

Carbon–Carbon Bond Forming Desulphurisation of a Tetrathiane

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The 1,2,4,5-tetrathiane (3), readily formed from amido ester (2) and disulphur dichloride, undergoes immediate reaction with potassium hydroxide in ethanol at room temperature to form sulphur and the maleimide salt (6) which is characterised as its *S*-benzyl and *S*-methyl (4) derivatives; a mechanism is proposed for this mild carbon–carbon bond forming desulphurisation reaction.

In connection with our synthesis of 1,3,5,2,4-trithiadiazines¹ we needed a route to 1,1-bis-sulphenyl chlorides, and one attractive possibility was the chlorinolysis of 1,2,4,5-tetrathianes such as (1) and (3). Kutney and Still² have shown that treatment of malondiamides with disulphur dichloride gives these tetrathianes directly, and we extended this to the conversion of half-amide (2) into the mixed tetrathiane (3) (89%). We planned to use amido ester (3) as starting material for other tetrathianes, and hence trithiadiazines, but on attempted alkaline hydrolysis of the ester groups we uncovered an unusual ring contraction reaction.

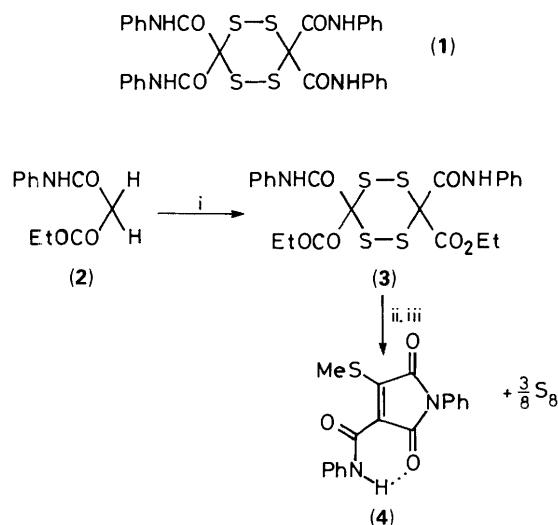
When tetrathiane (3) was treated with one equivalent of potassium hydroxide in dilute ethanolic solution at room temperature an immediate reaction occurred. The colourless solution became blood-red and an orange precipitate was formed. Since this appeared to be a potassium salt it was treated with benzyl bromide to give an orange crystalline compound, m.p. 209–211 °C, shown to be C₂₄H₁₈N₂O₃S from elemental analysis and high resolution mass spectrometry. I.r. spectroscopy showed an amide NH stretch at 3332 cm⁻¹, one sharp

carbonyl absorption at 1708 cm⁻¹, and the absence of ester carbonyl groups. The last observation was confirmed by ¹H n.m.r. which showed two benzylic protons (δ 4.84), 15 aromatic protons (δ 7.0–7.77), and one amide proton (δ 9.75) only. The original tetrathiane (3) had thus lost ethoxycarbonyl, ethanol, and three of the four sulphur atoms, some of which (at least) appeared as elemental sulphur. It was difficult to reconcile possible structures for the reaction product with the presence of only one strong carbonyl absorption in the infrared.

We also treated the potassium salt with iodomethane to form the corresponding methylated compound, m.p. 198–199 °C, (56%) and sulphur (54%). The analytical and spectroscopic properties of the methyl compound were entirely analogous to those of the benzyl derivative. On mechanistic grounds the maleimide structure (4) was deduced for the methyl compound but, because of doubts associated with the carbonyl absorption in the i.r. region, the product was submitted to X-ray structure determination.³ This confirmed structure (4), and showed the presence of an intramolecular H-bond between the anilide NH and a maleimide carbonyl group, which persisted in dilute chloroform solution.

Formation of the methylthiomaleimide (4) from tetrathiane (3) so rapidly under such mild conditions (Scheme 1) is a mechanistically intriguing reaction; it is also potentially useful since the tetrathianes are readily prepared in one step from the appropriate malonic acid derivative and disulphur dichloride. We assume that the key reaction intermediate is the thioenolate salt (5) which cyclises to the maleimide (6) and is then alkylated on sulphur. Thus three of the four sulphur atoms of the tetrathiane (3) have been excised, with the formation of a new carbon–carbon double bond bearing the remaining sulphur atom in place of the lost ethoxycarbonyl group.

We propose the mechanism shown in Scheme 2 for this transformation. In view of the speed of the reaction, and the sensitivity towards alkali of disulphides⁴ and particularly of 1,2,4-trithioles⁵ (the nearest analogue of our tetrathiane), the first step is thought to be opening of the heterocyclic ring by nucleophilic attack on sulphur. This is followed by rapid cleavage of the ethoxycarbonyl group from the reactive sulphenic acid intermediate, and ring closure to form a trithiole which loses sulphur and collapses to a thiiran, thus forming the first carbon–carbon bond. The double bond is then formed by sulphur extrusion to give the highly stabilised thioenolate salt



Scheme 1. Reagents: i, S₂Cl₂; ii, KOH, EtOH, 20 °C; iii, MeI

