

Formation of 2,3-Bis(methoxycarbonyl)-1,4-benzodithiins by reaction of 1,4,2-Benzodithiazines with Dimethyl Acetylenedicarboxylate

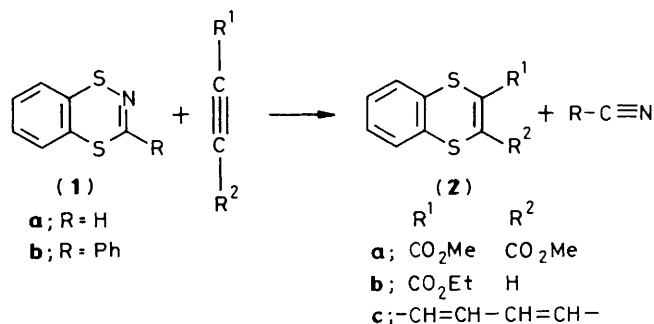
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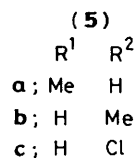
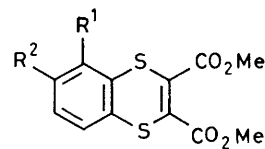
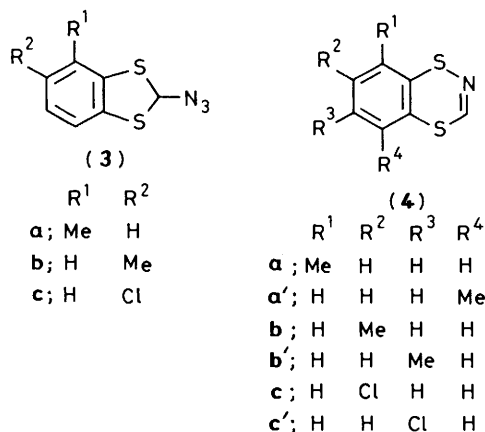
1,4,2-Benzodithiazines reacted with dimethyl acetylenedicarboxylate in boiling *o*-dichlorobenzene to give 2,3-bis(methoxycarbonyl)-1,4-benzodithiins in good yields with elimination of hydrogen cyanide or a nitrile.

Reactions of dimethyl acetylenedicarboxylate (DMAD) with heterocycles have provided useful methods for the preparation of a wide variety of novel compounds.¹ We report an unprecedented type of cycloaddition-elimination reaction of DMAD with 1,4,2-benzodithiazines which provides a general synthesis of 2,3-bis(methoxycarbonyl)-1,4-benzodithiins.

Heating 1,4,2-benzodithiazine (1a), which recently became readily obtainable,² with 3 mol. equiv. of DMAD† in boiling *o*-dichlorobenzene for 6 h afforded 2,3-bis(methoxycarbonyl)-1,4-benzodithiin (2a), ‡ m.p. 59–60 °C,³ in 75–80% yield, with evolution of hydrogen cyanide which could be trapped as silver cyanide in *ca.* 80% yield. 3-Phenyl-1,4,2-benzodithiazine (1b)² and 3 mol. equiv. of DMAD, on being heated at 195 °C without solvent for 3 h, gave the dithiin (2a) (90%) and benzonitrile.

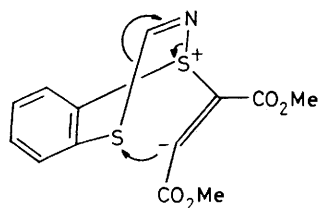


Prolonged heating of (1a) with an excess of ethyl propiolate in refluxing *o*-dichlorobenzene gave 2-(ethoxycarbonyl)-1,4-benzodithiin (2b), b.p. 110 °C/0.2 mmHg (Kugelrohr), in 34% yield. Benzyne, generated by thermal decomposition of benzenediazonium-2-carboxylate in boiling dichloromethane,⁴



† The use of an equimolar amount of DMAD gave (2a) in a decreased yield (46%).

‡ Satisfactory elemental analyses and supporting spectral data were obtained for all dithiins.



(6)

reacted with (1a) to give a low yield of thianthrene (2c) along with some other products. Dimethyl fumarate and diethyl azodicarboxylate, however, failed to react with (1a), the starting materials being recovered unchanged.

Thermolysis of the azide (3a), prepared from 4-methyl-1,3-benzodithiolylium tetrafluoroborate⁵ and sodium azide, in refluxing toluene afforded an isomeric mixture of (4a) and (4a') (ratio of *ca.* 1:1) in an 80% yield. Similarly the thermolyses of azides (3b) and (3c) gave isomeric mixtures of (4b) and (4b') and of (4c) and (4c'). Heating mixtures of (4a) and (4a'), (4b) and (4b'), and of (4c) and (4c') with 3 mol. equiv. of DMAD in boiling *o*-dichlorobenzene for 6–7 h yielded dithiins (5a), m.p. 88–89 °C, (65%), (5b), b.p. 170 °C/0.5 mmHg (Kugelrohr), (79%), and (5c), m.p. 73.5–74 °C, (66%), respectively.

The initial reaction of DMAD with heterocycles containing both nitrogen and sulphur (*e.g.*, thiazoles) takes place at the nitrogen atom.¹ In the present case, however, any product associated with this process was not obtained. We therefore tentatively propose an intermediate like (6).

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References

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- 3 de Mayo *et al.* obtained (2a) as a light yellow oil by prolonged irradiation of 1,3-benzodithiol-2-one in the presence of DMAD. Spectral data of our compound are fully consistent with those reported. P. de Mayo, A. C. Weedon, and G. S. K. Wong, *J. Org. Chem.*, 1979, **44**, 1977. Isomeric 2-bis(methoxycarbonyl)methylene-1,3-benzodithiole, prepared by condensation of 2-methylthio-1,3-benzodithiolylium perchlorate and dimethyl malonate, melts at 153.5–154 °C.
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