6,8-Dimethyl-3-chloropyrimido-[4,5-c]pyridazin-5,7(6H,8H)dione reacts with 2,6-dimethylaniline and 2-methyl-2-propionphenylcarbanion in the presence of sodium methoxide and potassium amide in methanol to give compounds 2a-c and 3a-c, respectively, with yields of 82 and 43% for 2a-c and 3a-c, respectively. Attempts to form products with less acidic nucleophiles led to lower yields, with the most acidic ethyl cyanoacetate leading to the lowest yield of 32%.

No clear dependence between the CH-acidity of the nucleophile and the results of the reaction was observed. Evidently both the possibility of forming the carbanion and its nucleophilicity are important. For example, in the case of malonodinitrile (pK_a 11.2) the yields of compounds 2a and 3a were 82 and 43% respectively, whereas for the less acidic cyanoacetic esters (pK_a ~ 12) the yield did not exceed 32%. Attempts to

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carry out analogous reactions with ethyl acetoacetate, acetylacetone (pKₐ 9.0), and nitromethane (pKₐ 10.2), which form less nucleophilic anions, were not successful: no reaction occurred at all at room temperature while considerable resinification was observed on prolonged heating. However reaction of the pyridazinouracil 1 with nitromethane is possible in liquid ammonia in the presence of potassium amide to give a 79% yield of the 3-nitromethyl derivative 4. Some characteristics of the compounds synthesized are given in Tables 1-3.

Since methyl–methylidene tautomerism is possible for compounds 2 and 4 we also examined the question as to which of the two tautomeric structures, 2 or 2', 4 or 4', was preferred.

In the IR spectra of compounds 2 and 4 the C=O (1645 cm⁻¹) and C=N (2150-2200 cm⁻¹) stretching frequencies are significantly lowered which indicates that they are included in a conjugated chain, which is only possible for the methylidene form 2'. In the same way in the ¹H NMR spectra of compounds 2 and 4 in DMSO-d₆, the signal for a methyne proton is absent, which corresponds to an aromatic structure. In the cases of compounds 2b, 2c, and 4 the chelated forms 2'b,c and 4 apparently exist as indicated by the weak field shift of the NH proton signal (δ 13-14 ppm).

Methyl–methylidene tautomerism is very sensitive to the solvent [5-7]. Compounds 2a and 4 are practically insoluble in chloroform, therefore the ¹H NMR spectrum in CDCl₃ was successfully obtained only for 2b,c. However, as in DMSO-d₆, the signal of the methyne proton was absent, but the signal for the 4-H proton was split into a doublet (J = 1.5-2.3 Hz) by spin-spin interaction with the NH proton. Thus compounds 2b and 2c exist in the methylidene form in chloroform solution as well. The UV spectra of the synthesized compounds confirm this conclusion (Table 2). Compounds 2-4 are brightly colored, the colors of the chelated compounds 2'b,c being noticeably deeper than that of the dicyanomethyl derivative 2'a for which formation of a chelate structure is impossible (the difference in λₘₐₓ for the long wave absorption bands is 65-100 nm). The values of λₘₐₓ for compounds 2b,c in CHCl₃ and DMSO solutions are close to the same. In methanol a hypsochromic shift of the