The Chemistry of a 1,3,4-Thiadiazin-6-one

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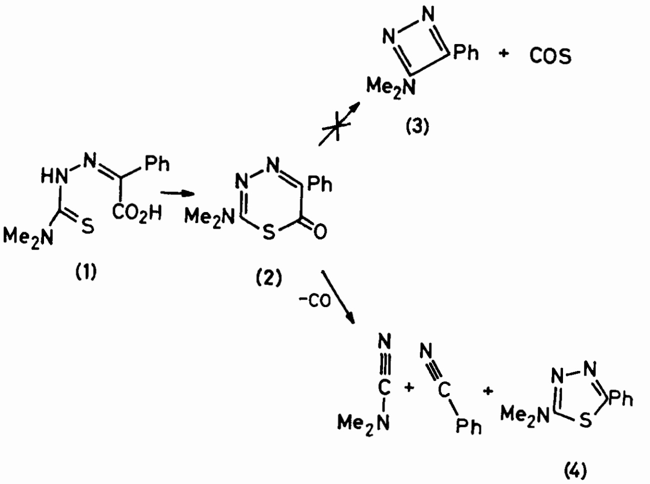
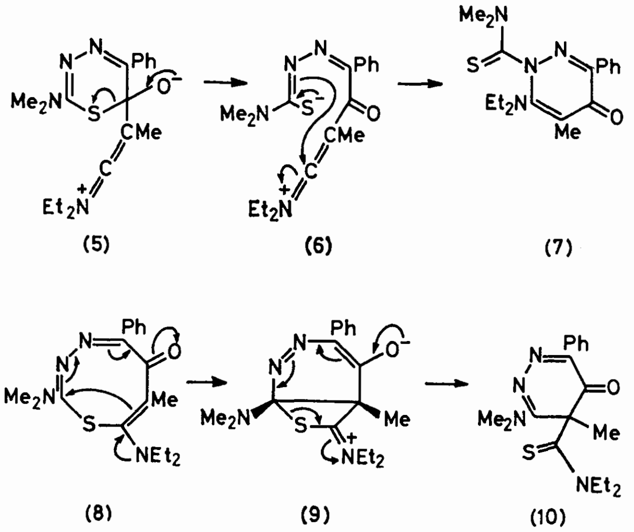
Summary 2-Dimethylamino-5-phenyl-1,3,4-thiadiazin-6-one (**2**), the first representative of this ring system, undergoes thermal fragmentation to yield benzonitrile, dimethylcyanamide, and 2-dimethylamino-5-phenyl-1,3,4-thiadiazole; its reaction with 1-diethylaminopropyne results in a mixture of adducts, the 1*H*-pyridazin-4-one (**7**) and the 5*H*-pyridazin-4-one (**10**).

1,3,4-THIADIAZIN-6-ONES have not been reported previously. We were interested in these compounds as potential precursors of 1,2-diazetes. The yellow 2-dimethylamino-5-phenyl derivative (**2**),† m.p. 105—106 °C, ν_{max} 1640 and 1530 cm^{-1}, was obtained in 92% yield by treating the 4,4-dimethylthiosemicarbazone (**1**)† of benzoylformic acid with dicyclohexylcarbodiimide. Its mass spectrum showed prominent peaks due to $(M - CO)^{\cdot +}$ and $(M - NMe_2)^{\cdot +}$ but no fragment resulting from loss of carbonyl sulphide. Flash-vacuum pyrolysis at 550 °C and 0·08 Torr likewise gave no indication of the formation of the diazete (**3**); the pyrolysate consisted essentially of a mixture of benzonitrile, dimethylcyanamide, and 2-dimethylamino-5-phenyl-1,3,4-thiadiazole (**4**),[1] which were identified by direct comparison with authentic specimens. Extrusion of carbon monoxide, accompanied by ring contraction, is a common feature of the mass spectra of six-membered heterocyclic 2-ones,[2] but does not appear to have been observed previously in the thermolysis of such compounds.


(1) (2) (3) (4)


(5) (6) (7)
(8) (9) (10)

SCHEME

Attempts to carry out Diels–Alder additions to the thiadiazinone (**2**) gave unexpected results. There was no reaction with the electron-poor dienophiles dimethyl

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† Satisfactory analytical and spectroscopic data were obtained for all new compounds.

acetylenedicarboxylate, *N*-phenylmaleimide, diethyl azodicarboxylate, or 4-phenyl-1,2,4-triazoline-3,5-dione; the electron-rich 1-diethylaminopropyne, on the other hand, gave a mixture of two adducts, neither of which appeared to be a simple cycloadduct. The structures were solved by *X*-ray analysis, details of which will be published elsewhere. The major (72%), yellow product, m.p. 145—146 °C, ν_{max} 1609 and 1595 cm^{-1}, proved to be the 1*H*-pyridazin-4-one (**7**),† and the minor (2%), orange isomer, m.p. 187—188 °C, ν_{max} 1668 and 1550 cm^{-1}, the 5*H*-pyridazin-4-one (**10**).†

We suggest that the formation of both compounds is best explained by initial addition of the ynamine to yield the dipolar intermediate (**5**), which undergoes ring-opening to the thiolate (**6**) (Scheme). The latter can recyclise in two ways: carbon–nitrogen bond formation leads directly to the major product (**7**) as shown; the alternative ring-closure from carbon to sulphur gives the transient eight-membered heterocycle (**8**), which undergoes a symmetry-allowed disrotatory electrocyclisation to the bicyclic oxide (**9**); this subsequently collapses to the minor isomer (**10**). The structure of this pyridazinone is remarkable for the presence of the tetrahedral carbon atom in the ring. The compound presumably owes its existence to the fact that it may not isomerise to a fully conjugated 1*H*-pyridazin-4-one or derivative of 4-hydroxypyridazine, because such rearrangements would require suprafacial [1,3] or [1,7] shifts, respectively, of the diethylthiocarbamoyl (or methyl) groups, which are precluded by the rules of orbital symmetry.

The behaviour of the thiadiazinone (**2**) is in marked contrast with that of the related 2,5-diphenyl-1,3,4-oxadiazin-6-one, which is reported[3] to undergo initial Diels–Alder additions to electron-poor acetylenes as well as to diethylaminopropyne.

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[1] E. Hoggarth, *J. Chem. Soc.*, 1949, 1163.

[2] See, for example, the formation of benzo[*b*]thiophen ion in the mass spectrum of thiocoumarin (O. Meth-Cohn and B. Tarnowski, *Adv. Heterocycl. Chem.*, 1980, **26**, 123).

[3] W. Steglish, E. Buschmann, G. Gansen, and L. Wilschowitz, *Synthesis*, 1977, 252.