Tetrahedron Letters No.24, pp. 1961-1964, 1965. Pergamon Press Ltd.
Printed in Great Britain.

A NEW THIOTHIOPHTHENE

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(Received 15 April 1965)

Several reports have appeared of the condensation of trithiones (1,2-dithiole-3-thiones) or their S-methyl derivatives (3-methylthio-1,2-dithiolium salts) with "active" methylene compounds.[1,2] We have found that oxazolones of type (V) may be prepared by suitable adaptations of known procedures but that intensely-coloured by-products are also formed. We wish to report here, particularly, on the nature of one of these, a red compound, m.p. 163-4°, first isolated in low yield from the reaction between the metho-sulphate (I) and aceturic acid in the presence of acetic anhydride and trimethylamine. Further experiments showed that the same compound was produced by the action of warm pyridine on the metho-sulphate, the main product being 5-phenyl-1,2-dithiole-3-thione.*

The red product, m.p. 163-4°, isolated by chromatography on alumina, was shown to have the formula $C_{19}H_{14}OS_4$ by analysis and mass spectrometry. The infrared spectrum suggested the

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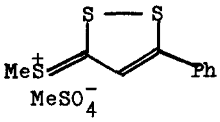
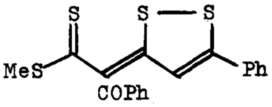
* The decomposition of a trithione metho-salt to the trithione with pyridine under somewhat different conditions has been previously described.[3]



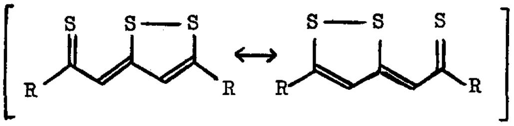
(I)



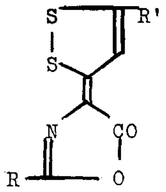
(II)

$Ph.CO.CH_2.CS_2Me$

(III)



(IV)

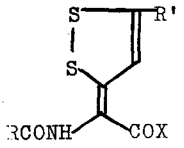


(V)

(Va). R=R'=Ph

(Vb) R=Me, R'=Ph

(Vc) R=Ph, R'=H



(VI)

(VIa) R=R'=Ph, X=NHMe

(VIb) R=Me, R'=Ph, $X=NHNH_2$

(VIc) R=Me, R'=Ph, $X=N_3$

presence of an extensively conjugated carbonyl group (ν_{max} 1660 cm.$^{-1}$) and a sharp singlet in the N.M.R. spectrum (measured in $CDCl_3$ solution) at τ 7.45 (three protons), considered in conjunction with the mass spectrum, indicated the presence of a methylthio-group. The N.M.R. spectrum also showed eleven protons in the aromatic region, two of these appearing at distinctly lower field than the remainder, a feature characteristic of protons _ortho_ to an electron--withdrawing group attached to an aromatic ring.

On this evidence, the red compound was tentatively formulated as (II) and this structure was easily confirmed by an unambiguous synthesis. The metho-sulphate (I) condensed smoothly with methyl benzoyldithioacetate (III), in acetic acid containing a little pyridine, giving the desired product in 80% yield. The compound thus appears to be a new example of the interesting "no-bond resonance" thiothiophthene system (IV) recently studied by Klingsberg,[2] Lozac'h[4] and by Behringer.[5] The ultraviolet and visible absorption spectrum of (II) shows marked similarities to those recorded[5] for thiothiophthenes. We regard the relative resistance of our product towards alkaline hydrolysis, in contrast to the expected reactivity of a dithio-ester, as evidence that it exists in the resonance-stabilized form equivalent to (IV).

Detailed discussion of the mechanism of the pyridine--trithione metho-salt reaction is deferred, but it is clear that a reactive intermediate, possibly (III) or a related compound, is generated presumably by nucleophilic attack at the 5-position of the metho-salt.[6]

Oxazolones prepared in the dithiole series include compounds (Va), (Vb) and (Vc). The first of these is most easily obtained from 5-phenyl-1,2-dithiol-3-one and hippuric acid in the presence of phosphorus oxychloride, a method which also succeeds with 1,2-dithiol-3-one, furnishing the oxazolone (Vc) (only one geometric isomer is shown in each case). The oxazolones react in the expected way with nucleophiles, yielding derivatives of type (VI), some of which are of interest in showing structural similarities to antibiotics of the thiolutin-holomycin group.*

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* The possibility of utilising the azide (VIc) to synthesise a holomycin analogue is being investigated.