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ISOLATION OF A CRYSTALLINE THIETE AND ITS 'OPEN' ISOMER; PHOTOPRODUCTS OF XANTHENETHIONE AND BIS(*tert*-BUTYLTHIO)ETHYNE

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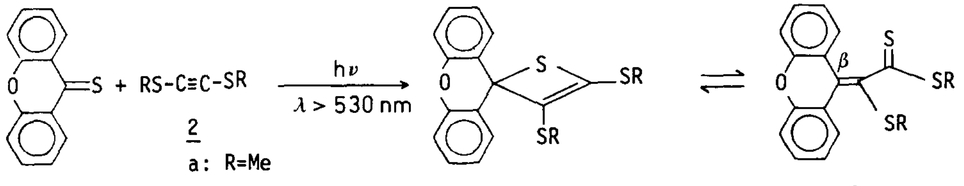
Summary; Irradiation of xanthenethione 1 with bis(*tert*-butylthio)ethyne 2 yielded both the expected α,β-unsaturated dithioester 4b and surprisingly its proposed intermediate thiete 3b as crystalline compounds. In solution an equilibrium between both compounds has been observed.

In a previous article [1)] we reported the isolation of the crystalline α,β-unsaturated dithioester 4a, after irradiating a solution of xanthenethione 1 and bis(methylthio)ethyne 2a. The intermediacy of a (2+2)cycloadduct, thiete 3a, was proposed to rationalise its formation.



1 + 2 (a: R=Me; b: R=*t*-Bu) → 3 ⇌ 4

About two years ago, Gotthardt and Nieberl [2)] described the photochemical adducts of xanthenethione and 1,3-dimethyl 2-thioparabanate with Ph-C≡C-Ph and Ph-C≡C-$COOC_2H_5$.
In a private communication they told us that the previously assigned structures are in fact thiete derivatives, as indicated by an X-ray crystal structure determination [3)].

In this paper we present the isolation of the stable thiete 3b and its 'open' isomer 4b, from the irradiated dichloromethane solution of xanthenethione 1 and bis(*tert*-butylthio)-ethyne 2b.

After chromatography (silicagel, benzene/pentane 1:8) an orange-red oil was obtained in 90% yield, which on crystallisation (CH_2Cl_2/pentane) initially gave red needles; m.p. 131-133°.

Recrystallisation of this red compound and further crystallisation of the mother liquor, yielded yellow crystals; m.p. 119-120° (the melt turned red).

Both compounds have the same mass spectra [4)], exhibiting important peaks at *m/e* 414 $[M]^{+\cdot}$, 212 $[C_{13}H_8OS]^{+\cdot}$,(thione 1) and 202 $[C_{10}H_{18}S_2]^{+\cdot}$, (acetylene 2b).

The yellow crystalline thiete 3b shows characteristic bands in the IR spectrum (KBr) at 1570 cm^{-1} (C=C), whereas the red dithioester 4b absorbs at 1530 cm^{-1} (C=C) and at 1120 cm^{-1} (probably C=S).

The IR spectrum of a CH_2Cl_2 solution of each compound looks like a superimposed spectrum of the spectra (KBr) of the red and the yellow compound. Thus suggesting an equilibrium between thiete 3b and the α,β-unsaturated dithioester 4b in solution at room temperature.

The ^1H NMR spectra of both compounds (CS_2) are identical and the signals for the aromatic protons in the region 7.0-8.5 ppm and for the protons of the two *tert*-butyl groups at 1.52 ppm (9H) and 1.02 ppm (9H), do not reveal the presence of thiete 3b and the unsaturated dithioester 4b. However, lowering the temperature to -50° , the signal at 1.02 ppm resolves (*via* coalescence) into two separate peaks at 1.10 ppm and 0.91 ppm with an intensity ratio of 40:60.

The ^{13}C NMR spectrum of the yellow compound in $CDCl_3$ at room temperature can be interpreted by assuming a fast equilibrium between 3b and 4b. At -30° two new signals become visible at 66.6 ppm and at 156.9 ppm assigned to the spiro-carbon atom of 3b and the β-carbon atom of 4b respectively. The signal at 224.6 ppm justifies the assumed presence of 4b.

The above mentioned observations lead to the conclusion that in solution we are dealing with a relatively fast equilibrium between thiete 3b and the α,β-unsaturated dithioester 4b. Out of a solution each isomer can crystallise. A molecular weight of 420, determined in boiling benzene,excludes the existence of an equilibrium between 4b and some dimeric structure [5)].

At this moment we are studying the details of this equilibrium especially with respect to the substituents of the thiete ring.

References:

1. A.C. Brouwer and H.J. T. Bos, Tetrahedron Lett., 1976, 206
2. H. Gotthardt and S. Nieberl, *ibid.*, 1976, 3566
3. H. Gotthardt and O.M. Huss, *ibid* , 1978, 3617 ; we thank prof. Gotthardt for sending us the manuscript
4. The samples were introduced as solids; exact mass measurements were carried out by C. Versluis from the 'Analytisch Chemisch Laboratorium', on a AEI-MS-902 mass spectrometer
5. There seems to be a negligible temperature effect on the equilibrium as was deduced from the low temperature ^1H NMR spectra down to -90°

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