine *S*-oxide structure **4** was based on its spectroscopic properties and confirmed by X-ray crystallography.[5] The sulfoxide group suggested that formation of **4** had involved oxidation, possibly during isolation; an examination of the five products **2**–**6** showed that all were stable to air except for the brown compound **5** which was oxidised to **4** when adsorbed on silica. Compound **5** was rapidly and cleanly converted into **4** by MCPBA in CH_2Cl_2 at room temperature. Link scan mass spectrometry showed that **4** and **5** gave the same pattern of daughter ions, the same species ($C_{16}H_{10}N_2S_3$) being



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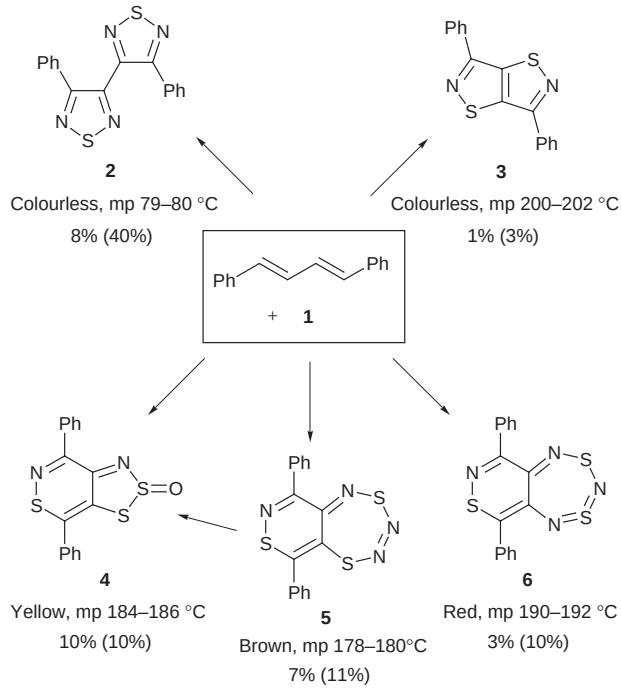
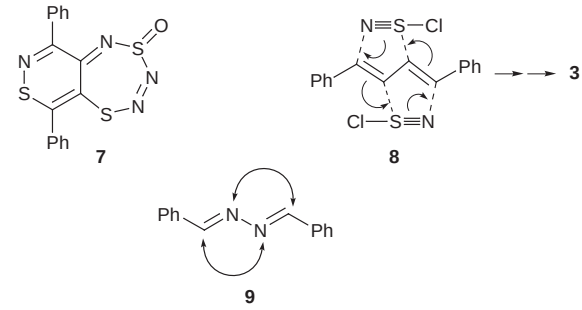
Scheme 1



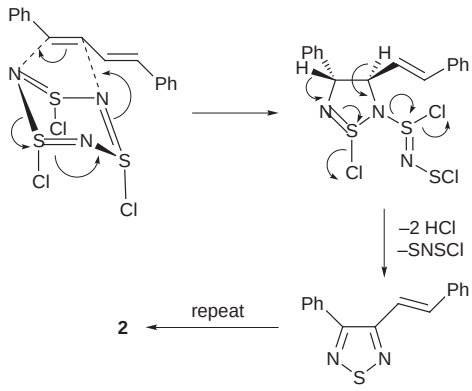
Scheme 2

formed from **4** by loss of O and from **5** by loss of N_2. This suggested the new thiazinodithiatriazepine structure **5** for the brown product, which agreed with all its spectroscopic properties, including the dominant loss of N_2 in the mass spectrum. Conversion of **5** into **4** could result from oxidation at the least hindered sulfur atom, to give **7**, followed by extrusion of N_2.



The structure of the final product **6**, which is isomeric with **5**, was assigned on the basis of spectroscopic properties and a chemical degradation. Its molecular ion was much stronger than that of **5** and showed no loss of N_2.

The formation of all five products can be explained by initial 1,2-, 1,3- and 1,4-cycloaddition processes (Scheme 1). The bi(thiadiazole) **2** is probably formed by addition of the trimer, as



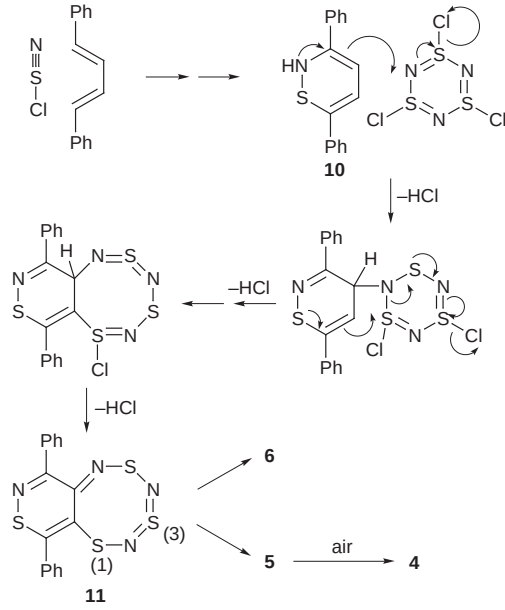
Scheme 3

an N–S–N unit, across C_1–C_2 and C_3–C_4, exactly as for monoenes[2] and pyrroles,[3] as shown in Scheme 3.

The structure of the isothiazoloisothiazole **3** suggests the addition of S–N units, possibly the monomeric species N≡SCl, across C_1–C_3 and C_2–C_4, as shown in **8**. Subsequent elimination of HCl and oxidation, possibly *via* chlorination, would give the stable aromatic system **3**. Such 'criss-cross' cycloadditions[6] have been reported for azabutadienes, particularly for azines such as 1,4-diphenyl-2,3-diazabuta-1,3-diene **9**,[7] but the present reaction is, we believe, the first example of a criss-cross cycloaddition to an all-carbon diene.

The 1,2-thiazine ring common to the remaining products suggests the 1,4-addition of an N–S unit, probably the monomer, to the diene. Since at least four molecules of monomer are required to form compounds **5** and **6**, it is possible that the Diels–Alder process is followed by reaction with a molecule of trimer, with overall elimination of 4 HCl units to give the intermediate **11** (Scheme 4). Initial Diels–Alder reaction, elimination of HCl and a hydrogen shift would give 3,6-diphenyl-1,2-thiazine **10**, which is nucleophilic at C_4. Attack on the trimer **1** at nitrogen, followed by a second nucleophilic attack by C_5 at sulfur and elimination of the remaining HCl, could give the key intermediate **11**. This is formally a 16π antiaromatic system which could become 14π by extrusion of any one of the sulfur atoms. Extrusion of S_3 or S_1 would then lead to the observed products **5** and **6**, respectively, and **4** has been shown to arise by oxidation and N_2 extrusion from **5**.

Thus the initially puzzling array of products from this one diene can be explained by invoking all three cycloaddition modes of the diene with the reactive trimer **1** and its more reactive monomer. At present the only product produced in high yield is the bi(1,2,5-thiadiazole) **2**, under more vigorous conditions; the analogous di-*p*-tolyl compound was also the main product from the same reaction of the corresponding butadiene.



Scheme 4

It is hoped that similar reactions of unsymmetrical and functionalised conjugated dienes will prove to be more selective and hence of synthetic as well as mechanistic value.

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Notes and References

† Yields are based on the minimum amount of trimer **1**, which is in deficiency, required to give each product.

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