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### Introduction.

In an earlier lecture in this series [1] we described the synthesis and properties of some novel polysulfur-nitrogen heterocyclic systems which are stable in spite of having a high ratio of heteroatoms to carbon atoms. Such systems were initially formed by the introduction of one or two carbon atoms into wholly inorganic heterocyclic rings, such as the cyclic sulfur nitrides (cyclothiazenes). In the course of this work we studied the reactivity of some inorganic "reagents" notably tetrasulfur tetranitride and trithiazyl trichloride **1** with organic substrates, particularly in cycloaddition reactions. We found that the more reactive and much less well studied trithiazyl trichloride **1** reacts in various ways with a wide range of simple organic compounds and has considerable potential for the synthesis of organic sulfur-nitrogen compounds, particularly heterocyclic rings containing S-N, N-S-N, and S-N-S units (Scheme 2).

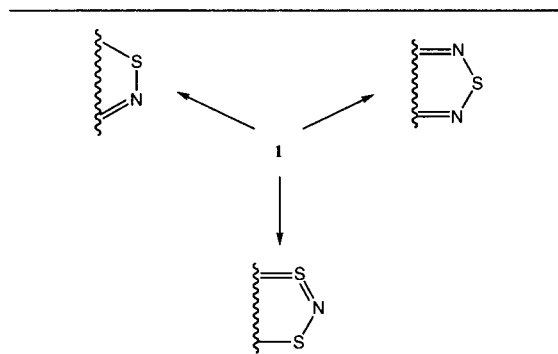
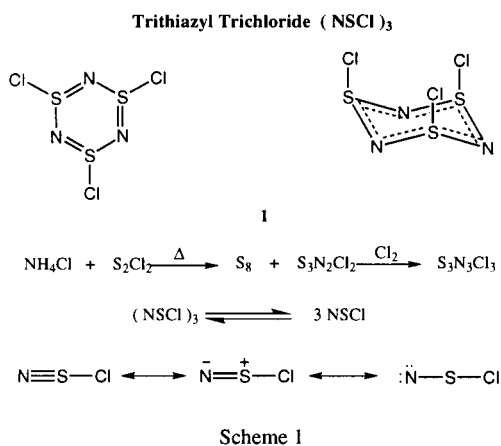
Trithiazyl trichloride [2] is a stable, but moisture-sensitive yellow crystalline solid which is prepared by heating ammonium chloride with disulfur dichloride, followed by chlorination of the initially formed salt,  $S_3N_2Cl_2$  (Scheme 1). Its six-membered ring has a somewhat flattened chair conformation with all three chlorines axial and on the same side of the ring, conveniently leaving the other side exposed for substitution and cycloaddition reactions. The ring bonds are delocalised, all being of equal length. The cyclic species (the "trimer") **1** is in equilibrium with the monomer, thiazyl chloride, NSCl, and on heating in inert organic solvents to about 60°C the monomer imparts a characteristic green colour to the solution [2]. Various canonical forms can be written for the monomer (Scheme 1) which is highly reactive. The inorganic chemistry of **1** has been extensively studied, but its reactions with organic substrates are relatively rare and usually complex and low yielding, and their generality has not been established [2].

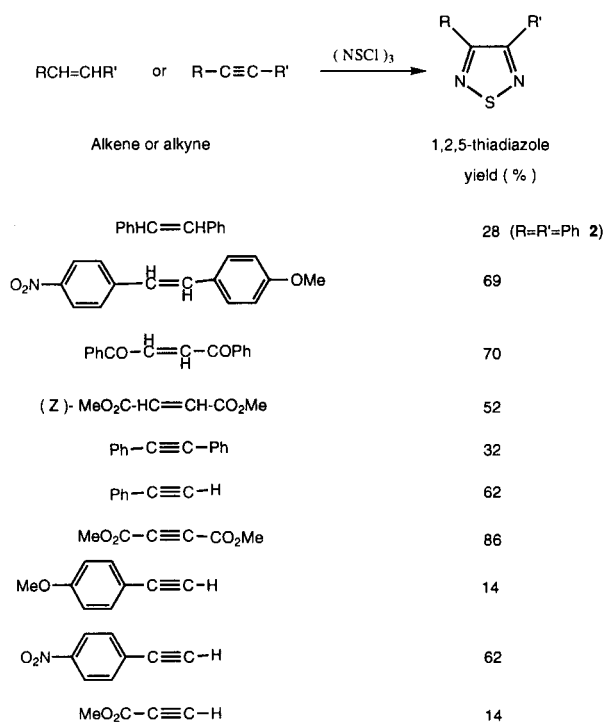
### Reaction with Alkenes and Alkynes.

One of the simplest and most useful reactions of the trimer **1** is with alkenes and alkynes, to give 1,2,5-thiadiazoles (Scheme 3). Early examples of this reaction with *trans*-stilbene and acenaphthylene in boiling chloroform to give 3,4-diphenyl-1,2,5-thiadiazole **2** and the fused thiadiazole, respectively, in low to moderate yields were reported by Barton and Bubb [3]. The yield of **2** (14%) can be increased a little (to 28%) by running the reaction in boiling toluene. We have extended the range of alkenes and alkynes converted into 1,2,5-thiadiazoles, under mild conditions. The mixture of reactants was stirred in benzene at room temperature overnight and then heated at reflux for an hour to complete the reaction. The yields of thiadiazoles so obtained are shown in Scheme 3.

Terminal alkynes tend to give low yields of the mono-substituted thiadiazoles, apparently because of competing polymerisation of the alkyne. Dimethyl maleate gave a reasonable yield of the thiadiazole but dimethyl fumarate and fumaronitrile did not react. The 4-methoxy-4'-nitro derivative of *trans*-stilbene, where the double bond is activated by "push-pull" substituents, gave a much better yield than stilbene.

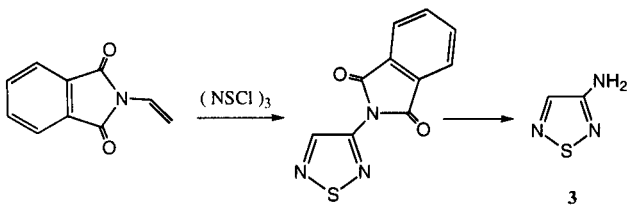
We were able to apply this trimer-alkene reaction to the synthesis of 3-amino-1,2,5-thiadiazole **3** which was needed for another purpose. This amine has been prepared [4] from aminoacetamide and  $S_2Cl_2$ , but synthesis of the amidine requires several steps and the  $S_2Cl_2$  reaction





Scheme 3

can give problems. Treatment of *N*-vinylphthalimide with (NSCl)<sub>3</sub> in boiling THF in the presence of 4 Å molecular sieves (which often improve trimer reactions) gave the desired 3-phthalimido-1,2,5-thiadiazole (38%) which was deprotected with methylhydrazine in benzene at room temperature to give 3-amino-1,2,5-thiadiazole (90%) (Scheme 4). This two-step synthesis in 34% yield compares favourably with the literature method from aminoacetamide.



Scheme 4

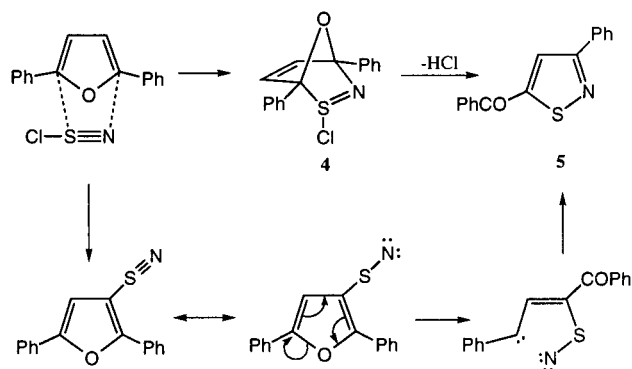
### Reaction with Pyrroles.

In the earlier lecture [1] we described the ready conversion of imines, R-CH=N-CH<sub>2</sub>-R', into 1,2,4-thiadiazoles on treatment with (NSCl)<sub>3</sub> in boiling chloroform in the presence of pyridine (Scheme 5). Since this thermal reaction could have involved the monomer, we sought independent evidence for NSCl by attempted Diels-Alder



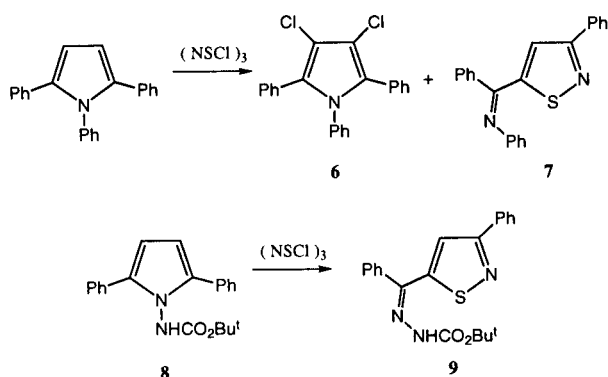
Scheme 5

reaction with a furan. 2,5-Diphenylfuran and the trimer (0.33 mole) reacted cleanly to give high yields of (> 80%) of 5-benzoyl-3-phenylisothiazole **5** which could indeed have been formed by rearrangement of the initial Diels-Alder adduct **4** with loss of HCl. However, an alternative mechanism could involve electrophilic attack of the furan by NSCl (equivalent to NS<sup>+</sup> Cl<sup>-</sup>) through sulfur at the unsubstituted β-position as shown (Scheme 6) or through nitrogen at the α-position. The reaction was regio-specific, giving none of the 3-benzoyl-5-phenyl isomer of **5**, and it provides an entirely new route to isothiazoles. Exactly the same product was obtained, though in lower yields, when the furan was replaced by 2,5-diphenylthiophene; we believe that the analogous product 3-phenyl-5-thiobenzoylisothiazole is formed but is oxidised very rapidly, like other thioketones, by the trimer to give the 5-benzoyl compound on work up.



Scheme 6

With these mechanistic possibilities in mind, we thought it of interest to extend the trimer reactions to pyrroles, where the enhanced sensitivity of the ring to electrophilic attack might be expected to favour that mechanism over cycloaddition, and where we have an extra mechanistic probe in variation of the *N*-substituent. By analogy with the above furan and thiophene, we first studied 1,2,5-triphenylpyrrole, with an "inert" *N*-substituent. After treatment of this with trimer (0.33 mole) in boiling CCl<sub>4</sub> for 12 hours, starting material (40%) was recovered together with the 3,4-dichlorinated product **6** (17%) and the *N*-phenylimine **7** (32%), which hydrolysed readily to the ketone **5**. Formation of a significant amount of a chlorinated product here accords with the well known



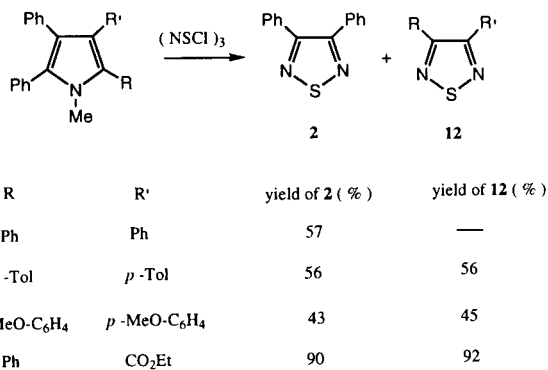
ease of halogenation of pyrroles; interestingly only the dichlorinated compound was observed. Formation of the *N*-phenylimine **7** is entirely analogous to the diphenylfuran and thiophene reactions and probably occurs by the same mechanism. The reaction conditions were varied in an attempt to increase the product yields; 2 moles of trimer in boiling  $\text{CCl}_4$  in the presence of dried 4 Å molecular sieves gave the imine **7** (48%) and the dichloropyrrole **6** (41%). We have found molecular sieves, which adsorb the HCl generated, to be beneficial in many trimer reactions, sometimes spectacularly so, and much better than the addition of bases such as pyridine. The same reaction of the analogous *N*-(*p*-methoxyphenyl) and *N*-(*p*-nitrophenyl) pyrroles gave broadly similar results; the *N*-arylimines also hydrolysed readily to the ketone **5**. The *N*-methoxycarbonyl pyrrole gave the ketone **5** directly, in high yield (78%), even at room temperature, the intermediate imine being entirely hydrolysed on work up. The *N*-*t*-butoxycarbonylamino compound **8** reacted similarly to give the stable product **9** (61%) as a mixture of the two geometrical isomers.

When the above *N*-substituents were replaced by primary alkyl groups an entirely new and unexpected reaction was observed. Treatment of 1-methyl-2,5-diphenylpyrrole **10** with trimer (2 moles) in boiling  $\text{CCl}_4$  for 12 hours gave only traces of 5-benzoyl-3-phenylisothiazole **5**, the major product (45%) being a colourless, crystalline solid with one less carbon atom and with four nitrogen and two sulfur atoms in its molecular formula. Assuming that the Me-N unit was lost, and the remaining carbon connectivity was retained, the bis-1,2,5-thiadiazole structure **11** seemed possible. Following the formation of 1,2,5-thiadiazoles from alkynes and trimer described

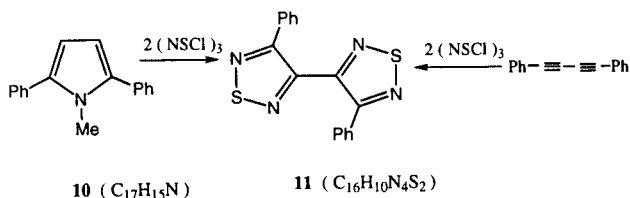
earlier, we treated 1,4-diphenylbuta-1,3-diyne under the same conditions and obtained the identical product **11** in very similar yield. The structure **11** has been confirmed by X-ray crystallography. When either of these trimer reactions was run in the presence of 4 Å molecular sieves the yield of **11** increased to about 70%. Product **11** was also obtained when the pyrrole *N*-methyl group was replaced by ethyl, benzyl, *p*-methoxybenzyl and *p*-nitrobenzyl, though in lower yield with the benzylic compounds since dichlorination of the starting pyrrole was once more a substantial reaction.

With these *N*-alkylpyrroles it appears that the trimer adds an N-S-N unit across the 2,3- and 4,5- "double bonds" of the pyrrole with opening of the pyrrole ring by excision of the nitrogen and its attached alkyl group. We showed that in the *N*-methyl case the carbon and nitrogen atoms are lost as HCN, (by the *p*-nitrobenzaldehyde colour test) and a mechanism for this is proposed later. The hydrogen atoms at the pyrrole 3- and 4- positions are also lost in the formation of **11**, probably by elimination as HCl as the trimer reaction proceeds, and we thought that substitution of these hydrogens for other groups would suppress this pyrrole ring opening process.

We therefore treated 1-methyl-2,3,4,5-tetraphenylpyrrole with trimer (2 moles) in boiling  $\text{CCl}_4$  in the presence of molecular sieves to find that a reaction did ensue, to give 3,4-diphenyl-1,2,5-thiadiazole **2** in 57% yield. Thus the trimer has caused complete fragmentation of the pyrrole ring, again by presumed cycloaddition across the carbon "double bonds" and with loss of the N-Me unit.



Scheme 7

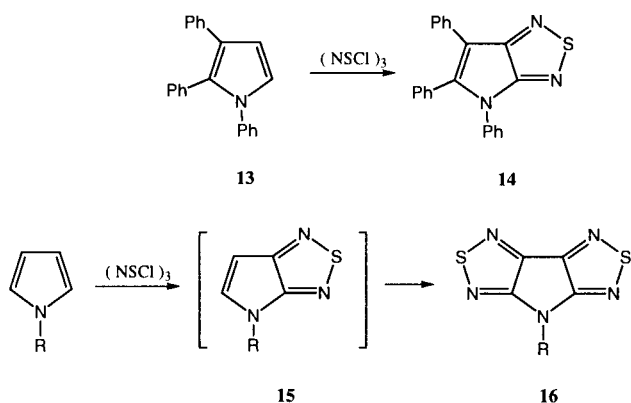


However, in this case the unit was not lost as HCN and this clearly has mechanistic implications as we shall see. In order to shed more light on this pyrrole ring cleavage, less symmetrical tetra-substituted *N*-methyl compounds were prepared and treated identically with trimer. The results all indicated the same cleavage of the pyrrole, into 2,3- and 4,5- derived fragments, as shown in Scheme 7.

With the phenyl, *p*-tolyl, and *p*-anisyl groups the yields of the thiadiazoles were about 50%, but with an electron-withdrawing ethoxycarbonyl group the yields were very high, showing just how efficient this unusual and extensive dissection of the pyrrole ring can be. In no case was there any evidence for thiadiazoles formed by cycloaddition, formal or otherwise, across other positions of the pyrrole ring. A mechanism will be proposed for this reaction later.

So far, all of the pyrroles investigated have had substituents in the  $\alpha$ -, if not the  $\beta$ -positions. What would happen if adjacent  $\alpha$ - and  $\beta$ -positions are unsubstituted? When 1,2,3-triphenylpyrrole **13** was treated with trimer under the above "standard" conditions 4,5,6-triphenylpyrrolo[2,3-*c*]-1,2,5-thiadiazole **14** was obtained in high yield (77%) as pale yellow crystals which are highly fluorescent (green) in solution. Thus, in this new and very simple reaction the reagent has fused a 1,2,5-thiadiazole ring across the unsubstituted 2,3-pyrrole bond. It is interesting to note that none of the analogous 3,4-fused thiadiazole was observed in the same reaction of 1,2,5-triphenylpyrrole or any other *N*-substituted 2,5-diphenylpyrrole that we have investigated. This is, of course, in complete agreement with the influence of the ring  $\pi$ -bond orders on the chemistry of pyrroles generally.

We then extended this trimer reaction to some pyrroles with no substituents on carbon. The trimer (2 moles) added to both the 2,3- and the 4,5 bonds of *N*-phenylpyrrole to give two fused thiadiazole rings, **16**, R=Ph (43%). In this simple one-pot process a new tricyclic ring system is produced in which all of the ring carbon atoms have been functionalised. We could not isolate, nor saw any sign of the bicyclic system **15** with one thiadiazole fused onto the pyrrole. *N*-Methylpyrrole gave the analogous product **16**, R=Me, in slightly lower yield (31%). We then



turned our attention to the synthesis of the parent ring system, 7*H*-pyrrolo[2,3-*c*:4,5-*c'*]bis-1,2,5-thiadiazole **16**, R=H. Pyrrole itself with the trimer gave a complex reaction mixture from which no pure products could be iso-

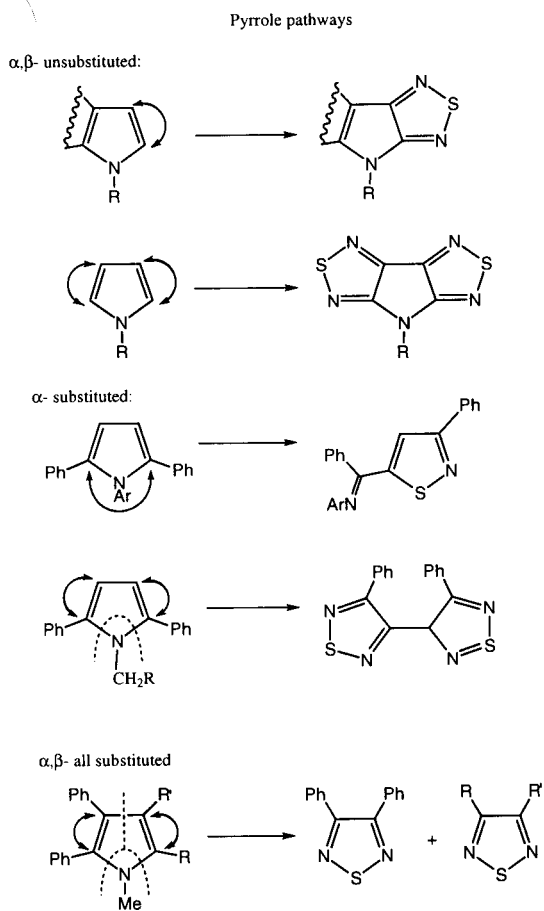
lated; pyrrole is presumably too sensitive to the reagent and to the acidic conditions which develop in its reactions. We treated various *N*-protected pyrroles similarly; a small amount of the parent system **16**, R=H (8%), was isolated from the *N*-tri-isopropyl derivative which was extensively decomposed by the trimer. The reaction of *N*-methoxycarbonylpyrrole was also complex but a very little of the corresponding pyrrolo-bistriazole **16**, R=CO<sub>2</sub>Me (4%) was isolated.

We discovered a somewhat surprising way of obtaining the tricyclic compounds **16** in much better yield, as follows. We assumed that the bicyclic species **15** was an intermediate in the reaction, although it was not observed, presumably because the remaining pyrrole carbon-carbon double bond, now being part of an enamine, reacts much faster with trimer than did the starting pyrrole. We hoped to be able to block the second thiadiazole ring fusion process by brominating the pyrrole in the 2-position. However, we found that a 2-bromine does not block thiadiazole formation on 2,3-side of the pyrrole but, to our initial surprise, it actually accelerates this process. The trimer reaction was faster and cleaner with 2-bromo-1-phenylpyrrole than with 1-phenylpyrrole, and gave the same tricyclic compound **16**, R=Ph, in considerably greater yield (70%). Even 2,3,4,5-tetrabromo-1-phenylpyrrole gave the same product in 62% yield. With 2,5-dibromo-1-methylpyrrole the yield of **16**, R=Me, was similarly increased to 74% (from 31%). Thus these pyrrolo-bis-thiadiazoles **16** can be made in good yield in a one-pot reaction of trimer with the readily formed bromopyrroles. A rationalisation of this beneficial effect will be suggested shortly.

#### Pyrrole-trimer Reaction Pathways.

The rather rich diversity of reaction modes between the trimer and variously substituted pyrroles can be summarised as shown in Scheme 8. If the 2,3-positions are free a 1,2,5-thiadiazole is fused across them; if all four carbons are unsubstituted, two thiadiazoles are fused across the 2,3- and 4,5-positions. With 2,5-diphenylpyrroles the course of the trimer reaction depends critically upon the nature of the *N*-substituent; *N*-aryl compounds undergo a rearrangement to an isothiazole imine, entirely analogous to the diphenyl furan and thiophene reactions. With *N*-alkyl compounds (with an  $\alpha$ -methylene group) the nitrogen atom and the alkyl group are excised with opening of the pyrrole ring and the (formally) resulting Ph-C-C-C-C-Ph unit is converted into a bis-1,2,5-thiadiazole. When all the ring carbons are substituted the *N*-alkyl portion is again lost but the pyrrole ring is cleaved further (between C<sub>3</sub> and C<sub>4</sub>) to give two separate thiadiazoles.

Apart from the novelty of the pyrrole chemistry illustrated in Scheme 8, these processes all represent different

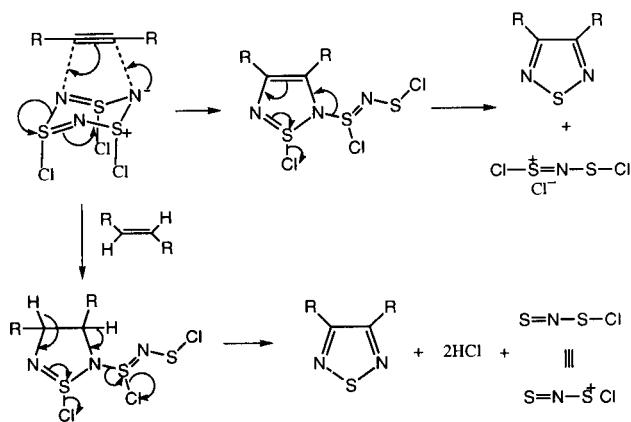


Scheme 8

ways of functionalising the pyrrole ring carbon atoms. This is of potential interest in synthesis generally since the 1,2,5-thiadiazoles, so readily formed from the trimer may be reductively desulfurised [5], for example by  $\text{LiAlH}_4$  [6],  $\text{Sn-HCl}$  [7] and Raney nickel [8], to give 1,2-diamines. Thus a fused thiadiazolo-pyrimidine has been converted into a 4,5-diaminopyrimidine [8] and reduction of tris-1,2,5-thiadiazolobenzene provides a valuable route to hexaaminobenzene [7].

#### Trimer Reaction Mechanisms.

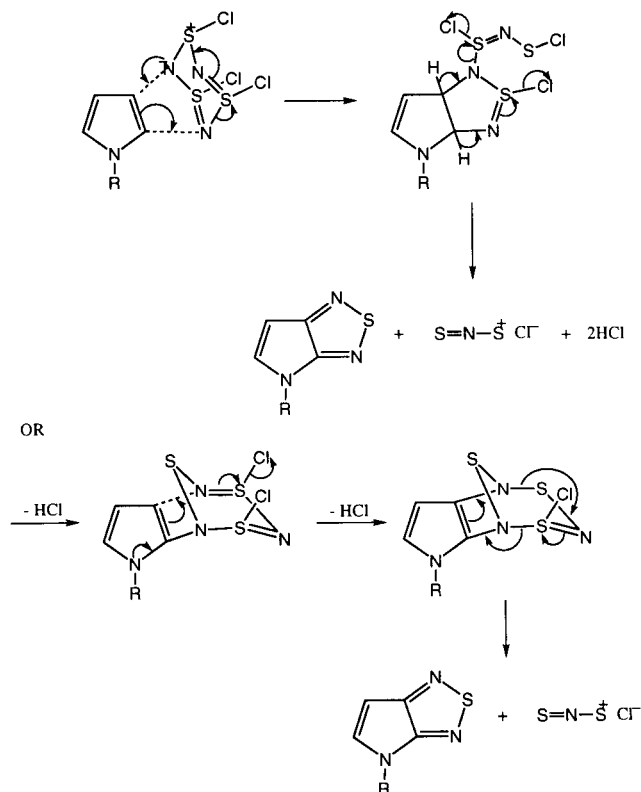
At present we have no direct evidence for the mechanism of these trimer reactions but it is helpful to consider the possibilities and we tentatively propose a reasonably unified set of schemes here. The first question is whether the organic substrate is reacting with the intact trimer and/or the monomer; if the reagent contributes an N-S-N unit then the simplest proposal is initial reaction with the trimer, possibly by a 1,3-dipolar cycloaddition type of process. Thus conversion of alkynes and alkenes to 1,2,5-thiadiazoles could proceed as shown in Scheme 9. These



Scheme 9

reactions utilise an N-S-N unit from the trimer, and the remaining S-N-S portions could possibly separate off as the known cations  $\text{ClSNSCl}^+$  and  $\text{SNS}^+$ .

The alkene reaction could apply equally well to cycloaddition to an  $\alpha,\beta$ -unsubstituted pyrrole, though now the possibility of a double electrophilic attack on pyrrole is presumably a more serious competitor (Scheme 10).

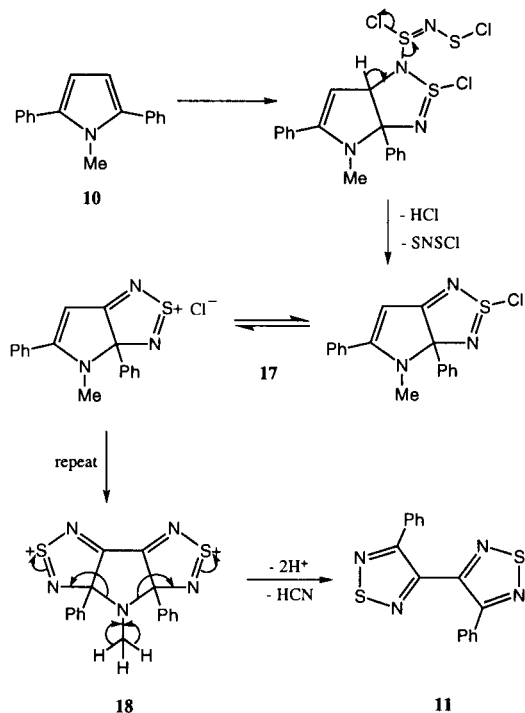


Scheme 10

We saw earlier that replacement of hydrogen by bromine on the pyrrole ring led to faster reactions giving

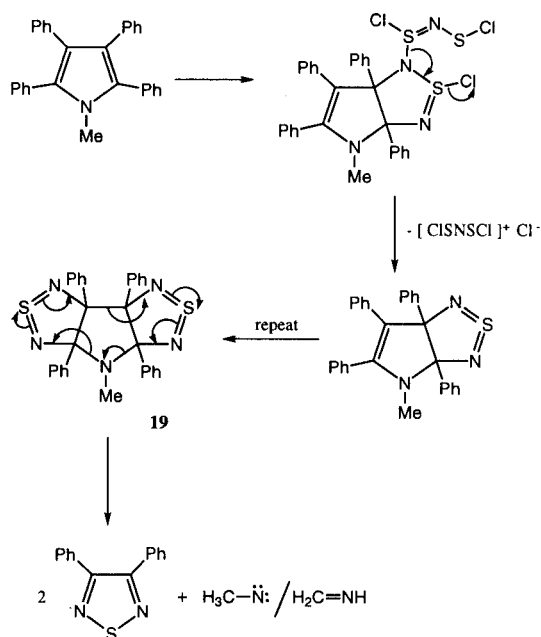
higher yields of the pyrrolo-bisthiadiazoles **16**. This could possibly result from more rapid elimination (of HBr or Br<sub>2</sub>) in the cycloaddition intermediates (Scheme 10) when bromine is present at the ring junction positions.

Formation of the bis-1,2,5-thiadiazole **11** from 1-methyl-2,5-diphenylpyrrole **10** is more puzzling at first sight, but the same initial cycloaddition process would give the bicyclic intermediate **17** which, with the  $\alpha$ -positions substituted, cannot aromatise to a pyrrolo-thiadiazole. A second cycloaddition to **17** at the reactive enamine double bond would then give the tricyclic system **18**. This can aromatise only by breaking the pyrrolic C-N bonds, as shown in Scheme 11, to give the very stable bis-thiadiazole **11** and HCN which was detected. Similar treatment



Scheme 11

of the fully substituted pyrroles such as 1-methyl-2,3,4,5-tetraphenylpyrrole led to even more extensive fragmentation of the pyrrole ring to give two 1,2,5-thiadiazoles, again with loss of the MeN unit. Interestingly, this result follows quite reasonably by application of the same mechanistic process as in Scheme 11, as can be seen in Scheme 12. The tricyclic intermediate **19**, analogous to **18** in Scheme 11, cannot now aromatise solely by elimination of the MeN unit. Formation of the very stable thiadiazoles requires cleavage of the central C-C bond and extrusion of MeN, formally, at least, as methyl nitrene or formaldehyde imine. Careful analysis of the gaseous products of this reaction failed to reveal any HCN, in agreement with this proposal. Possible Diels-Alder or

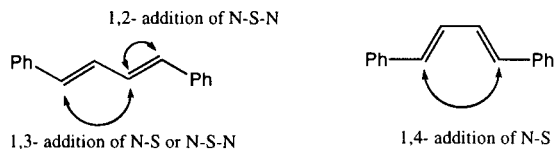


Scheme 12

electrophilic substitution mechanisms for the formation of the isothiazole **5** from furans and thiophenes, were proposed in our earlier lecture [1].

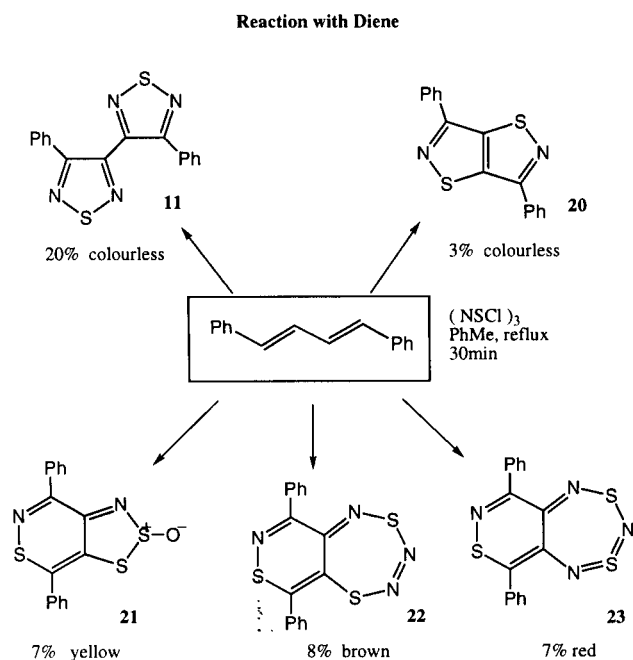
Reaction with Conjugated Dienes.

We have seen that mono-enes and mono-yne are converted by trithiazyl trichloride **1** into 1,2,5-thiadiazoles. Furthermore certain 2,5-diphenylpyrroles are converted into the bis-1,2,5-thiadiazole **11**, thus reacting like a masked 1,3-diene. We thought that it would be interesting, therefore, to explore the reactions of conjugated dienes with trimer, especially since 1,2-, 1,3- and 1,4-cycloadditions to such dienes can all be envisaged (Scheme 13). We started with *E*, *E*-1,4-diphenylbuta-1,3-diene. When this



Scheme 13

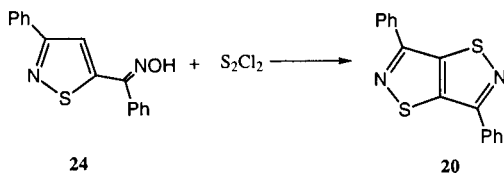
was treated with trimer (1 mole) in refluxing CCl<sub>4</sub> a rapid and complex reaction ensued from which five crystalline sulfur-nitrogen containing organic compounds were isolated. We hoped that the characterisation of these products would shed light on the different modes of reaction of the trimer with conjugated dienes. The yields and colours of



Scheme 14

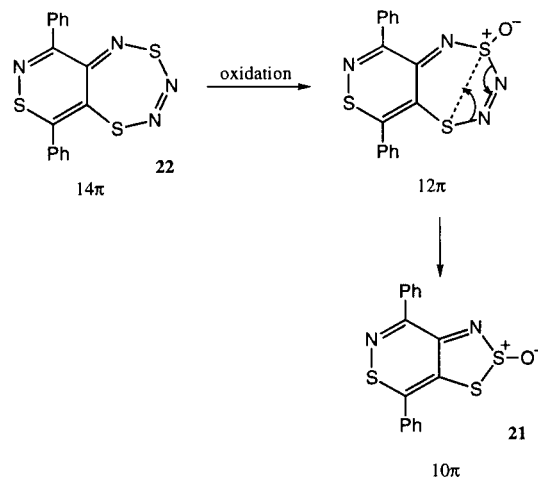
the products are shown in Scheme 14; in spite of their varied structures the carbon skeleton of the starting diene has been retained in all of them. The bis-1,2,5-thiadiazole **11** identical with that formed from *N*-alkyl-2,5-diphenylpyrroles was the major product; when an excess of trimer (3 moles) was used at a higher temperature for a longer time (boiling toluene, 16 hours) the reaction was much simpler and the bis-thiadiazole was isolated in 59%.

The isothiazolo-isothiazole structure **20** was suggested by its high stability and symmetry (<sup>1</sup>H and <sup>13</sup>C NMR) and its mass spectrum which showed fragments for PhCN and C<sub>2</sub>S<sub>2</sub>. It was synthesised independently by treatment of the oximes **24** of 5-benzoyl-3-phenylisothiazole **5** (very readily prepared from 2,5-diphenylfuran and trimer) with S<sub>2</sub>Cl<sub>2</sub> in DMF at 100°C, which gave the identical product **20** (19%). This low yield probably stems from the low proportion of the oxime isomer required for cyclisation, and the relatively low reactivity of the isothiazole ring towards the electrophilic cyclisation process.



The dithiazolothiazine *S*-oxide structure **21** was established by X-ray crystallography. The sulfoxide group suggested that the formation of this product has involved oxida-

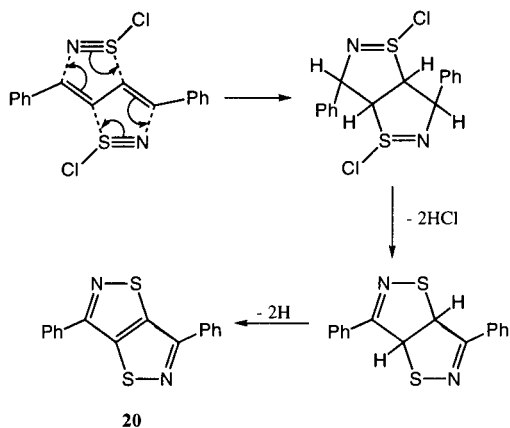
tion, either by the trimer or during work up. An examination of the five diene-trimer products showed that all were stable to air except the brown compound **22** which was oxidised to **21** when adsorbed on silica. When the diene-trimer reaction work up was delayed, with greater exposure to air, we isolated less of the brown product **22** and correspondingly more of the yellow product **21**. When a solution of **22** in dichloromethane was treated with *m*-chloroperbenzoic acid at room temperature its colour changed immediately and it was converted very cleanly into **21**. Link scan mass spectrometry showed that these two compounds gave the same pattern of daughter ions by thermal decomposition indicating that the same product, C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>S<sub>3</sub> was formed from **21** by loss of an oxygen atom and from **22** by loss of dinitrogen. From this we deduced that the brown product almost certainly had the thiazino-dithiazepine structure **22**, which agrees with all its spectroscopic properties, including the dominant loss of dinitrogen from the molecular ion in the mass spectrum. Its conversion into the dithiazole-*S*-oxide **21** can be rationalised by oxidation of the less hindered sulfur atom followed by extrusion of dinitrogen (Scheme 15). The 6-7 fused ring system of **22** is 14 π aromatic and



Scheme 15

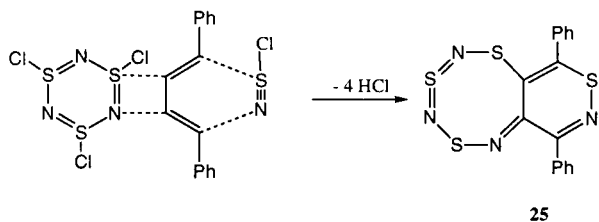
this will be disrupted by the *S*-oxidation, but loss of N<sub>2</sub> as shown will produce the 10 π aromatic **21**, providing a driving force for the conversion. Almost certainly **22** is a direct product of the diene-trimer reaction and the yellow compound **21** is derived from **22**. The final, red, product is isomeric with **22** and structurally closely related to it. It was assigned structure **23** on the basis of its spectroscopic properties; its molecular ion in the mass spectrum was much stronger than that of **22** and no loss of N<sub>2</sub> was observed.

We believe that the formation of all five isolated products can be readily rationalised in terms of the 1,2-, 1,3- and 1,4-cycloaddition process suggested earlier (Scheme 13). The bis-thiadiazole **11** is presumably formed by addition of an N-S-N unit from the trimer across C<sub>1</sub>-C<sub>2</sub> and then C<sub>3</sub>-C<sub>4</sub>, exactly as for alkenes (Scheme 9) and pyrroles (Scheme 10). The structure of isothiazoloisothiazole **20** suggests 1,3- addition of S-N units to the diene. This kind of "cross-cross" cycloaddition is rare but examples have been reported, such as in the reaction of 1,4-diphenyl-2,3-diazabutadiene with methyl acrylate [9]. Similar cycloaddition of two molecules of the monomer, followed by elimination of HCl and oxidation (possibly by chlorination and dehydrochlorination) would give the very stable fused aromatic compound **20** (Scheme 16). The thiazine ring common to the remaining products



Scheme 16

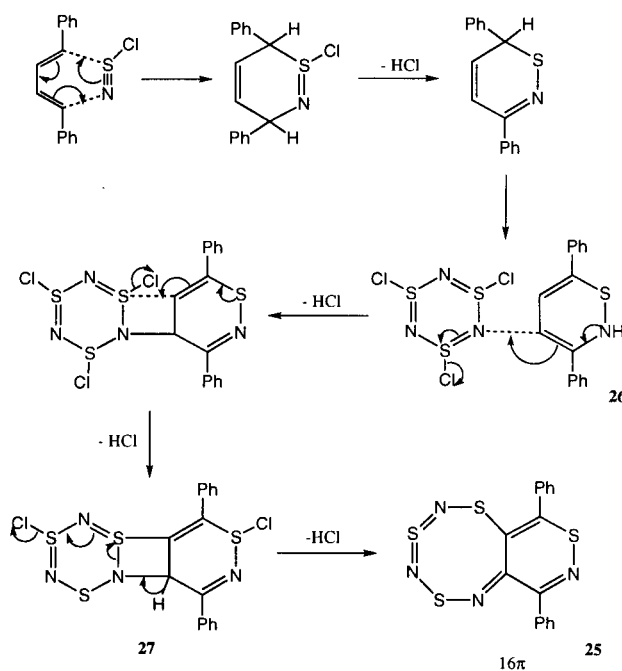
suggests a 1,4-cycloaddition of the monomer to the diene. Since all four alkene hydrogens are lost on reaction with trimer and since four molecules of monomer are required to form these N<sub>4</sub>S<sub>3</sub> compounds, **22** and **23**, it is possible that after the Diels-Alder reaction the remaining carbon-carbon double bond reacts with one molecule of trimer, with the overall elimination of 4HCl to form **25** (Scheme 17).



Scheme 17

A more detailed mechanism for the formation of **25** is proposed in Scheme 18. Initial Diels-Alder reaction fol-

lowed by elimination of HCl and hydrogen shift could give 3,6-diphenyl-1,2-thiazine **26**, which is nucleophilic at C-4. Nucleophilic attack on the trimer at nitrogen, followed by a second nucleophilic attack by C-5, would give the tricyclic intermediate **27**, with elimination of two molecules of HCl. Elimination of the final HCl opens the 4-membered ring to give the 6-8 fused ring system **25** which is formally 16 $\pi$  antiaromatic. The inherent instability of this could result in extrusion of sulfur. Extrusion of S-1 leads to the red 14 $\pi$  **23** and extrusion of S-3 leads to the brown 14 $\pi$  **22** which by oxidation is converted into the remaining product **21**, as explained above (Scheme 15).

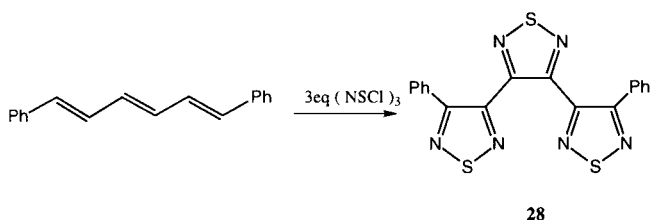


Scheme 18

Thus we see that the initially bewildering array of products from this one diene and the trimer can be rationalised by involving all of the cycloaddition modes possible, which include the pathways described earlier for furans, thiophenes, and pyrroles. It could be interesting to extend this reaction to other, functionalised butadienes and to see if such reactions could be made more selective and hence more useful synthetically. At present the only product which can be produced in substantial yield is the bis-1,2,5-thiadiazole **11**, under fairly vigorous conditions. An initial experiment with 1,6-diphenylhexa-1,3,5-triene produced a complex reaction mixture from which only the tris-1,2,5-thiadiazole **28** has been isolated and characterised.

Very recently Katz and coworkers reported the fascinating observation that in the conversion of quinones by





the trimer into 1,2,5-thiadiazoloquinones, the trimer can, with much convenience, be replaced by a combination of an alkyl carbamate, thionyl chloride and pyridine [10]. It will be very interesting to see if this combination is equally effective in the transformations which we have described.

#### Conclusion.

The reactions described in this lecture illustrate the versatility of trithiazyl trichloride **1** in forming a range of 5-, 6- and 7-membered sulfur-nitrogen heterocyclic systems from very readily available organic substrates such as alkenes, alkynes, dienes, furans and pyrroles in simple one-pot reactions.

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#### REFERENCES

- [1] Polysulfur-nitrogen Heterocyclic Chemistry, C. W. Rees, *J. Heterocyclic Chem.*, **29**, 639 (1992).
- [2] Gmelin Handbook of Inorganic Chemistry, 8th Ed, Sulfur-Nitrogen Compounds, Part 2, Springer-Verlag, Berlin, 1985, p 92.
- [3] D. H. R. Barton and W. A. Bubb, *J. Chem. Soc., Perkin Trans. 1*, 916 (1977).
- [4] L. M. Weinstock, P. Davis, B. Handelsman and R. Tull, *J. Org. Chem.*, **32**, 2823 (1967).
- [5] L. M. Weinstock and I. Shinkai in Comprehensive Heterocyclic Chemistry, Vol. 6, K. T. Potts, ed, Pergamon Press, Oxford, 1984, p 528.
- [6] T. Suzuki, T. Okubo, A. Okada, Y. Yamashita and T. Miyashi, *Heterocycles*, **35**, 395 (1993).
- [7] S. Mataka, H. Eguchi, K. Takahashi, T. Hatta and M. Tashiro, *Bull. Chem. Soc. Japan*, **62**, 3127 (1989).
- [8] G. D. Hartman, S. E. Biffar, L. M. Weinstock and R. Tull, *J. Org. Chem.*, **43**, 960 (1978).
- [9] T. Wagner-Jauregg, *Synthesis*, 349 (1976).
- [10] S. Shi, T. J. Katz, B. V. Yang and L. Liu, *J. Org. Chem.*, **60**, 1285 (1995).