Organic Heterocyclothiazenes. Part 2.[1] Reaction of Tetrasulphur Tetranitride with Phenylacetylene and Diphenylacetylene

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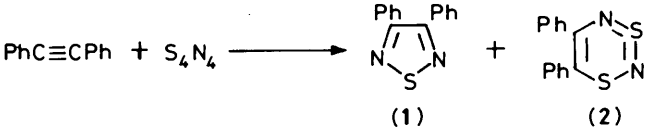
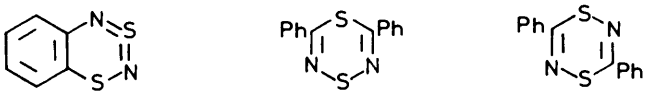
The reaction of S_4N_4 with diphenylacetylene in boiling toluene has been found to give 3,4-diphenyl-1,2,5-thiadiazole (**1**) as the major product and 3,5-diphenyl-1,4,2,6-dithiadiazine (**4**), a new heterocyclic system, as a minor product. The same reaction with phenyacetylene gives 3-phenyl-1,2,5-thiadiazole (**12**) and the novel 1,3,2-dithiazolylimine (**16**), the first example of this mesoionic ring. These new structures correct literature assignments. Reaction mechanisms are proposed for the formation of the products.

In a continued investigation of the reactions of tetrasulphur tetranitride with alkynes, we have uncovered further products with unusual heterocyclic structures which are wrongly assigned in the literature. We describe such reactions of mono- and di-phenylacetylene in this paper.

S_4N_4 *and* PhC≡CPh.—The reaction of S_4N_4 with diphenylacetylene in boiling toluene was reported[2] to give 3,4-diphenyl-1,2,5-thiadiazole (**1**) (87%), and 5,6-diphenyl-1,3$\lambda^4\delta^2$,2,4-dithiadiazine (**2**) as stable orange needles, m.p. 79—80.5 °C, in less than 1% yield. The same products were reported[3] for the reaction of S_4N_4 with benzil bishydrazone. Structure (**2**) was of considerable interest since the ring system was hitherto unknown and it would, if planar, be an 8π-electron antiaromatic system. However, the little evidence presented for the assignment of structure (**2**) was later eliminated by the ^{13}C n.m.r. spectrum which showed the 2 phenyl rings to be magnetically equivalent.[2] The first authentic derivative of the 1,3$\lambda^4\delta^2$,2,4-dithiadiazine ring, the benzo compound (**3**), has since been described by Koenig and Oakley;[4] compound (**3**) is deep blue, as befits a species with antiaromatic character.



(**1**) (**2**)



(**3**) (**4**) (**5**)

Whilst several structures can be written for the orange product (**2**), $Ph_2C_2N_2S_2$, with the symmetrical starting arrangement of carbon atoms retained, none of these appear to be thermally stable. So we wondered if the triple bond of the diphenylacetylene had become cleaved but with the two halves retained in the product, similar to a rearrangement observed in the reaction of S_4N_4 with dimethyl acetylenedicarboxylate.[1]

We therefore repeated the diphenylacetylene and benzil bishydrazone reactions with S_4N_4 and obtained the same two products as the Japanese workers.[3] The mass spectrum of the highly crystalline orange compound, $Ph_2C_2N_2S_2$, suggested the absence of N–N and the original acetylenic C–C bonds, and the i.r. spectrum suggested the absence of a sulphur di-imide, N=S=N, unit. We therefore considered the dithiadiazine structures (**4**) and (**5**) to be likely candidates. Both were unknown at the time, though the 1,4,2,5-dithiadiazine (**5**), m.p. 102—104 °C, has since been prepared by Lenz and Zwanenburg by an entirely different route.[5] Thermal and photochemical decomposition (see below) of the orange compound to give the 1,2,5-thiadiazole (**1**) favoured structure (**4**), which was confirmed by *X*-ray diffraction.[6] The 3,5-diphenyl-1,4,2,6-dithiadiazine (**4**) has a symmetrical 'open-book' conformation with the atoms in each half being coplanar; the heterocyclic ring adopts a boat conformation, similar to that of the simpler dithiins.[7]

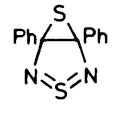
Dithiadiazine (**4**) was also produced, though again only as a minor product (*ca.* 1%) in the reaction of diphenylacetylene and S_4N_4 in the presence of aluminium chloride, and of dimorpholino disulphide, and in the reaction of diphenylcyclopropenone with S_4N_4. However, when the molar ratio S_4N_4:PhC≡CPh was changed from 1:2 to 2:1, the yield of (**4**) increased to 7%. Dithiadiazine (**4**) was independently prepared by the reaction of thiobenzamide, sulphur dichloride, and triethylamine in ether, but again the yield was low (8%) since the major product here, and in several other reactions designed to give (**4**), was 3,5-diphenyl-1,2,4-thiadiazole, a known product of thiobenzamide oxidation.[8]

Compared with 1,4-dithiins[9] and 1,4,2-dithiazines,[10] the dithiadiazine (**4**) is surprisingly stable thermally. It is unchanged on prolonged heating in xylene and decomposes only slowly in boiling decalin (190 °C); after 6 h, 10% has decomposed to the 1,2,5-thiadiazole (**1**). None of the isomeric 1,3,4-thiadiazole is formed, presumably because desulphurisation proceeds through the bicyclic sulphur di-imide structure (**6**) rather than the much less stable thiocarbonyl ylide structure (**7**). Upon irradiation at 300 nm in light petroleum the dithiadiazine (**4**) gave the same thiadiazole (**1**), much more rapidly.

Following a report[11] that 1,4,2-benzodithiazines (**9**) react with dimethyl acetylenedicarboxylate (DMAD) in boiling *o*-dichlorobenzene to give dimethyl 1,4-benzodithiin-2,3-dicarboxylate (**10**) with the elimination of RCN, we treated the dithiadiazine (**4**) with DMAD similarly. The dithiin tetracarboxylate (**11**) was formed, both possible molecules of benzonitrile having been eliminated.

Whilst 1,4-dithiins[9] and 1,4,2-dithiazines[10] have been widely studied, 1,4,2,6-dithiadiazines are virtually unknown, only the dioxide (**8**) having previously been reported.[12] As mentioned above, the isomeric diaryl 1,4,2,5-dithiadiazines such as (**5**) have recently been described.[6]

S_4N_4 *and* PhC≡CH.—Tashiro and co-workers also treated S_4N_4 with phenylacetylene in boiling toluene for 6 h and obtained 3-phenyl-1,2,5-thiadiazole (**12**) (16%), 3-amino-4-phenyl-1,2,5-thiadiazole (**13**) (5%), and a deep violet compound,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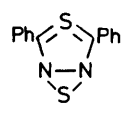
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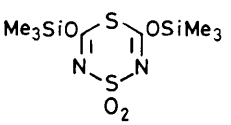
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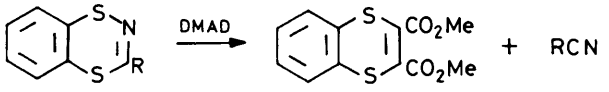
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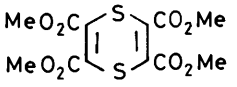
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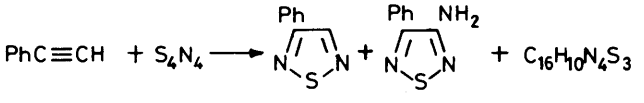
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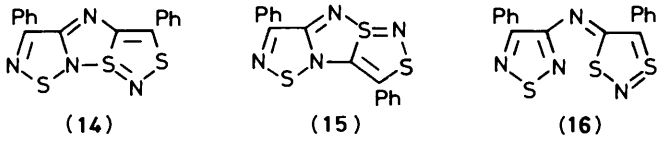
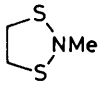

(14) (15) (16)

$C_{16}H_{10}N_4S_3$ (8%), m.p. 178—179 °C, for which they proposed either structure (**14**) or (**15**).[3] They obtained the three analogous products from a similar reaction with *p*-tolylacetylene, though all in substantially lower yields. Either tricyclic structure (**14**) or (**15**) would be an interesting product since, formally, seven of the eight atoms of S_4N_4 have been retained, H_2S having been lost from a 2:1 acetylene:S_4N_4 adduct; and either structure, if near to planar, could be a delocalised 14π-electron aromatic system. We therefore repeated this reaction and isolated the same minor product, $C_{16}H_{10}N_4S_3$, in a similar yield, though we found that its yield was increased to 21% in the presence of aluminium chloride. The structure of this compound was solved by *X*-ray diffraction after suitable crystals were obtained by very slow evaporation of a solution in chloroform containing 30% ethanol. A large range of other solvents, with slow cooling and solvent diffusion techniques, and sublimation, had all given minute twinned crystals unsuitable for crystallography. The compound has the bicyclic structure (**16**),[6] similar to the Japanese structure (**14**) but with no central N–S bond. One five-membered ring is a simple aromatic 1,2,5-thiadiazole, but the other is an example of the rare 1,3,2-dithiazole ring system, the only others reported being the saturated compound (**17**)[13] and its (*N*-aryl)benzo derivatives,[14] persistent nitrogen-centred radicals of structure (**18**),[15] the 1,3,2-dithiazolium salt (**19**)[16] and its benzo derivative,[17] and persistent radicals [*e.g.* (**20**)] derived from them by reduction.[16,17]

In structure (**16**) all the atoms in the five-membered rings and the linking nitrogen are accurately coplanar; the two phenyl rings are nearly parallel and rotated out of this plane by *ca.* 30°. Compound (**16**) is thus the imine derived from the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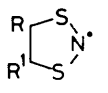
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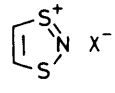
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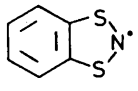
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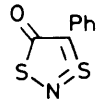
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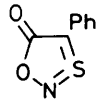

(22)

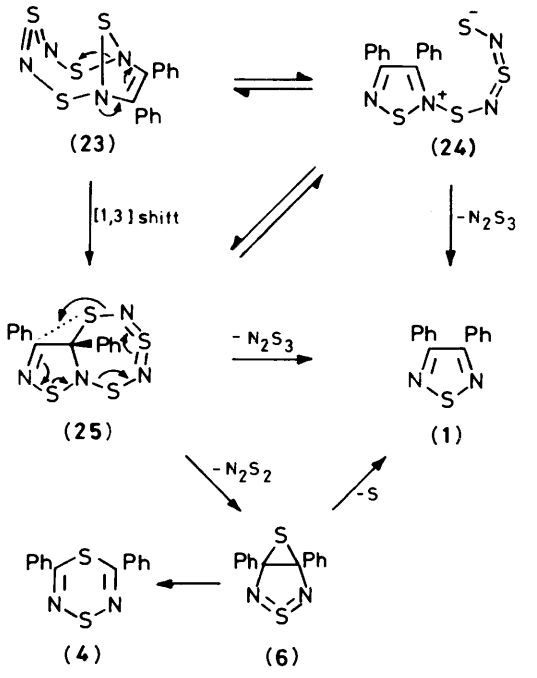
aminothiadiazole (**13**) and 4-phenyl-1,3,2-dithiazol-5-one (**21**). The latter is unknown though the analogous mesoionic 4-phenyl-1,3,2-oxathiazol-5-one (**22**) has been quite well studied.[18] The imine structure (**16**) explains the formation of the aminothiadiazole (**13**) (64%) and phenylacetic acid (a trace) on treatment of this product with ethanolic potassium hydroxide.[2]

Compound (**16**) is surprisingly stable thermally, decomposing only slowly in boiling decalin (190 °C). This stability, and the molecular planarity, suggests a possible contribution from the tricyclic 14π structure (**14**). However, *X*-ray results[6] show that such a contribution must be small since the interannular N–S separation is 2.70 Å (*cf.* an N–S single bond length of 1.74 Å and the sum of the van der Waals radii of 3.35 Å). Furthermore, the compound was completely decolourised by *m*-chloroperbenzoic acid in dichloromethane at room temperature in 2 h, showing it to be considerably more reactive than the monocyclic 10π systems reported in Part 1.[1]

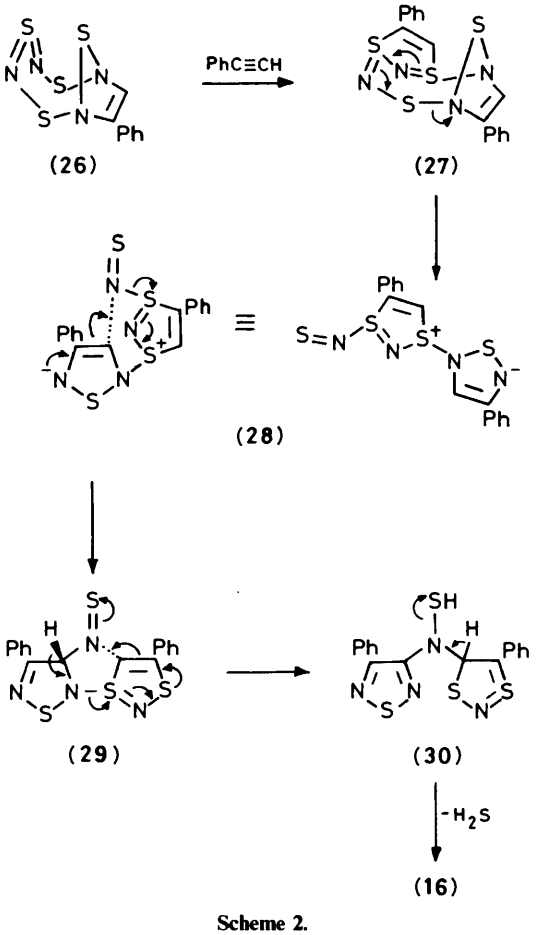
Reaction Mechanisms.—As in the reaction of S_4N_4 with dimethyl acetylenedicarboxylate,[1] the simplest mechanistic proposal (Scheme 1) for the diphenylacetylene reaction is initial cycloaddition of the triple bond across N(2)–N(4), to give the adduct (**23**). Cycloaddition of a second acetylene, across N(6)–N(8), would give a 2:1 adduct which could readily extrude sulphur to give two molecules of the very stable thiadiazole product (**1**). The 1:1 adduct (**23**) could also ring open to give the zwitterion (**24**), where a now localised, and weakened, N–S single bond has been cleaved to give the aromatic thiazolium ring. This could then lose N_2S_3 to give thiadiazole (**1**), either before or after collapse to the bicyclic intermediate (**25**).* Intermediate (**25**) could rearrange with loss of N_2S_2 [arrows in (**25**)] to yield the sulphur di-imide (**6**) which can, in turn, lose sulphur to give more of the major product (**1**), or rearrange to the dithiadiazine (**4**).

In the monophenylacetylene reaction, the thiadiazole (**12**) is presumably formed in an analogous manner to the diphenyl compound (**1**). Formation of the product (**16**) requires a more complex rearrangement and the mechanism proposed in Scheme 2 is speculative. Initial cycloaddition of the acetylene to S_4N_4 is again across nitrogen to give the adduct (**26**). The structure of (**16**) then suggests that the next 1,3-dipolar cycloaddition of the acetylene is to sulphur atoms to give the adduct (**27**), with the regiochemistry controlled by steric factors. Intermediate (**27**) could ring open to give (**28**) which could then collapse to give structure (**29**), with transfer of the thionitroso group in a six-centred transition state (Scheme 2). The final nitrogen bridge can then form as shown by the arrows in (**29**) followed by elimination of H_2S from (**30**) to give the stable, mesoionic system (**16**) isolated. The thio-oxime tautomer of (**29**)

* Alternatively, conversion of adduct (**23**) into (**25**) could be by direct [1,3] sigmatropic shift of the S–N single bond from nitrogen to carbon.



Scheme 1.



Scheme 2.

could also be involved, either in an electrocyclic process to give (**30**), or by homolysis of the weak N–S bond, followed by radical cyclisation. It is hoped that further work will clarify some of the rather novel features of this rearrangement.

Experimental

For general points see reference 1.

3,5-*Diphenyl*-1,4,2,6-*dithiadiazine* (**4**).—(a) Benzil bishydrazone (1.16 g, 5 mmol) and tetrasulphur tetranitride (0.46 g, 2.5 mmol) were heated at reflux in toluene (25 ml) for 6 h. The solvent was evaporated and the residue chromatographed on silica gel (25 g). Elution with light petroleum–chloroform (9:1) gave the title compound (**4**), purified by p.l.c., as orange needles (9.1 mg, 1.5%), m.p. 78—80 °C (lit.,[2] 78—80.5 °C) $\lambda_{max.}$(EtOH) 234 (log ε 4.26), 272 (4.31) and 454 nm (3.42); $\nu_{max.}$(KBr disc) 1 445, 1 208, 1 175, 900, 760, 675, and 585; δ_H [250 MHz; CCl_4–$(CD_3)_2CO$] 7.45—7.55 (3 H, m) and 7.98 (2 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 126.9, 128.6, 131.7, 135.9, and 151.8; *m/z* 270 (M^+), 167, 121, 103, and 77. Further elution with light petroleum–chloroform (9:1) gave 3,4-diphenyl-1,2,5-thiadiazole (**1**) (0.25 g), m.p. 84—86 °C (lit.,[19] 85—86 °C).

(b) Thiobenzamide (0.50 g, 3.64 mmol) and triethylamine (0.87 g, 8.6 mmol) in dry ether (50 ml) were stirred under nitrogen at −78 °C for 5 min. Sulphur dichloride (0.46 ml, 7.28 mmol) was then added from a syringe over 2 min and the mixture stirred at −78 °C for a further 15 min. The mixture was allowed to attain room temperature and then heated at reflux, under nitrogen, for 30 min. The solution was washed with water, dried ($MgSO_4$), and chromatographed on silica gel (20 g). Elution with light petroleum–chloroform (9:1) gave the title compound (**4**) (41 mg, 8%), m.p. 76—79 °C. Elution with light petroleum–chloroform (7:3) gave 3,5-diphenyl-1,2,4-thiadiazole (83 mg, 19%), m.p. 86—88 °C (lit.,[20] 86—88 °C).

Reaction of Tetrasulphur Tetranitride with Diphenylacetylene.—(a) *With aluminium trichloride.* Diphenylacetylene (1.78 g, 10 mmol), S_4N_4 (0.92 g, 5 mmol), and aluminium trichloride (0.66 g, 5 mmol) were heated at reflux in toluene for 13 h. Chromatography on silica gel gave unchanged diphenylacetylene (44%) and 3,5-diphenyl-1,4,2,6-dithiadiazine (**4**) (43 mg, 1.5%) as the only identifiable products.

(b) *With dimorpholino disulphide.* Diphenylacetylene (0.89 g, 5 mmol), S_4N_4 (0.46 g, 2.5 mmol), and dimorpholino disulphide (0.59 g, 2.5 mmol) were heated at reflux in toluene (25 ml) for 48 h. Chromatography as before gave 3,5-diphenyl-1,4,2,6-dithiadiazine (**4**) (14 mg, 1%) and 3,4-diphenyl-1,2,5-thiadiazole (**1**) (0.86 g, 72%) as the only identifiable products.

Reaction of Tetrasulphur Tetranitride with Diphenylcyclopropenone.—Diphenylcyclopropenone (1.0 g, 4.85 mmol) and S_4N_4 (0.44 g, 2.42 mmol) were heated at reflux in toluene (25 ml) for 48 h. Chromatography as before gave 3,5-diphenyl-1,4,2,6-dithiadiazine (**4**) (19 mg, 1.5%), unchanged diphenylcyclopropenone (40%), and 3,4-diphenyl-1,2,5-thiadiazole (**1**) (96 mg, 8%) as the only identifiable products.

Thermolysis of 3,5-*Diphenyl*-1,4,2,6-*dithiadiazine* (**4**).—Dithiadiazine (**4**) (20 mg) was heated at reflux in decalin (10 ml) under nitrogen for 6 h. H.p.l.c. analysis indicated that 10% of the starting material had decomposed to the thiadiazole (**1**) which was identified by co-injection. No decomposition was detected when compound (**4**) was heated at reflux in xylene for 15 h.

Photolysis of 3,5-*Diphenyl*-1,4,2,6-*dithiadiazine* (**4**).—Dithiadiazine (**4**) (13.9 mg) in light petroleum (b.p. 60—80 °C) was irradiated at 300 nm for 2 h. The solution was filtered from an insoluble residue (5 mg) and the solvent removed under reduced pressure to give almost pure 3,4-diphenyl-1,2,5-thiadiazole (**1**) (5.8 mg, 48%).

Reaction of 3,5-*Diphenyl*-1,4,2,6-*dithiadiazine* (**4**) *with dimethyl acetylenedicarboxylate.*—Dithiadiazine (**4**) (13.6 mg)

and DMAD (19 μl, 3 equiv.) were heated at reflux in *o*-dichlorobenzene (2.5 ml) under nitrogen. The solvent was removed under reduced pressure and the resulting oil purified by p.l.c. on alumina to give 3,4-diphenyl-1,2,5-thiadiazole (**1**) (1.2 mg, 8%) and crude tetramethyl 1,4-dithiintetracarboxylate (**11**), purified by further p.l.c., as a pale yellow solid (8.4 mg, 48%), m.p. 122—125 °C (lit.,[21] 126—127 °C).

*5-Phenyl-*N*-(4-phenyl-1,2,5-thiadiazol-3-yl)-1,3,2-dithiazol-4-imine* (**16**)—Phenylacetylene (1.02 g, 10 mmol) and S_4N_4 (0.92 g, 5 mmol) were heated at reflux in toluene (20 ml) under nitrogen for 6 h. The solvent was evaporated and the residue chromatographed on silica gel (40 g). Elution with light petroleum–chloroform (9:1) gave 3-phenyl-1,2,5-thiadiazole (**12**) (0.18 g, 11%) as crystals from ether, m.p. 42—43 °C (lit.,[2] 43—44 °C). Elution with light petroleum–chloroform (7:3) gave *5-phenyl-*N*-(4-phenyl-1,2,5-thiadiazol-3-yl)-1,3,2-dithiazol-4-imine* (**16**) (89 mg, 5%) as deep violet needles from light petroleum (b.p. 60—80 °C), m.p. 190—195 °C (lit.,[2] 178—179 °C) (Found: C, 53.9; H, 2.8; N, 16.0. $C_{16}H_{10}N_4S_3$ requires C, 54.2; H, 2.8; N, 15.8%); $\lambda_{max.}$(EtOH) 234 (4.22), 254 (4.13), 358 (4.02), and 516 nm (3.48); $\nu_{max.}$(Nujol) 1 415, 1 155, 925, 895, 820, 780, 760, 735, 720, and 690; δ_H(250 MHz, $CDCl_3$) 7.42 (3 H, m), 7.55 (3 H, m), 8.10 (2 H, m), and 8.50 (2 H, m); δ_C($CDCl_3$) 128.2, 128.5, 128.8, 129.2, 129.4, 131.0, 132.9, 153.8, 160.6, 164.8, and 178.4; *m/z* 354 (M^+), 308, 275, 237, 233, 178, 177, 135, 121, 103, and 77.

Thermolysis of the Imine (**16**).—The imine (**16**) (23 mg) was heated at reflux in decalin (4 ml) under nitrogen for 80 h. T.l.c. analysis (silica, chloroform) showed that much of the starting material remained but some extensive decomposition had occurred.

Reaction of Phenylacetylene and Tetrasulphur Tetranitride in the presence of Aluminium Trichloride.—Aluminium trichloride (0.66 g, 5 mmol) was added to a solution of phenylacetylene (1.02 g, 10 mmol) in toluene (20 ml) to give a blood red solution. S_4N_4 (0.92 g, 5 mmol) was added and the mixture heated at reflux for 3 h. The solvent was evaporated and the residue chromatographed on silica (40 g). Elution, as in the above experiment without aluminium chloride, gave 3-phenyl-1,2,5-thiadiazole (**12**) (52 mg, 3%) and the imine (**16**) (0.38 g, 21%) as the only identifiable products.

Reaction of the Imine (**16**) *with* m-*Chloroperbenzoic Acid.*—The imine (**16**) (16 mg) and *m*-chloroperbenzoic acid (18 mg, 2 equiv.) in dichloromethane (3 ml) were stirred at room temperature for 2 h. The initial deep purple colour of the solution began to fade after 10 min and gradually diminished to pale yellow after 2 h. T.l.c. analysis (silica, chloroform) showed that the imine was consumed to give a complex mixture.

Acknowledgements

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