

1,3-Dipolar Reactivity of 1,2-Dithiole-3-thiones and 1,3-Dithiolan-2-thiones

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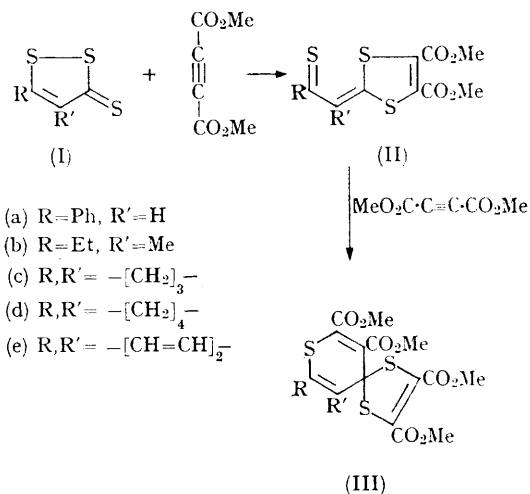
BEHRINGER and WIEDENMANN¹ recently reported the formation of 1:1-adducts (*e.g.*, II) from 1,2-dithiole-3-thiones (I) and dipolarophilic acetylenes. We have obtained similar reddish-brown adducts by reaction of the thiones (Ia—Id) with dimethyl acetylenedicarboxylate, in benzene at room temperature, and have adduced similar evidence for their structures. In most instances, however, we observed also the formation of small amounts of pale yellow, thione-ester 1:2-adducts which became the main products when a two-fold or greater excess of the ester was used. In accord with the German workers' failure to isolate a 1:1-adduct from the benzodithiolethione (Ie), we could obtain only a 1:2-adduct from this compound.

Desulphurisation of the 1:2-adducts from the thiones (Ia) and (Ie), with Raney nickel, gave dimethyl (3-phenylpropyl)succinate and dimethyl benzylsuccinate, respectively, together with dimethyl succinate. On the basis of this evidence we assign the structures (IIIa—IIIe) to the 1:2-adducts. Evidently these adducts are formed by 1,4-cyclo-addition of the acetylenic ester to the enethione grouping of the 1:1-adducts. The *o*-quinonoid structure (IIIe)¹ of the expected 1:1-adduct from the thione (Ie) probably accounts for its rapid disappearance by further cyclo-addition.

1,3-Dithiolan-2-thione (IV) reacted rapidly with dimethyl acetylenedicarboxylate at 140° to give the 1,3-dithiole-2-thione (V), in almost quantitative yield, together with ethylene, characterised as its

adduct² with 2,4-dinitrobenzenesulphenyl chloride. In view of the recent stereospecific conversion³ of dithiolanthiones into olefins by treatment with trialkyl phosphites, it was of interest to investigate the steric course of this alternative method for elimination of the trithiocarbonate grouping. The only result available at the present time indicates that the reaction is not stereospecific since *cis*-4,5-diphenyl-1,3-dithiolan-2-thione gave *cis*- and *trans*-stilbene, in the ratio 42:58, together with the thione (V). *cis*-Stilbene was shown not to isomerise under the reaction conditions.

Reaction of the thione (Ia) with benzyne,

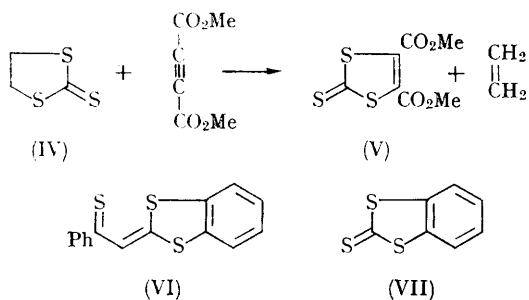


- (a) R=Ph, R'=H
 (b) R=Et, R'=Me
 (c) R,R' = $-\text{[CH}_2\text{]}_3-$
 (d) R,R' = $-\text{[CH}_2\text{]}_4-$
 (e) R,R' = $-\text{[CH=CH]}_2-$

¹ H. Behringer and R. Wiedenmann, *Tetrahedron Letters*, 1965, 3705.

² N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724.

³ E. J. Corey, F. A. Carey and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, **87**, 934.



generated⁴ from anthranilic acid and isopentyl nitrite in boiling benzene, gave a 28% yield of a 1:1-adduct (VI), identical with an authentic specimen prepared from benzo-1,3-dithiole-2-thione (VII) by the general method previously reported.⁵ 1,3-Dithiolan-2-thione yielded no characterisable product under these conditions but with benzyne generated⁶ from 2-phenyliodonio benzene-1-carboxylate in boiling γ -butyrolactone, it gave the thione (VII) in 9% yield.

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⁴ L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

⁵ D. Leaver and D. M. McKinnon, *Chem. and Ind.*, 1964, 461.

⁶ F. M. Beringer and S. J. Huang, *J. Org. Chem.*, 1964, **29**, 445.