

Meso-ionic 1,3,4-Thiadiazoles, Reaction with Methyl Azodicarboxylate

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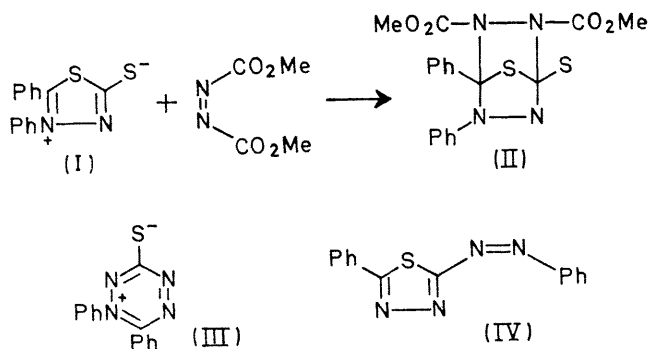
Summary The reaction of 4,5-diphenyl-1,3,4-thiadiazolium-2-thiolate (I) with methyl azodicarboxylate, previously reported to yield a 6-membered meso-ionic system (III), is here shown to produce an azothiadiazole derivative (IV).

$C_{14}H_{10}N_4S$ and the i.r. spectrum was identical with that of the compound prepared from (I), which we must now represent by structure (IV). The reduction of the product to a dihydro-derivative and the simple cleavage of this to an amino-aryl-1,3,4-thiadiazole¹ are more easily explicable upon the basis of structure (IV) than (III).

RECENTLY, the reactions of two 4,5-diaryl-1,3,4-thiadiazolium-2-thiolates with azodicarboxylic ester were described,¹ and the products postulated to be meso-ionic tetrazine derivatives. We have attempted to reproduce this work

Heating (I) under reflux with a two-fold excess of dimethyl azodicarboxylate in benzene for 12 h as described¹ gave, we found, a quantitative recovery of unchanged (I). However, the use of (higher boiling) toluene afforded a 30% yield of product, m.p. 173–174°, λ_{max} 265 (log ϵ 4.45) and 365 nm (3.81). Microanalyses supported the formula $C_{14}H_{10}N_4S$ and mass spectrography gave a molecular weight of 266.

All these data are in reasonable agreement with those of Moriarty *et al.*¹ However, we were unable to prepare the methiodide of (III), which they describe, recovering only unchanged material. It seemed that the proposed¹ intermediate (II) might collapse to products other than (III), such as (IV). An unambiguous route to (IV) appeared to be through condensation of the known² 2-amino-5-phenyl-1,3,4-thiadiazole with nitrosobenzene. We thus obtained an 88% yield of golden orange crystals, m.p. 173–174°. The microanalyses again showed the composition to be



It thus appears that an authentic representative of the meso-ionic system (III) has yet to be described.

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¹ R. M. Moriarty, J. M. Kliegman, and R. B. Desai, *Chem. Comm.*, 1967, 1045.

² E. Hoggarth, *J. Chem. Soc.*, 1949, 1163.