

SYNTHESIS AND DESULFURIZATION OF PYRIDAZINO[4,5-e]
[1,3,4]THIADIAZINES

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Sulfur-containing heterocyclic compounds have been converted, through extrusion of sulfur, into another heterocycles, by several appropriate methods. According to the scheme shown below, synthesis of some derivatives of the novel ring, pyridazino[4,5-e][1,3,4]thiadiazine, and their ring contraction to those of pyrazolo[3,4-d]pyridazine have been successfully effected.

5-(α -Bromo-benzylidenehydrazino)-4-halo-2-substituted 3(2H)-pyridazinones reacted with potassium thioacetate in boiling acetonitrile, followed by acidic hydrolysis to yield 4-H-2-phenyl-7-substituted pyridazino[4,5-e][1,3,4]thiadiazines (I). 8-Hydroxy derivative (I: $R^1=H$) was chlorinated with phosphorus oxychloride, then aminated to give 8-chloro- and 8-amino-pyridazino-thiadiazine derivatives (II).

Oxidative cyclization of 5-thiosemicarbazide-pyridazinones with N-bromosuccinimide (NBS) in chloroform afforded 2-amino-pyridazino[4,5-e][1,3,4]thiadiazines (III), whilst, reaction of 5-hydrazino-pyridazinones with carbon disulfide in the presence of sodium hydroxide in dimethylformamide, with subsequent alkylation, gave 2-alkylthio-pyridazino[4,5-e][1,3,4]thiadiazine derivatives (IV).

A series of pyridazino[4,5-e][1,3,4]thiadiazines (I~IV: $R^2=H$) described above were satisfactorily converted, in appropriate basic conditions, into the corresponding 1-H-3,5-disubstituted pyrazolo[3,4-d]pyridazin-4(5H)-ones (V) or 3,4-disubstituted pyrazolo[3,4-d]pyridazines (VI) through removal of the sulfur atom. Such a ring contraction also took place thermally in suitable solvents leading to the desulfurized products (V, VI: $R^2=H$ or CH_3).

