〔J. Heterocyclic Chem., **22**, 161 (1985)〕

3-Alkylthio and 3-Aminopyrazolo〔3, 4-*d*〕pyridazines. Ring Contraction of Pyridazino〔4, 5-*e*〕〔1, 3, 4〕thiadiazines *via* Extrusion of Sulfur.

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Reaction of 5-(1-methylhydrazino)-3(2*H*)-pyridazinone derivative (**1**) with carbone disulfide followed by alkylation yielded 2-alkylthio-4*H*-pyridazino〔4, 5-*e*〕〔1, 3, 4〕thiadiazines (**2**). Oxidative cyclization of 5-(4-substituted 1-methylthiosemicarbazido)-3(2*H*)-pyridazinone derivatives (**4**) with *N*-bromosuccinimde also gave 2-substituted amino-4*H*-pyridazino〔4, 5-*e*〕〔1, 3, 4〕thiadiazines (**5**). Heating of **2** and **5** resulted in ring contraction to afford the corresponding pyrazolo〔3, 4-*d*〕pyridazine derivatives (**6**, **7**) *via* sulfur extrusion. A possible machanism for the desulfurization reaction is discussed, comparing with a structual difference between a type of pyridazino〔4, 5-*e*〕〔1, 3, 4〕thiadiazine (**2**, **5**) and another one (**9**, **11**, **13**, **15**).

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Synthesis of Pyrazolo〔3, 4-*d*〕pyridaznes from 5-(Methylhydrazino)-pyridazines by Means of the Vilsmeier-Haack Reaction.

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Reaction of 2-substituted 5-(1-methylhydrazino)-3(2*H*)-pyridazinones (**2**) with dimethylformamide-phosphorus oxychloride afforded 5-substituted 1, 5-dihydro-1-methyl-4*H*-pyrazolo〔3, 4-*d*〕-pyridazin-4-ones (**3**) in good yields. However, concurrent formation of 5-substituted 2, 5-dihydro-2-(2-substituted 1-chlorovinyl)-4*H*-pyrazolo〔3, 4-*d*〕pyridazin-4-ones (**6**, **12**, **13**) (minor products) and the 1-methyl-4*H*-derivatives (**3**) (major ones) was observed, when starting with the corresponding 2-substituted 5-(2-acyl-1-methylhydrazino)-3(2*H*)-pyridazinones (**5**, **9**, **10**) under similar reaction conditions. A plausible machanism for the reaction is proposed.

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The Structure-Reactivity-Chemoselectivity Relationship on the Reactions of 1-Unsubstituted Tautomeric 2-Pyridones with Benzyne.

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The reactions of 2-pyridones with benzyne were investigated in order to gain some insight into the structure-reactivity-chemoselectivity relationship involved in the tautomeric systems. All reactions examined have resulted in the formation of Diels-Alder and Michael-type adducts. It has been shown that the Diels-Alder reactivities were well correlated with the HOMO energy levels of the 2-pyridone form and the yields of the Michael-type adduct were closely associated with the tautomeric equilibria. In summary, the chemoselectivities of 2-pyridones in the reaction with benzyne were largely affected by the tautomeric properties.