Reaction of a 2-Iminothione with Dimethyl Acetylenedicarboxylate to give a Pyridine Derivative

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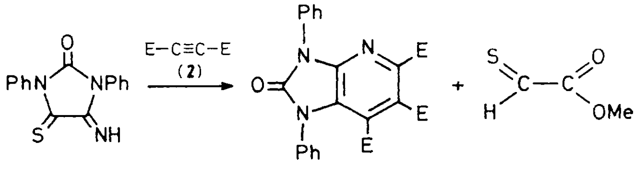
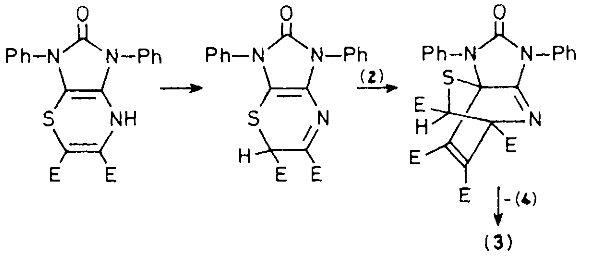
Reactions of 5-imino-1,3-diphenyl-4-thioxoimidazolidin-2-one (**1**) and 5-imino-3-phenyl-4-(*N*-phenylimino)-thiazolidine-2-thione (**6**) provide 5,7-dihydro-2,3,4-tris(methoxycarbonyl)-5,7-diphenyl-6*H*-imidazo[4,5-*b*]-pyridin-6-one (**3**) and 6,7-dihydro-2,3,4-tris(methoxycarbonyl)-7-phenylthiazolo[4,5-*b*]pyridine-6-thione (**7**), respectively, when heated with dimethyl acetylenedicarboxylate.

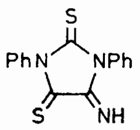
During the course of investigating the synthetic utility of the 2-iminothione system[1,2] we heated compound (**1**) in the presence of dimethyl acetylenedicarboxylate (**2**) in the hope of trapping a suspected iminocarbene intermediate. We observed instead a product (m.p. 220—222 °C) from which sulphur had indeed been lost but which contained not two but three methoxycarbonyl substituents. This product can be assigned the imidazopyridine structure (**3**) on the basis of its n.m.r. (methyl singlets at δ 3.91, 3.88, and 3.18) and mass spectra [M^+, m/z 461.11979, calc. 461.12231; M^+– PhN–C(:O)–NPh, m/z 251.04513, calc. 251.04299] and elemental analysis. Similar products were obtained, also in low yield, from



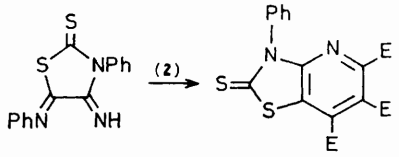
(**1**) (**3**) (**4**)

E = CO_2Me





(5)



(6) (7)

analogues of (**1**) having methyl groups in place of one or both phenyl groups in the starting heterocycle.

Products of this type may be viewed as resulting from a Diels–Alder reaction of the iminothione as a heterodiene followed by a prototropic shift, a second Diels–Alder addition, and a retrograde Diels–Alder reaction in which the thioaldehydic ester (**4**) is lost. Other systems in which thiones have constituted part of a heterodiene have also been reported.[3,4]

In an attempt to extend the reaction to what we had previously thought was the 2-thione analogue of (**1**), *i.e.* (**5**),[1] we obtained a product, m.p. 202—204 °C, which did not lose sulphur but instead lost an *N*-phenylimino-group and still contained the three methoxycarbonyl substituents (n.m.r. methyl singlets at δ 4.04, 3.99, and 3.83; mass spectrum, M^+, m/z 418.02987, calc. 418.02937; $PhNCS_2^+$, m/z 166.98778 calc. 166.98634).

These observations require that the substance previously thought to be (**5**)[1] must be reformulated as the di-imino-compound (**6**). It too reacts as a heterodiene and with the acetylenic dienophile gives the thiazolopyridine derivative (**7**) by a pathway similar to that suggested for (**1**) → (**3**).

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