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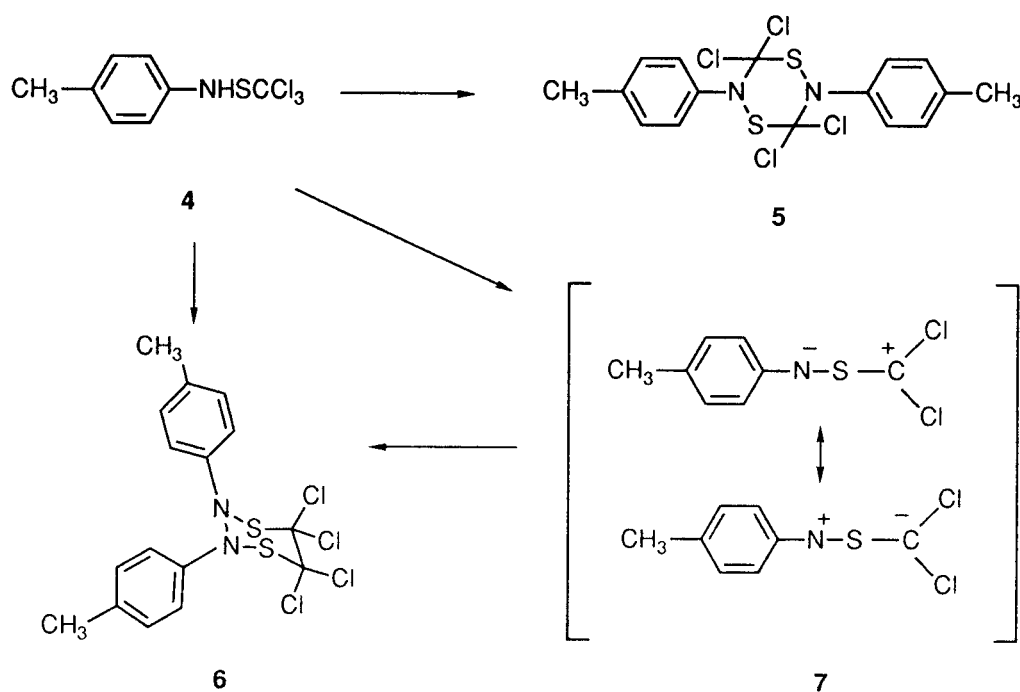
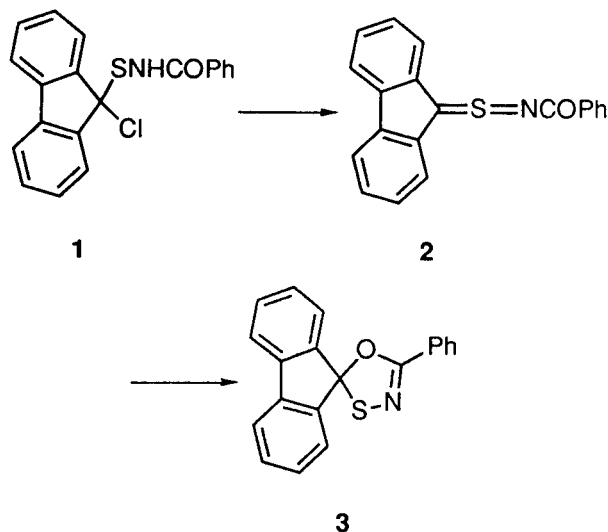
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N-(*p*-Tolyl)trichloromethane sulfenamide when treated with potassium hydroxide in an ether-alcohol mixture resulted in the formation in solution of a red, transient thione-S-imide which underwent a head-to-head dimerization to 2,3-di(*p*-tolyl)-5,5,6,6-tetrachloro-1,4,2,3-dithiadiazine whose structure was established by a single crystal X-ray determination. A variety of sulfenamides derived from aryl-substituted primary aromatic amines and alcoholic potassium hydroxide undergo this reaction with the formation of analogous structures. This thiocarbonyl imine dipole could not be trapped with alkenic or alkynic dipolarophiles.

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Thione-S-imides, in contrast to other sulfur containing 1,3-dipoles, are relatively unknown. An interesting example is the 9-fluorenone thione *S*-benzoylimide (**2**), prepared [1] in THF solution from the action of triethylamine on the sulfenamide **1**. Anhydrous hydrogen chloride (-78°) on this THF solution led to the rapid regeneration of the sulfenamide **1**, and when the solution of **2** was warmed to *ca.* -30° the deep-red color of **2** was lost and the oxathiazole **3** was obtained *via* an electrocyclic ring closure of **2**.

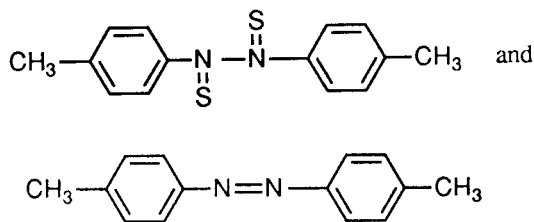
Potential methods of generating the thiocarbonylimine dipole such as the reaction of a nitrene with a thiocarbonyl group were unsuccessful [2], although related approaches have been successful in forming carbonyl ylides [3] and thiocarbonyl ylides [4] contained in heteroaromatic betaines. We have found [5] that trichloromethanesulfonyl chloride is an especially useful reagent for the annulation of a 1,3,4-thiadiazole ring to a 2-aminoheterocycle analog.



gous to 2-aminopyridine. Speculation about the mechanism of this ring annulation led us to consider sulfenamides derived from trichloromethanesulfonyl chloride as potential precursors to the thiocarbonyl imine dipole. This publication describes the transient generation of such a dipole and its extremely facile head to head dimerization to yield an interesting 1,4,2,3-dithiadiazine.

Aromatic primary amines and trichloromethanesulfonyl chloride were reported [6] to undergo ready reaction to form secondary sulfenamides **4**. On treating an ether solution of **4** with alcoholic potassium hydroxide solution Connolly and Dyson in 1934 isolated [7] a colorless, crystalline product after observing a transient deep-red coloration of the reaction mixture. On the basis of analytical data, molecular weight data, and several degradative experiments, structure **5** was assigned to this colorless product.

Repetition of this reaction resulted in a crystalline product with physical constants consistent with those described earlier [7]. In our hands degradative experiments were inconclusive for structural determination. The ^1H nmr spectrum showed aromatic and methyl protons (4:3); however, important information was obtained from the mass spectrum (E.I., direct insertion probe, heating $30^\circ/\text{min}$ to 150°). The molecular ion at m/z 438 showed chlorine isotopes consistent with the presence of more than three chlorine atoms. Particularly informative were fragment ions showing the presence of an $-N-N-$ bond: ions at m/z 274 and 210 are consistent with structural entities



respectively. Also, tetrachloroethylene and thiophosgene ions were observed at m/z 164 and 114, respectively. These mass spectral results are inconsistent with structure **5** but are readily accommodated by the 1,4,2,3-dithiadiazine ring system **6** and this was confirmed by the single crystal X-ray structural determination shown in Figure 1. The only example of the 1,4,2,3-dithiadiazine ring system known [8] is the corresponding diester which was prepared from ethane-1,2-bis(sulfonyl chloride) and ethyl hydrazodicarboxylate.

The dithiadiazine **6** is most likely formed by a head-to-head dimerization of a transient thione-S-imide **7** generated from **4** by the potassium hydroxide. The formation of **7** is consistent with the observance of an immediate transient red color when **4** was treated with base. Attempts to trap this dipole with alkenic and alkynic dipolarophiles

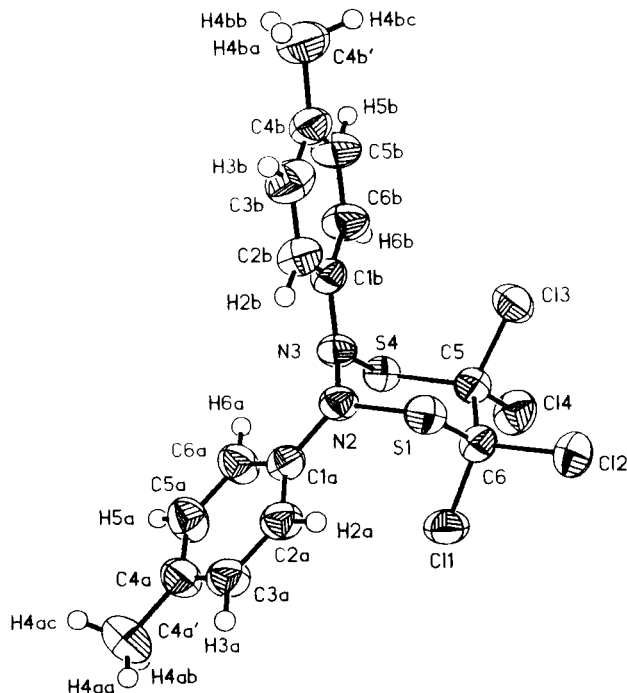


Figure 1. Ortep representation of 2,3-di(*p*-tolyl)-5,5,6,6-tetrachloro-1,4,2,3-dithiadiazine **6**.

were unsuccessful, dimerization being the preferred reaction pathway. Such head-to-head dimerizations of 1,3-dipoles are not unknown [9], and what is especially interesting in this case is the formation of an $N-N$ bond in a four heteroatom contiguous linkage.

It is interesting to note in the above context that when a primary aromatic amide is treated with trichloromethanesulfonyl chloride under thermal conditions in an inert solvent (dioxane, tetrachloroethylene) the reaction takes a different course. In this instance a 5-aryl-1,3,4-oxathiazol-2-one and the corresponding nitrile were obtained [10]. A variety of 1,3,4-oxathiazole derivatives may be prepared from amides and chlorosulfonyl chlorides, these being

Table 1	
Selected Bond Lengths (Å) and Bond Angles ($^\circ$) for 2, 3-Di-(<i>p</i> -tolyl)-5, 5, 6, 6-tetrachloro-1, 4, 2, 3-dithiadiazine (6)	
Bond Lengths Å	Bond Angles $^\circ$
N2-N3 : 1.413	N2-S1-C6: 101.2
S1-N2: 1.703	N2-N3-S4: 114.9
N3-S4: 1.686	S4-C5-C6: 110.5
S4-C5: 1.821	S1-C6-C5: 110.5
C5-C6: 1.771	S1-N2-N3: 114.7
S1-C6: 1.833	N3-S4-C5: 102.7

valuable as a source of the nitrile sulfide dipole [11].

Several sulfenamides derived from substituted-aryl primary aromatic amines under these reaction conditions result in products analogous to **6** above and their structures should be revised accordingly. Similarly the product obtained [12] by treatment of the sulfenamide derived from 2-aminopyridine with potassium carbonate should also have its structure revised in view of these present results.

EXPERIMENTAL [13]

2,3-Di(*p*-tolyl)-5,5,6,6-tetrachloro-1,4,2,3-dithiadiazine (**6**).

A solution of potassium hydroxide (8.0 g) in ethanol (75 ml) was added dropwise to an ether solution of *N*-(*p*-tolyl)trichloromethane sulfenamide (**4**, 2.6 g) with stirring at room temperature. On the addition of base an immediate orange-red coloration developed and this color faded after the base addition was completed. After stirring the reaction mixture for 4 hours, the colorless precipitate of potassium chloride was removed and the solvent evaporated under reduced pressure at room temperature. The residue was dissolved in boiling ethanol from which it separated as colorless needles, mp 142° with sudden and copious gas evolution (lit [7] mp 142.5°).

Anal. Calcd. for C₁₆H₁₄Cl₄N₂S₂: C, 43.65; H, 3.21; N, 6.36. Found: C, 43.86; H, 3.27; N, 6.24.

Acknowledgement.

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Supplemental Material Available.

Tables of crystal data, positional parameters and isotropic thermal parameters, bond lengths, bond angles, anisotropic ther-

mal parameters, and hydrogen atom parameters (4 pages) are available from the authors.

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