

Orthoamide, LXIX [1]. Beiträge zur Synthese N,N,N',N',N'' -peralkylierter Guanidine und N,N,N',N',N'',N'' -persubstituierter Guanidiniumsalze

Orthoamides, LXIX [1]. Contributions to the Synthesis of N,N,N',N',N'' -peralkylated Guanidines and N,N,N',N',N'',N'' -persubstituted Guanidinium Salts

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N,N,N',N' -Tetraalkyl-chloroformamidinium chlorides **6** are prepared from N,N,N',N' -tetraalkylureas **5** and phosgene in acetonitrile. The iminium salts **6** react with primary and secondary amines in the presence of triethylamine to give N,N,N',N',N'' -pentasubstituted and N,N,N',N',N'',N'' -hexasubstituted guanidinium salts **7** and **8**, respectively. Treatment of the guanidinium salts **7** with sodium hydroxide in excess affords the N,N,N',N',N'' -pentasubstituted guanidines **9a–9aa**. Additionally, the N,N,N',N',N'' -pentasubstituted and N,N,N',N',N'',N'' -hexasubstituted guanidinium salts **7l'**, **7p'** and **8a–c** can be obtained from the reaction mixtures by addition of stoichiometric amounts of sodium hydroxide. A modified method is described for the preparation of guanidinium salts possessing dialkylamino substituents consisting of two long-chain alkyl groups ($> C_{14}$). Some guanidines **9** were alkylated with allyl chloride and bromide, ethyl bromide, butyl bromide, benzyl bromide and chloride, dimethyl sulfate, diethyl sulfate, and methyl methanesulfonate to give the corresponding guanidinium salts **11–15**. By alkylation of the N,N,N',N',N'' -pentasubstituted guanidine **9v** with triethylxonium tetrafluoroborate the guanidinium tetrafluoroborate **16a** is accessible. N -Functionalized guanidinium salts **17–18a–c** result from the reaction of N,N,N',N',N'' -pentasubstituted guanidines with ethyl bromoacetate and bromoacetonitrile, respectively, and subsequent anion exchange with sodium tetraphenylborate. N,N,N',N' -Tetramethylguanidine (**21**) adds to ethyl acrylate to give the labile guanidine **22**, which forms the guanidinium salt **23a** on treatment with methyl iodide. Zwitterionic guanidinium salts **25** result, when N,N,N',N',N'' -pentasubstituted guanidines are treated with sultones **24**.

Key words: N,N,N',N' -Tetraalkyl-chloroformamidinium Salts, Alkylation, N,N,N',N',N'' -Pentasubstituted Guanidines, N,N,N',N',N'',N'' -Persubstituted Guanidinium Salts, Crystal Structures, Zwitterionic Guanidinium Salts