## Orthoamide, LXV [1]. Kondensationsreaktionen von Amidinen, Guanidinen, Hydrazin und Hydrazin-Derivaten mit Orthoamiden von Alkincarbonsäuren

Orthoamides, LXV [1]. Condensation Reactions of Amidines, Guanidines, Hydrazine and Hydrazine Derivatives with Orthoamides of Alkyne Carboxylic Acids

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The orthoamide derivatives 4 react with amidines 10 and guanidines 11 to give 4-dimethylaminopyrimidines 12. The 3-dimethylamino-pyrazoles 13a - c can be prepared from orthoamides 4 and hydrazine. The hydrazine derivative 14, whose constitution was established by crystal structure analysis, is obtained in low yield when hydrazine is added dropwise to a boiling solution of 4d in THF.

Methyl- and phenylhydrazine, undergo reaction with the orthoamides 4a, c yielding mixtures of the isomeric pyrazoles 19 and 20. The reaction of 4c with acylhydrazines 21a - e affords the pyrazole 13b. The pyrazole 26 is produced in the reaction of 4a and acet-hydrazide according to this scheme, whereas 4a reacts with aromatic acid hydrazides 21c - e to give condensation products, which are presumably amidrazones 28. The 4,5-diaza-octatetraene derivative 30 results from the reaction of 4c with *p*-toluenesulfonylhydrazide. Ketene aminals 34a - c are the products of the reaction of the orthoamides 4b - d with 4,4-dimethylthiosemicarbazide 34, which cyclize on heating to give highmelting pyrazolethiones 35a - c. According to the crystal structure analysis of 35c the compounds have zwitterionic character and are associated *via* hydrogen bridges in the solid state.

Key words: Orthoamides of Alkynecarboxylic Acids, Ketene Aminals,

2,3-Dihydro-pyrazolethiones, Crystal Structure Analysis