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SYNTHESIS OF THIAZOLO[3,2-b]PYRIDAZINIUM AND THIAZOLO[2,3-a]PHTHALAZINIUM SALTS AND THEIR REACTIONS WITH NUCLEOPHILES

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Thiazolo[3,2-b]pyridazinium salts (1) and thiazolo[2,3-a]phthalazinium salts (2) were synthesized by alkylation of *anhydro*-6-mercaptothiazolo[3,2-b]pyridazinium hydroxides and *anhydro*-6-mercaptothiazolo[2,3-a]phthalazinium hydroxides (3), and also by acid-cyclization of 3-(2-oxoalkylthio)-6-methyl- and 6-phenylpyridazines.

On reaction with sodium hydrosulfide or with sodium salt of ethyl cyanoacetate, 2 afforded 6-thione ylide (3) or 6-(α-cyano-α-ethoxycarbonyl)methylidene ylide through *AE*-mechanism, nucleophilic addition taking place at C_6-position to form thiazole-*N*-imine-type intermediate. On the contrary, pyridazinium salts (1) gave, on reaction with sodium cyanide, 8-cyano-4,7-dihydrothiazolo[3,2-b]pyridazine-7-ones and *anhydro*-7-cyano-5,8-dihydrothiazolo[3,2-b]pyridazinium hydroxides through oxidative substitution mechanism *via* radical intermediates induced by atmospheric oxigen, nucleophilic addition taking place either at C_8 or at C_7-position. On reaction with sodium hydrosulfide or with sodium salts of active methylene compounds, 1 gave in the similar manner *anhydro*-8-mercaptothiazolo[3,2-b]pyridazinium hydroxides or *anhydro*-5,8-dihydro-8-(α,α-disubstituted)methylidenethiazolo[3,2-b]pyridazinium hydroxides, respectively.