

Mechanism of the Reaction of Amines with 5-[(Aryl- or Alkylamino)hydroxymethylene]-2,2-dimethyl-1,3-dioxane-4,6-diones in the Presence of Chlorotrimethylsilane (Me₃SiCl)

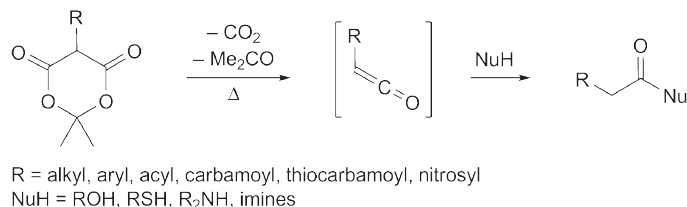
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Addition of chlorotrimethylsilane (Me₃SiCl) to the mixture of a carbamoyl-substituted *Meldrum's* acid, *i.e.*, a 5-[(arylamino)hydroxymethylene]-2,2-dimethyl-1,3-dioxane-4,6-dione of type **1** and a secondary amine as nucleophile strongly accelerated the rate of their reaction. The reason for this phenomenon observed, during our previous research, remained, however, unclear. To elucidate the mechanism of this reaction, we assumed and verified three possible pathways for the action of Me₃SiCl (*cf.* *Scheme 2*): The acceleration of the reaction is caused *i*) by formation of a *O*-trimethylsilylated *Meldrum's* acid of type **2**, *ii*) by the silylated amine **3**, or *iii*) by the presence of HCl liberated from Me₃SiCl. The performed experiments revealed that the faster course of reaction is caused by the formation of *N*-trimethylsilylated amines of type **3**.

Introduction. – *Meldrum's* acid derivatives have a broad scope of application in organic synthesis [1]. The most explored feature of these compounds is the ability to form ketenes in the course of thermal decomposition, which can be trapped with various nucleophiles (*Scheme 1*). Depending on the type of *Meldrum's* substrate, pyrolysis can lead to formation of oxo ketenes [2], carbamoyl ketenes [3], thiocarbamoyl ketenes [4], iminopropadienones [5], or even nitroso ketenes [6]. Practical application of the thus formed ketenes allow the preparation of various useful compounds, as *e.g.*, 3-substituted β -lactams [3][7], isoxazolols [8], pilicides [9], 1,3-oxazinones [10], or derivatives of tetramic acid [11].

Scheme 1



In our laboratory, we have focused on the reactivity and synthetic application of carbamoyl ketenes generated from 5-[hydroxy(aryl- or alkylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones. In contrast to acyl-substituted *Meldrum's* acids, which became the subject of many publications including detailed mechanistic studies [12],