

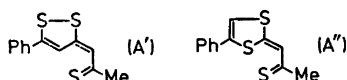
Short Communications

Formation of α -(5-Phenyl-1,3-dithiol-2-ylidene)propanethione from Thioacetic Acid and Phenylacetylene

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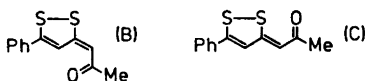
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It has been reported that the reaction of thioacetic acid with phenylacetylene in the presence of anhydrous sodium acetate resulted in the formation of an intensely coloured compound, $C_{13}H_{10}S_3$, (A).¹ This compound has later been assigned the *trans* trithiapentalene structure (A').²⁻⁴

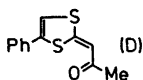


We want to present evidence which conclusively establishes the structure α -(5-phenyl-1,3-dithiol-2-ylidene)propanethione (A'') for this substance.

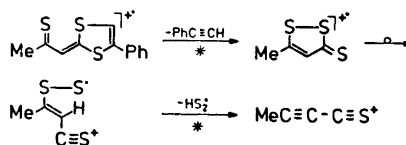
If compound (A) is dissolved in concentrated sulfuric acid a compound with the composition $C_{13}H_{10}OS_2$ can be isolated after dilution with water. The compound has been assigned the structure (B).²⁻⁴



This structure is unlikely since dithiolydene ketones (C) have been shown to photoisomerize to *trans* compounds of the same type as (B).^{5,6} These *trans* isomers, however, are not stable but revert to starting material *via* a thermal process. The lifetime of the *trans* isomers varies from milliseconds to some minutes. The compound obtained by partial desulfurization is actually α -(5-phenyl-1,3-dithiol-2-ylidene)propanone (D).⁷



The mass spectrum of (A), Fig. 1, is fully in accordance with structure (A''). The dominant fragmentation is loss of phenylacetylene from the molecular ion, a metastable peak corresponding to this fragmentation being present. The loss of acetylenes has been observed to be a general for 1,3-dithioles of the same type as (A'').⁸ The $[\text{M}-\text{PhC}\equiv\text{CH}]^+$ ion further loses HS_2 to give rise to the abundant ion m/e 83. These fragmentations can be rationalized for structure (A'') in the following way.



The loss of HS_2 is characteristic for 5-substituted 1,2-dithiol-3-thiones.⁹

When compound (A) is refluxed for several hours in xylene very little isomerisation to the corresponding 2-methyl-5-phenyl-1,6,6a Δ VS-trithiapentalene occurs; however, if thioacetamide is added to the refluxing solution rapid isomerisation takes place in accordance with previous observations.¹⁰⁻¹²

1,2-Dithiol-3-thiones react with activated acetylenes in a cycloaddition reaction forming α -(1,3-dithiol-2-ylidene)thioketones.^{10,13,14} We have succeeded in preparing a compound identical with (A) by reacting 5-methyl-1,2-dithiol-3-thione with phenylacetylene in boiling xylene. By partial desulfurization in concentrated sulfuric acid a compound identical to the compound which had been assigned structure (D) was obtained.

We have observed, that 5-methyl-1,2-dithiol-3-thione is formed in a refluxing solution of anhydrous sodium acetate in thioacetic acid. It has further been observed that the amount of 5-methyl-1,2-dithiol-3-thione is augmented by addition of diacetyl disulfide. We therefore propose that diacetyl disulfide is a precursor for the thione which reacts in a cycloaddition forming (A). This is further substantiated by the observation that the yield of (A) increased in proportion to the amount of diacetyl disulfide added to the reaction mixture.

Experimental. α -(5-Phenyl-1,3-dithiol-2-ylidene)propanethione (A''). Phenylacetylene (10 g), thioacetic acid (40 g), and anhydrous sodium acetate (1 g) were refluxed for 3 h, and the

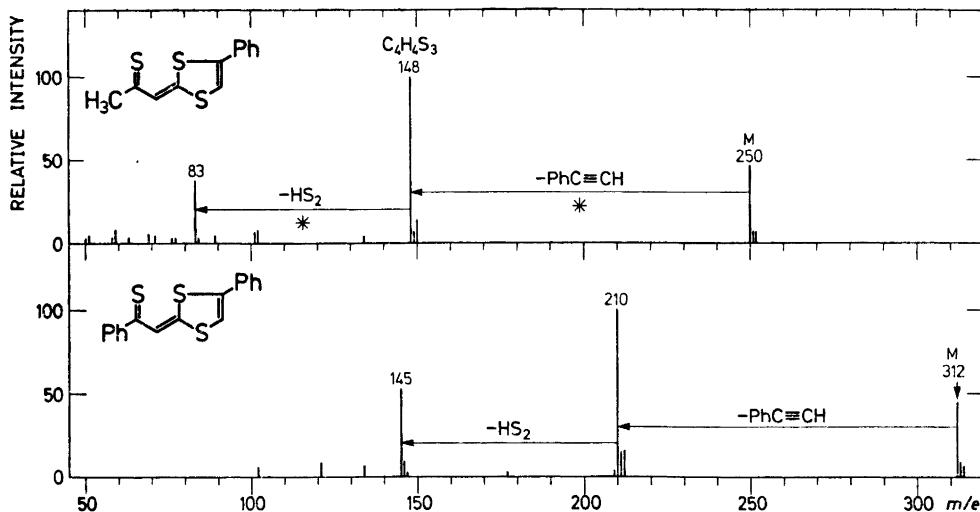


Fig. 1. Mass spectra of α -(5-phenyl-1,3-dithiol-2-ylidene)propanethione, and α -(5-phenyl-1,3-dithiol-2-ylidene)thioacetophenone.

reaction mixture was left over-night. The crystals that separated were washed with water. Yield 1.8 g, 7% based on phenylacetylene. Recrystallized from glacial acetic acid; m.p. 185–187 °C (isomerization). M^+ 249.9945; calc. for $C_{12}H_{10}S_3$ 249.9904, $M-102$ 148.0060; calc. for $C_6H_4S_3$ 148.0071. (Found: C 57.55; H 4.13; S 38.43. Calc. for $C_{12}H_{10}S_3$: C 57.60; H 4.03; S 38.37).

α -(5-Phenyl-1,3-dithiol-2-ylidene)propanone (D) (A'') (500 mg) was dissolved in cold concentrated sulfuric acid (10 ml); after 10 min at room temperature the yellow solution was warmed for 5 min on the water bath. After cooling the solution was poured into ice. The product was extracted with chloroform. After evaporation the compound was recrystallized from ethanol. Yield 300 mg; m.p. 157–158 °C, (lit. 157–158 °C,⁴ 152–154 °C⁷).

2-Methyl-5-phenyl-1,6,6a¹VS-trithiapentalene. Compound (A'') (300 mg) was refluxed in xylene (25 ml). After 4 h small amounts of trithiapentalene were detectable by means of TLC. Thioacetamide (300 mg) was added, and the solution was refluxed for a further 4 h, after which (A'') was 75% converted to trithiapentalene. After evaporation and chromatography on alumina 100 mg of crystals were isolated, Recrystallized from cyclohexane, m.p. 168–169 °C, (lit. 169 °C¹⁵).

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