SYNTHESIS OF CONDENSED PYRIDAZINE DERIVATIVES WITH THIAZOLE, 1,2,3-THIADIAZOLE, 1,4-THIAZINE AND 1,4-DITHIIN MOIETIES

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4-Benzyl- or 4-p-tolylmethylamino-5-chloro-2-substituted 3(2H)-pyridazinones reacted with sodium hydrosulphide by heating at 140-150°C in dimethyl sulphoxide, to afford, though in rather moderate yield in each case, the corresponding 2-phenyl-or 2-p-tolyl-5-substituted thiazolo[4,5-d]pyridazin-4(5H)-ones, instead of the usually expecting 5-mercapto-3(2H)-pyridazinones derivatives. 4-Mercapto-5-benzylamino-2-substituted3(2H)-pyridazinones gave also, in similar reaction conditions, the respective 2-phenyl-6-substituted thiazolo[4,5-d]pyridazin-7(6H)-ones. It might be reasonbly assumed that in these reactions the methylene group of benzylamino substituent on the substrates serves as a carbon unit for cyclisation to the thiazole part of products under an appropriate effect of dimethyl sulphoxide as oxidant.

Interaction of 4-amino- or 4-alkylamino-5-mercapto-3(2H)-pyridazinones with β-diketones(ethyl acetoacetate, benzoylacetone and dimedone) by heating in dimethyl sulphoxide has furnished a convenient synthetic route to 2,3,6-trisubstituted pyridazino[4,5-b][1,4]thiazin-5(6H)-ones.

On treatment of 4-amino-5-mercapto- or 4-mercapto-5-amino-2-substituted 3(2H)-pyridazinones with nitrous acid generated in situ, 5-substituted [1,2,3]thiadiazolo [4,5-d]pyridazin-4(5H)-ones or 6-methyl-[1,2,3]thiadiazolo[4,5-d]pyridazin-7(6H)-one were obtained respectively in fairly good yield. Photochemical irradiation(in acetone, in a stream of nitrogen, with a 100 W h.p. mercury lamp) on these [1,2,3]thiadiazolo [4,5-d]pyridazinone derivatives provided concurrent formations of 2,7-disubstituted pyridazo[4,5-b:4',5'-e][1,4]dithiin-1,6(2H,7H)-dione and 2,8-disubstituted dipyridazo [4,5-b:4',5'-e][1,4]dithiin-1,9(2H,8H)-dione in all cases. An attempted thermolysis of 5-benzyl-[1,2,3]thiadiazolo[4,5-d]pyridazin-4(5H)-one(in tetralin, at ca. 200°C) showed a similar result but a poor yield. A discussion on the mechanism involving counterparts of the thiketo carbene for these reactions is also proposed.