The orthoamide derivatives 4 react with amidines 10 and guanidines 11 to give 4-dimethylamino-pyrimidines 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 high-melting 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.