



## Boron difluoride complexes of carbamoyl Meldrum's acids

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### ABSTRACT

5-[Hydroxy(aryl/alkylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones react with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in mild conditions leading to the formation of boron difluoride complexes of carbamoyl Meldrum's acids. The X-ray structure has been obtained for one representative complex. The obtained new compounds are air and moisture stable at standard ambient conditions and easily isolable.

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### 1. Introduction

Acyl derivatives of Meldrum acids have a broad scope of applications in organic synthesis [1]. Their use in organic synthesis is mainly due to the ability to create ketenes in the course of thermal decomposition [2–4]. These ketenes as strongly acylating agents can react with a wide range of nucleophiles and as a result form various useful compounds such as, for example: 3-substituted- $\beta$ -lactams [5,6] isooxazolols [7], pilicides [8], and derivatives of tetramic acid [9]. However, the formation of ketenes is not the only useful reaction of derivatives of Meldrum's acids. The addition of metalorganic species or reduction of the conjugated double bond [10,11], also may take place. The least explored area is action of the Meldrum's acid derivatives as the nucleophilic reagents, only in the case of thiocarbamoyl Meldrum's acid the appropriate anion was used as nucleophilic agent [12] whereas in the case of the oxygene analog none example could be found.

### 2. Results and discussion

Recently we focused on the reactivity of carbamoyl ketenes generated from 5-[hydroxy(aryl/alkylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones **1**. Ketenes formed during thermal decomposition of **1** can acylate amines [13], alcohols and thiols [14] leading to the formation of malonamide derivatives, but, more

importantly, during our previous researches we observed that these ketenes can undergo cycloaddition to aldimines to form 3-carbamoyl- $\beta$ -lactams in the modified Staudinger reaction. The initial success in the field of synthesis of  $\beta$ -lactams encouraged us to try to develop a method of synthesis 4-unsubstituted-3-carbamoyl- $\beta$ -lactams. Preparation 4-unsubstituted- $\beta$ -lactams in the typical or modified Staudinger reaction carries difficulties associated with unstability of monomeric formaldehyde aldimines or necessity to use surrogates of formyl aldimines. In order to obtain 4-unsubstituted- $\beta$ -lactams we performed several unsuccessful experiments with ketenes generated from **1** and surrogates of formaldehyde aldimines described in literature, such as: dithiocarbamates [15], formaldehyde N,N-dialkylhydrazones [16], and glyoxal imines [17]. Eventually we ran a reaction of 1 equiv. of **1** in boiling toluene with 2 equiv. of N-methylene-tert-butylamine as a one of most stable formaldehyde aldimines. To ensure depolymerisation of imine we added 6 equiv. of boron trifluoride etherate as a well known agent for depolymerisation of hexahydro-1,3,5-triazines [18]. From the reaction mixture, beside a large amount of tar, we isolated a small amount of a new compound with the  $^1\text{H}$  NMR spectra almost identical with that of the starting material except for the lack of acidic proton; on the other hand TLC chromatography also showed that the new compound is not as acidic as 5-[hydroxy(aryl/alkylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones. A similar experiment conducted with HCl or  $\text{SnCl}_4$  instead of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  did not result in the formation of the new compound. Moreover, other experiments carried out between **1** and tripyrolidine in the presence of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in boiling toluene also demonstrated the formation of the same new compound (entry 1, Table 1). These aforementioned experiments strongly indicate that **1** and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  are necessary for formation of

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