Gas–Solid Chlorination of 4-Phenylthiazole-2(1*H*)-thione

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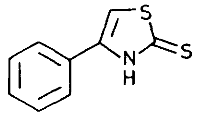
The title compound (**1**) is converted into an unusual chlorophenacyl disulphide (**2**) through a crystal structure controlled chlorination–oxidation reaction.

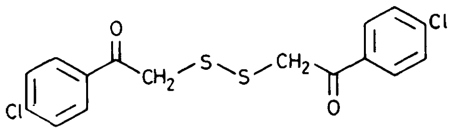
Organic gas–solid reactions are interesting from both mechanistic and stereochemical viewpoints. Recent work has shown that topochemical control plays an important role in determining the course and outcome of these reactions.[1—7] We report here a novel chlorination–oxidation of the title compound.

Colourless crystals of 4-phenylthiazole-2(1*H*)-thione, (**1**), recrystallized from benzene, were kept in an atmosphere of moist chlorine for several weeks at ambient temperature. Although a slight yellowing and pitting occurred, the overall crystal shape and size remained unaltered. However the material had been completely transformed; separation by t.l.c. (silica gel, 20% EtOAc–hexane) revealed two products with no traces of starting material. Oxidation of (**1**) in solution by Chloramine-T in EtOH–H_2O gave entirely different products which were not examined further.

The major compound from the gas–solid reaction, crystal-



(1)



(2)

lised from acetone as large colourless crystals (m.p. 118 °C), was identified as (4-chloro)phenacyl disulphide (**2**) [i.r. (KBr), 3060, 1670, 1595, 840 cm^{-1}; δ_H ($CDCl_3$) 7.75, 7.20 (m, AA'BB', 8H), 4.34 (s, 4H); δ_C ($CDCl_3$) 192.7, 140.0, 133.5, 129.9, 128.9, 78.3; *m/z* (70 eV) 370 (0.68%), 372 (0.51), both $M^{\cdot+}$; 139 (100) 141 (34.2) both $C_7H_4ClO^+$]. Since the formation of (**2**) was unexpected, the structure assignment was confirmed by an *X*-ray analysis of the recrystallised material.† The minor product, m.p. 54 °C, formed in trace amounts, was difficult to identify, with no characteristic n.m.r. spectral features, and only one notable i.r. absorption at 1900 cm^{-1}. It appears to be a low-molecular weight byproduct of the reaction. Interestingly, crystals of reacted (**1**) could be mounted and showed faint *X*-ray diffraction patterns. However, the unacceptably high mosaicity of these crystals precluded any attempt at data collection.

The *X*-ray structure determination of thione (**1**),[10] was undertaken since any attempt at understanding this chlorination–oxidation reaction must hinge on the molecular packing in the reactant crystal.† Figure 1 shows the arrangement of molecules as viewed down the [010] axis. The molecule exists as the thione tautomer and is centrosymmetrically C=S · · · H–N hydrogen bonded (N · · · S 3.29 Å). Such dimer pairs are arranged along the [100] axis to generate layers parallel to [001]. There is a well-defined interlamellar region which presumably permits easy access of the gaseous reagents Cl_2 and H_2O.

Two distinct gas–solid reactions, an electrophilic chlorination and a heterocyclic ring oxidation, must take place in the conversion of thione (**1**) into disulphide (**2**). The chlorination probably proceeds by an addition–elimination mechanism as

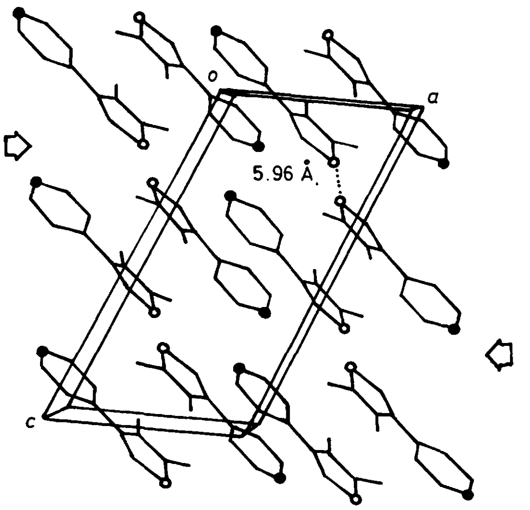
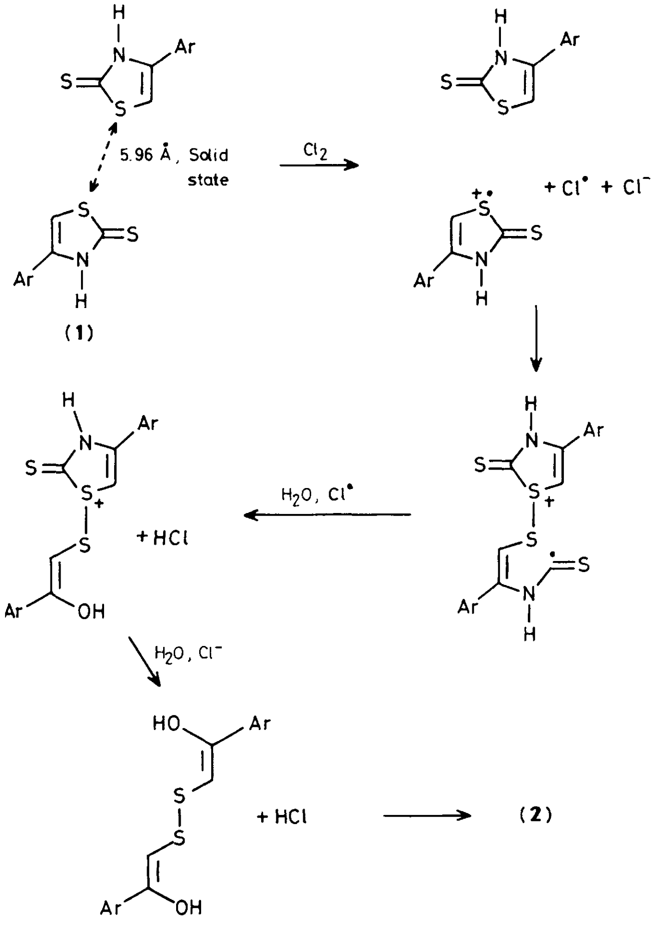


Figure 1. The crystal structure of thione (**1**) viewed down the [010] axis. Notice the layered arrangement of hydrogen bonded molecules. Heterocyclic S atoms and *para*-C atoms are indicated as empty and filled circles respectively. The arrows indicate possible entry directions for the gaseous reagents. S atoms separated by 5.96 Å in the crystal are linked to give disulphide (**2**).



Ar = Ph, p-ClC_6H_4

Scheme 1

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† *Crystal data* for (**2**): $C_{16}H_{12}Cl_2O_2S_2$, M = 370, monoclinic, space group $C2$, a = 30.952, b = 5.017, c = 5.337 Å, β = 90.67°, U = 829 Å^3, $F(000)$ = 380, Z = 2, D_c = 1.48, D_m = 1.44 g cm^{-3}, μ(Cu-K_α) = 57.12 cm^{-1}, Enraf-Nonius CAD-4 diffractometer, 937 independent reflections, 834 reflections with $I \geqslant 3.0\sigma(I)$, structure solution with MULTAN 78,[8] anisotropic refinement with SHELX 76,[9] with hydrogens placed in calculated positions, R = 0.071, R_w = 0.068; the molecule lies on the two-fold axis.

Crystal data for (**1**): $C_9H_7NS_2$, M = 193, monoclinic, space group $P2_1/n$, a = 6.210, b = 11.556, c = 12.763 Å, β = 101.62°, U = 897 Å^3, $F(000)$ = 400, Z = 4, D_c = 1.47, D_m = 1.43 g cm^{-3}, μ(Mo-K_α) = 4.72 cm^{-1}, Enraf-Nonius CAD-4 diffractometer, 1305 independent reflections, 758 reflections with $I \geqslant 3.0\sigma(I)$, structure solution with MULTAN 80,[8] anisotropic refinement with SHELX 76,[9] thioamide hydrogen refined isotropically, other hydrogens placed in calculated positions, R = 0.051.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

reported for crystalline chloro- and methyl phenols.[6,7] The *para*-position is adjacent to the interlamellar region and is quite accessible to electrophilic attack by Cl_2 compared with the *ortho* positions. Therefore, electronic factors apart, there is a good topochemical reason for the formation of the *para*-chloro derivative. This is found to be the exclusive substitution product, no *ortho*-isomer being produced in detectable amounts.

The heterocyclic S atoms also adjoin the interlayer region and should be amenable to oxidation by Cl_2. Bonding between two such S atoms is necessary to form disulphide (**2**) and probably accompanies such an oxidation. The nearest such $S\cdots S$ approach in crystalline (**1**) is across a distance of 5.96 Å between screw-axis related neighbours as indicated in Figure 1. Conversion of (**1**) into (**2**) must involve, in addition, the hydrolysis of two C–N bonds and the elimination of the minor product (**3**). Scheme 1 sets out a tentative mechanism with the order of some of the steps being flexible. Such a sequence would result in the di-enol form of (**2**). It should be noted that the isolation of (**2**) as the major solid state product indicates that (a) $S\cdots S$ bond formation is probably crystal lattice controlled, (b) hydrolysis on either side of the disulphide bridge occurs readily, and (c) chlorination and oxidation occur at comparable rates.

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