Cycloaddition Reactions of Thioacylketen Thioacetals[1]

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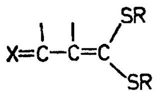
Summary Thioacylketen thioacetals undergo 1,4-cycloaddition with electron-deficient olefins and sulphene, and 1,2-cycloaddition with tetracyanoethylene and diphenyldiazomethane.

The preparation and synthetic applications of conjugated keten thioacetals such as vinylketen (I)[2] and α-keto-keten thioacetals (II) have recently been reported.[3] However, for thioacylketen thioacetals (III), only the reactions with active acetylenes have been studied[4]† despite their considerable potential in synthesis.



(I) X=CR$_2$; (II) X=O; (III) X=S

We now report that the thioacylketen thioacetals (III) undergo 1,2- and 1,4-cycloaddition reactions with some types of reagents under fairly mild conditions. We chose 4,5-tetramethylene-2-thiobenzoylmethylene-1,3-dithiolan (IV)[6] as a suitable thioacylketen thioacetal because it is readily available from 5-phenyl-1,2-dithiole-3-thione. The results are summarized in the Scheme. The identity of the products was established by their analytical and spectral data.

The product (V) from tetracyanoethylene is presumably formed *via* 1,2-cycloaddition across the C=S bond, followed by elimination of $(CN)_2C{=}S$.[7]

The formation of compounds (V) and (VII) is a novel method of preparation of vinylketen thioacetals.

The possible conversion of a thioacetal to a carbonyl group[8] will also make these reactions useful for the synthesis of six-membered sulphur-heterocycles.

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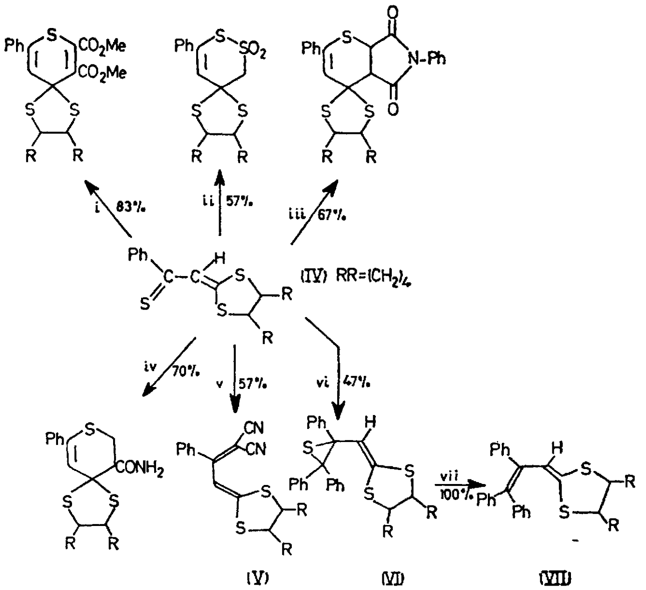

Scheme

(i) Dimethyl acetylenedicarboxylate in dichloromethane, room temp., 10 h; (ii) sulphene (methanesulphonyl chloride–triethylamine) in benzene, 5°, 1 h; (iii) *N*-phenylmaleimide in benzene, reflux, 4 h; (iv) acrylamide in xylene, reflux, 2 h; (v) tetracyanoethylene in acetonitrile, reflux, 2 h (or in dichloromethane, room temp., 5 days); (vi) diphenyldiazomethane in ether, room temp., 15 h; (vii) triphenylphosphine in benzene, room temp., 4 days.

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† Cycloadditions of activated acetylenes and *N*-phenylmaleimide to similar systems, *i.e.* *o*-thioquinomethides, have recently been reported.[1,5]

[1] Part of a series on conjugated keten thioacetals. For part 1 see: R. Okazaki and N. Inamoto, *Chem. Letters*, 1974, 1439.

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