Orthoamides and Iminium Salts, LXXV [1]. Contribution to the Formation of 2-Formyl-1,1,3,3-tetramethylguanidine and the Isomeric 1,1-Dimethyl-3-dimethylaminomethylene-urea

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2-Formyl-1,1,3,3-tetramethylguanidine (1) could be prepared from tris(dimethylamino)ethoxymethane (3a) and formamide (4). Surprisingly, guanidine 1 does not result from the reaction of 1,1,3,3-tetramethylguanidine with formylating reagents such as dimethylamino-methoxy-acetonitrile (8) or the *N*,*N*-dimethylformamide-dimethylsulfate adduct (9), rather the isomeric 1,1-dimethyl-3-dimethylaminomethylene-urea (2) is formed. The structure of 2 was confirmed by NMR spectroscopy and crystal structure analysis.

Key words: Guanidines, Formamide, DMF-DMS Adduct, 1,3-Hydride Shift