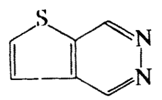
Thieno[3,2-c]pyridazine: a New Ring System related to Cinnoline

By A. J. Poole and F. L. Rose*

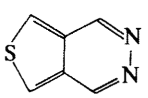
(*University of Manchester Institute of Science and Technology, P.O. Box 88, Sackville Street, Manchester, 3*)

Although five thienopyridazine ring systems are possible, only derivatives of thieno[2,3-*d*]- (I) and thieno[3,4-*d*]-pyridazine (II), have been reported. Of these, only the former has been described as the parent heterocycle.

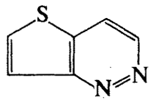
We have prepared the cinnoline analogue, thieno[3,2-*c*]-pyridazine (III). Juxtaposition of the heterocyclic nuclei was achieved in the hexahydro-forms [(VI), needles from MeOH, m.p. 136·5—137·5, and (IX), m.p. 119—120°, from MeOH] by the reaction of hydrazine acetate with the tetrahydrothiophen oxo-esters (V) and (VIII), themselves derived from the products of Dieckmann ring-closure, with magnesium ethoxide, of the hydrogen sulphide–ethyl acrylate (IV) and ethyl acrylate–ethyl maleate (VII) condensates. The carboxylic ester series (IX) proved more amenable to dehydrogenation and this was achieved as follows. Treatment with *N*-bromosuccinimide in dry acetone gave the tetrahydro-derivative [(X) from MeOH, m.p. 207—208°]; excess of the same reagent in wet acetone, followed by decarboxylation, then yielded the oxo-compound [(XI), monohydrate, golden yellow needles from BuOH, m.p. 219—220°] which dehydrated at 180°/0·2 mm. The action of phosphoryl chloride on (XI) gave the chlorothienopyridazine, although it was difficult to remove reductively the chlorine substituent. However treatment of compound (XI) with LiAlH$_4$, followed by reaction of the prodispinol mercury(II) oxide, without characterisation of the intermediate oily product, gave the parent heterocycle (III) in reasonable yield. This compound formed colourless needles, m.p. 97·5—98·5°, from light petroleum. The spectral properties (i.r. and n.m.r.) were consistent with the proposed structure.



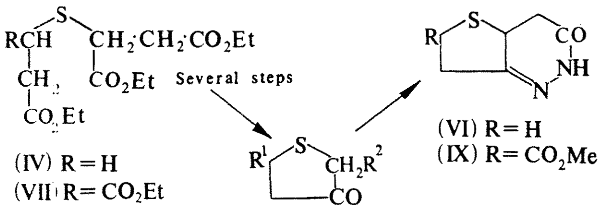
(I)



(II)



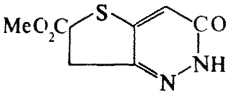
(III)



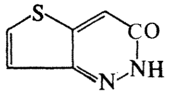
(IV) R = H
(VII) R = CO$_2$Et

(VI) R = H
(IX) R = CO$_2$Me

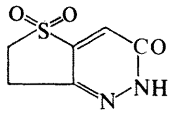
(V) R^1 = H, R^2 = CO$_2$Et
(VIII) R^1 = CO$_2$Me, R^2 = CO$_2$Me



(X)



(XI)



(XII)

Dehydrogenation of compounds (VI) and (IX) has also been achieved with other oxidants such as chloranil and hydrogen peroxide, in the latter instance to yield the sulphone (XII). The dihydro-derivative (XI) also gave a sulphone with hydrogen peroxide in hot glacial acetic acid.

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