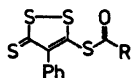


5-Acylthio-4-phenyl-1,2-dithiole-3-thiones; Thia Analogues of  $\alpha$ -(1,2-Dithiol-3-ylidene) Ketones

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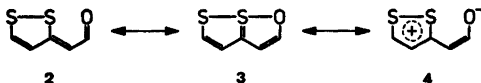
The reaction of dimethylammonium 4-phenyl-3-thioxo-1,2-dithiole-5-thiolate<sup>1,2</sup> with carboxylic acid chlorides results in the formation of 5-acylthio-4-phenyl-1,2-dithiole-3-thiones (1).



1

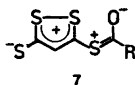
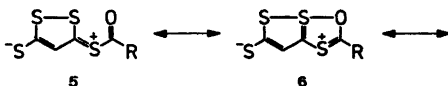
Although dialkylation of the 4-phenyl-3-thioxo-1,2-dithiole-5-thiolate ion has been described<sup>1</sup> diacylation has never been observed even with excess of acyl halide.

Compounds of type (1) may be considered as analogues to  $\alpha$ -(1,2-dithiol-3-ylidene) ketones (2) for which the resonance structures (3) and (4) have to be taken into consideration due to the absence of absorption bands in IR above



1600  $\text{cm}^{-1}$ <sup>3</sup> where the carbonyl absorption is normally observed. The lack of a normal carbonyl group in these compounds is also reflected in the O 1s binding energy observed in the ESCA spectra. An average value of 531.1 eV<sup>4</sup> has been found, which is considerably more negative than normal for carbonyl oxygen.

A series of analogous resonance structures (5), (6) and (7) can be written down for (1).



As seen from Table 1 these compounds show a normal carbonyl vibration in the 1600–1700

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Table 1. 5-Acylthio-4-phenyl-1,2-dithiole-3-thiones.

R	$\nu_{\text{CO}}/\text{cm}^{-1}$ (KBr)	M.P. <sup>a</sup> /°C	Yield/%
CD <sub>3</sub>	1700	131–132	69
CCl <sub>3</sub>	1725	118–119	55
CH <sub>3</sub>	1699	155–156	63
CH <sub>2</sub> CH <sub>3</sub>	1700	83–84	48
CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1681	100–101	55
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	1688	79–80	51
C(CH <sub>3</sub> ) <sub>3</sub>	1684	98–99	53
C <sub>6</sub> H <sub>5</sub>	1670	178–179	58
4-CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub>	1652	189–190	55

<sup>a</sup> All compounds show satisfactory elemental analysis.

$\text{cm}^{-1}$  region. This indicates that there is no conjugation through the exocyclic sulfide sulfur, i.e. no interaction between the dithiole ring sulfur and the carbonyl oxygen is present. From model considerations it is obvious that the carbonyl group has to be *cis* with respect to the dithiole sulfurs due to the sterical interaction of the 4-phenyl group.

This means that the resonance forms (6) and (7) only play a minor role in the description of these compounds.

**Experimental.** 5-Acylthio-4-phenyl-1,2-dithiole-3-thiones. (Table 1). Dimethylammonium 4-phenyl-3-thioxo-1,2-dithiole-5-thiolate<sup>1</sup> (0.01 mol) in acetonitrile (50 ml) was mixed at room temperature with a solution of the acid chloride (0.01 mol) in acetonitrile (50 ml). The mixture was stirred for 5 min; if no precipitate had occurred, the solution was cooled in an ice/acetone mixture. The precipitates were recrystallized from benzene or mixtures of benzene and ether (1:1).

The mass spectra of the compounds all exhibited abundant peaks corresponding to  $[\text{M}-\text{RCO}]^+$  as well as  $[\text{RCO}]^+$ .

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