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

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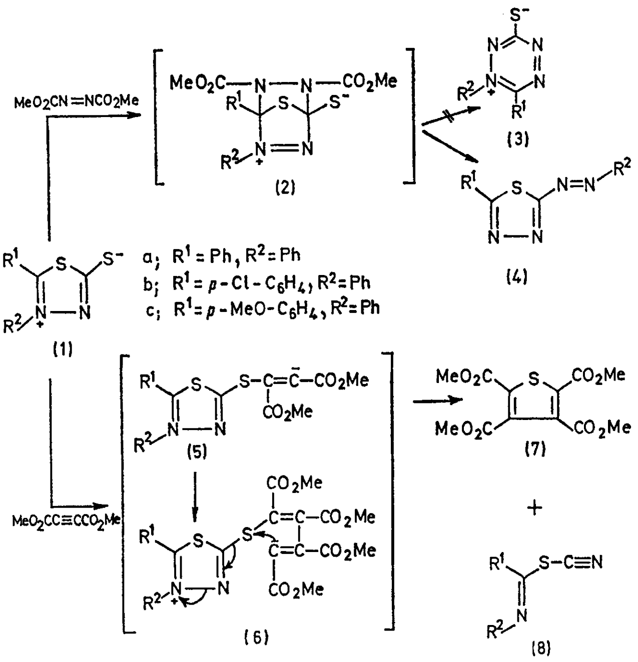
Summary Treatment of various mesoionic 1,3,4-thiadiazoles with dimethyl acetylenedicarboxylate yields tetramethylthiophen tetracarboxylate and the *S*-cyanothioimidate derivative; a mechanism involving fragmentation of the mesoionic ring is suggested.

The cycloaddition of mesoionic 1,3,4-thiadiazoles with dimethyl azodicarboxylate has previously been reported.[1] 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**).[2] 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. Pathway (**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.[3]



(*Received, 27th October* 1972; *Com.* 1826.)

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† In their attempts to repeat this work[2] they inexplicably failed to obtain a reaction under the described conditions,[1] 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.

[1] R. M. Moriarty, J. M. Kliegeman, and R. B. Desai, *Chem. Comm.*, 1967, 1045.
[2] W. L. Mosby and M. L. Vega, *Chem. Comm.*, 1971, 837.
[3] A. O. Illvespää, *Helv. Chim. Acta*, 1968, **51**, 1723.