

## A New Reaction of Mesoionic 1,3,4-Thiadiazoles. Attempted Cycloaddition with Dimethyl Acetylenedicarboxylate

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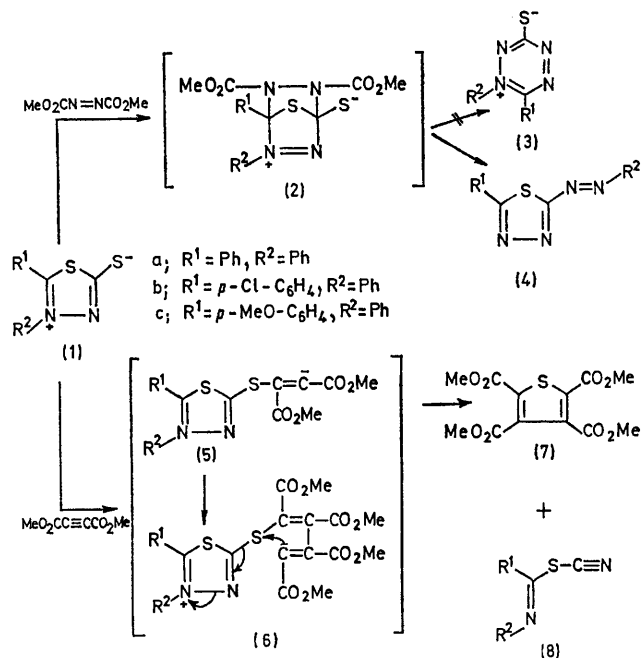
**Summary** Treatment of various mesoionic 1,3,4-thiadiazoles with dimethyl acetylenedicarboxylate yields tetramethylthiophen tetracarboxylate and the *S*-cyanothioimidate derivative; a mechanism involving fragmentation of the mesoionic ring is suggested.

THE cycloaddition of mesoionic 1,3,4-thiadiazoles with dimethyl azodicarboxylate has previously been reported.<sup>1</sup> Repetition of this work by Mosby and Vega led to a revision of the structure of the alleged mesoionic product (3) to a 5-phenyl-2-phenylazo-1,3,4-thiadiazole (4).<sup>2</sup> On reinvestigating this cycloaddition with several mesoionic 1,3,4-thiadiazoles we confirmed the revised structural assignments, although some important discrepancies remain.† Apparently the hypothetical intermediary product of 1,4-cycloaddition, (2), decomposes exclusively by the route (2) → (4).

We also investigated dimethyl acetylenedicarboxylate as a 1,4-dipolarophile in the hope of obtaining a reaction analogous to (1) → (2) → (4) from which a thiophen derivative would result.

We now report that a strikingly different reaction occurs which involves a hitherto unobserved mode of cleavage of the mesoionic 1,3,4-thiadiazole ring, embodied in the expression (6) → (7) + (8).

Treatment of (1a–c) with dimethyl acetylenedicarboxylate in 1:2 ratio in benzene under reflux for 6 h gave (7) in yields of ca. 30% and (8a–c)‡ in yields of ca. 50%. The *S*-cyanothioimidates underwent hydrolysis readily to give the corresponding amides; these compounds could be synthesized independently by treatment of the appropriate chloroimidate derivative with sodium thiocyanate. Path-



way (1) → (5) → (6) → (7) + (8) is speculative; no evidence for reaction intermediates has been obtained. A similar fragmentation reaction has been observed in the addition of amines to 2-bromo-5-nitrothiazole.<sup>3</sup>

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† In their attempts to repeat this work<sup>2</sup> they inexplicably failed to obtain a reaction under the described conditions,<sup>1</sup> namely heating (1) under reflux with dimethyl azodicarboxylate in 1:2 molar ratio in benzene, under nitrogen, for 12 h. Under these conditions the yields of (4a), (4b), and (4c) are 30, 32, and 41%, respectively. Also, (4a) forms a derivative with methyl iodide (sealed tube), m.p. 172–181°, m.p. 208–211°.

‡ Structures confirmed by elemental analysis and n.m.r. and m.s. data.

\* R. M. Moriarty, J. M. Kliegeman, and R. B. Desai, *Chem. Comm.*, 1967, 1045.

<sup>2</sup> W. L. Mosby and M. L. Vega, *Chem. Comm.*, 1971, 837.

<sup>3</sup> A. O. Illvespää, *Helv. Chim. Acta*, 1968, 51, 1723.