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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 $BF_3{\cdot}Et_2O$ 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.

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-β-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 metaloorganic 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 find.

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-b-lactams in the modified Staudinger reaction. The initial success in the field of synthesis of β-lactams encouraged us to try to develop a method of synthesis 4-unsubstituted-3-carbamoyl-β-lactams. Preparation 4-unsubstituted-β-lactams in the typical or modified Staudinger reaction carries difficulties associated with unstability of monomeric formaldehyde aldimines or necessity to use surogates of formyl aldimines. In order to obtain 4-unsubstituted-β-lactams we performed several unsuccessful experiments with ketenes generated from 1 and surogates 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 depolimerisation of imine we added 6 equiv. of boron trifluoride etherate as a well known agent for depolimerisation 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 ^1H 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 $SnCl_4$ instead of $BF_3{\cdot}Et_2O$ did not result in the formation of the new compound. Moreover, other experiments carried out between **1** and tripyrolidine in the presence of $BF_3{\cdot}Et_2O$ in boiling toluene also demonstrated the formation of the same new compound (entry 1, Table 1). These aforementioned experiments strongly indicate that **1** and $BF_3{\cdot}Et_2O$ are necessary for formation of

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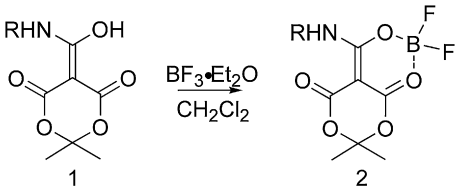
Table 1
Synthesis of boron difluoride complexes of carbamoyl Meldrum's acids.



.

Entry	1,2	R	Time (h)	Yield (%)
1[a]	a	Ph	4	27
2[b]	a	Ph	5	62
3	a	Ph	3	60
4[c]	a	Ph	4	15
5[d]	a	Ph	3.5	15
6[b]	b	3-ClC_6H_4	5	71
7	b	3-ClC_6H_4	3.5	45
8[e]	b	3-ClC_6H_4	4.5	66
9	c	Et	3	43
10[e]	c	Et	3	56
11	d	Cyclo-hexyl	2.5	36
12[e]	d	Cyclo-hexyl	2.5	79
13	e	Naphtyl	5	48
14[e]	e	Naphtyl	5	63
15	f	4-$NO_2C_6H_4$	4	14
16[e]	f	4-$NO_2C_6H_4$	4.5	55

[a] 0.33 equiv. of tripyrolidine was used, and toluene as a solvent.
[b] 2 equiv. of N-methylene-tert-butylamine was used.
[c] 3 equiv. of $HBF_4{\cdot}Et_2O$ was used.
[d] 6 equiv. of $HBF_4{\cdot}Et_2O$ was used.
[e] 2 equiv. of triethylamine was used.

the new compound. Structure elucidation with ^1H, ^{13}C and elemental analysis strongly suggested that the new formed compound might be a 5-[difluoroboroxy(phenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione **2a**. Which should be considered as a carbamoyl Meldrum's acid difluoroboric acid mixed anhydride.

Fortunately **2a** gave crystals suitable for X-ray crystallography. X-ray date has confirmed our previous suppositions, the acidic proton of the **2a** is replaced with BF_2 moiety which also coordinates to the adjacent carbonyl oxygen (Fig. 1).

To the best of our knowledge such a derivative of Meldrum's acids was not described up to now in chemical literature.

At this point we decided to check whether it is possible to increase the yield of **2** and whether the observed process is a general phenomenon or limited only to this model of reactants. At the beginning we decreased the temperature of the process as the observed reaction should not require as a high temperature as decomposition of Meldrum's acid derivative to ketene. We also anticipate that in boiling toluene part of the initially formed **2** may subsequently decompose to an ketene. Therefore, we performed two experiments in boiling dichloromethane using **1a** and **1b** as starting materials and leaving all other parameters of the reaction unchanged. After the disappearance of the starting material, which takes 3.5 h from the reaction mixtures, we isolated anhydrides **2a** and **2b** with high yield (entries 2 and 6, Table 1). We also ran the reaction of **1a** with 6 equiv. of $BF_3{\cdot}Et_2O$ in boiling DCE; however, as in the case of toluene we observed the formation of a large amount of byproducts.

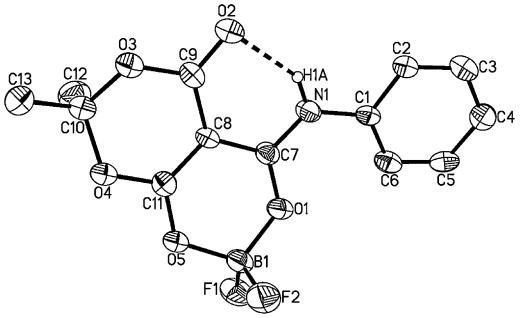


Fig. 1. X-ray crystal structure representation of the complex **2a** [22].

In subsequent studies we carried out a two series of reactions: first where **1a–f** were heated in boiling DCM only in the presence of 6 equiv. of $BF_3{\cdot}Et_2O$ (entries 3, 7, 9, 11, 13 and 15, Table 1) and the second series where **1a–f** were heated in boiling DCM with 6 equiv. of $BF_3{\cdot}Et_2O$ in the presence of 2 equiv. of triethyl amine (entries 8, 10, 12, 14 and 16, Table 1). In the case of the reactions carried out in the presence of tertiary amine yields of the **2** were even two to four fold higher that in the reaction without base. This fact clearly demonstrates that formation of anionic form of the carbamoyl Meldrum's acid strongly facilitates ligand substitution on the boron atom. Additionally we run the reaction of **1a** with in the strongly acidic solution of HBF4 in diethyl ether but in this case we observed formation only a small amount of **2a** (entries 4 and 5, Table 1).

The last aspect we decided to test was the problem if other acyl derivative of Meldrum's acid are also able to react in such a way and form chelates with boron trifluoride. We ran two reactions of 5-[hydroxy(phenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones with 6 equiv. of $BF_3{\cdot}Et_2O$, first was performed in boiling DCM and the second at room temperature.

In both cases the reaction led to consumption of the starting material what took respectively 5 and 24 h, and in both cases we isolated only acetophenone as the main product. We already observed that decomposition to ketene catalysed by acid is faster for usual acyl Meldrum's acids than in the case of carbamoyl derivatives; however it is surprising that even at room temperature this reaction path is overwhelming.

From the other hand, selective ability of carbamoyl Meldrum's acids for formation of difluoroboron complexes might be explained taking into account the presence of nitrogen atom with the lone electron pair at the end of the conjugated system which is capable for stabilizing such a complex.

In summary, the obtained difluoroboron complexes of carbamoyl Meldrum's can be considered as far analogies to difluoroboron complexes of 1,4-dihydro-4-oxoquinoline-3-carboxylic acid [19].

3. Conclusion

A new reaction of 5-[hydroxy(aryl/alkylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones **1** with $BF_3{\cdot}Et_2O$ in the presence of tertiary amine is reported. We obtain carbamoyl Meldrum's acid difluoroboric acid mixed anhydrides in mild conditions with high yield. The new product **2** is easily isolable and stable at room temperature.

4. Experimental

4.1. General experimental procedures

Reagents were purchased from Sigma–Aldrich. Toluene were distilled from potassium under argon. Dichloromethane and 1,2-dichloroethane was distilled from K_2CO_3 Analytical TLC was performed on aluminium sheets of silica gel UV-254 Merck. Flash chromatography was performed using 40–63 μm of Zeochem silica gel and with aluminium oxide neutral Grade I POCH. The 1H, 13C were recorded on Varian Gemini 200 and Varian Unity Plus 500, chemical shifts (δ) in ppm rel. to internal Me4Si; coupling constants J in Hz. Elemental analysis were performed on Vario El

Cube CHNS Elementar. High-resolution (HRMS) was recorded on MicroMas Quattro LCT mass spectrometer. Melting points were determined with Warsztat Elektromechaniczny W-wa apparatus and are not corrected. Commercially unavailable reagents were prepared using literature procedures as follows: 5-[hydroxy(phenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**1a**) [20], 5-{[hydroxy(3-chlorophenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**1b**) [6], 5-[Hydroxy(ethylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**1c**) [6], 5-[Hydroxy(cyclohexylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**1d**) [6], N-methylene-tert-butylamine [21].

4.2. Syntheses of carbamoylo Meldrums's acids (*1e–f*)

5-[Hydroxy(1-naphthylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**1e**). Following the typical literature procedure [6,20] for **1a–b** using Meldrum's acid (0.72 g, 5 mmol) anhyd. DMF (5 ml) Et_3N (1.4 ml, 10 mmol); naphtylisocyanate (0.845 g, 5 mmol,) yield 1.345 g (86%); Mp 119–120 °C. ^{1}H NMR (200 MHz, CDCl3): δ = 1.82 (s, 6 H), 7.48–7.62 (m, 3 H), 7.63–8.00 (m, 4 H), 11.60 (brs, 1 H), 13.62 (brs, 1 H). ^{13}C NMR (50 MHz, CDCl3): δ = 26.9, 74.3, 105.7, 121.7, 122.2, 125.8, 127.2, 127.7, 128.2, 128.7, 129.2, 130.4, 134.6, 165.1, 168.4, 171.2. HRMS (ESI-): *m/z* [M−H] calcd for $C_{13}H_{11}N_2O_7$: 307.0566; found: 307.0563.

5-[Hydroxy(4-nitrophenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**1f**). Following the typical literature procedure [6,20] for **1a–b** using Meldrum's acid (0.72 g, 5 mmol) anhyd. DMF (5 ml) Et_3N (1.4 ml, 10 mmol); p-nitro-phenylisocyanate (0.820 g, 5 mmol,) yield 1.243 g (80%); crystallized from CH_2Cl_2, mp 210–215 °C dec. ^{1}H NMR (500 MHz, CDCl3): δ = 1.78 (s, 6 H), 7.67 (d, J = 9.1 Hz, 2 H), 8.27 (d, J = 9.1 Hz, 2 H), 11.45 (brs, 1 H), 16.50 (brs, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.5, 74.9, 106.2, 121.8, 125.3, 141.1, 145.2, 164.3, 170.0, 171.6. HRMS (ESI-): *m/z* [M−H] calcd for $C_{17}H_{14}NO_5$: 312.0872; found: 312.0877.

4.3. Syntheses of 5-[Difluoroboroxy(aryl/alkylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones (*2a–f*)

4.3.1. General procedure

To a solution of **1** (1 mmol) in anhd. CH_2Cl_2 15 ml, 6 mmol $BF_3{\cdot}Et_2O$ was added, triethyl amine or N-methylene-*tert*-butylamine (2 mmol) was added if specified in Table 1. The resulting mixture was stirred and heated to reflux for the time specified in Table 1. After disappearance of starting material, reaction mixture was washed with sat. aq $NaHCO_3$ (5 ml) and if amine was added with 2 M aq HCl (5 ml). The organic solution was dried with $MgSO_4$, filtered and solvents was removed under reduced pressure, and the residue was purified as follow:

5-[Difluoroboroxy(phenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**2a**). Purification by flash column chromatography on silica gel (EtOAc-toluene, 1:7); mp 139–142 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.88 (s, 12 H), 7.28–7.54 (m, 10 H), 10.99 (s, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.4, 74.9, 109.6, 123.1, 128.2, 130.0, 134.0, 162.1, 164.4, 172.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ = −143.72. Anal. Calcd for $C_{13}H_{12}BF_2NO_5$: C, 50.20; H, 3.89; N, 4.50; Found: C, 49.89; H, 3.95; N, 4.59.

5-[Difluoroboroxy(3-chlorophenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**2b**). Purification by flash column chromatography on neutral aluminium oxide (EtOAc-toluene, 1:5); mp 136–139 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.87 (s, 12 H), 7.26–7.37 (m, 6 H), 7.40 (s, 2 H), 11.02 (brs, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.5, 75.0, 109.9, 121.3, 123.3, 128.3, 131.0, 135.0, 135.7, 162.0, 164.8, 171.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ = −143.40. Anal. Calcd for $C_{13}H_{11}BClF_2NO_5$: C, 45.19; H, 3.21; N, 4.05; Found: C, 45.18; H, 3.26; N, 4.04.

5-[Difluoroboroxy(ethylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**2c**). Purification by flash column chromatography on neutral aluminium oxide (EtOAc-toluene, 1:5); mp 145–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.3 Hz, 6 H), 1.81 (s, 12 H), 3.55–3.61 (m, 4 H), 9.13 (brs, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.6, 26.4, 36.7, 74.8, 109.2, 161.9, 165.9, 171.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ = −144.62. Anal. Calcd for $C_9H_{12}BF_2NO_5$: C, 41.10; H, 4.60; N, 5.33; Found: C, 39.67; H, 5.26; N, 5.73.

5-[Difluoroboroxy(cyclohexylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**2d**). Purification by flash column chromatography on neutral aluminium oxide (EtOAc-toluene, 1:5); mp 137–140 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.34–1.42 (m, 12 H), 1.62–1.75 (m, 4 H), 1.81 (s, 12 H), 1.96–2,01 (m, 4 H), 3.91–4.09 (m, 2 H), 9.12 (brs, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.7, 25.5, 26.4, 32.7, 51.0, 74.3, 109.2, 161.9, 164.5, 171.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ = −144.67. Anal. Calcd for $C_{13}H_{18}BF_2NO_5$: C, 49.24; H, 5.72; N, 4.42; Found: C, 49.37; H, 5.84; N, 4.66.

5-[Difluoroboroxy(naphtylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**2e**). Purification by flash column chromatography on neutral aluminium oxide (EtOAc-toluene, 1:5); mp 248–251 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.90 (s, 12 H), 7.49–7.60 (m, 6 H), 7.63–7.95 (m, 6 H), 11.43 (brs, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.5, 75.3, 109.8, 121.0, 122.9, 125.9, 127.2, 127.4, 128.2, 128.9, 129.1, 129.4, 134.4, 162.5, 165.5, 171.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ = −143.77. Anal. Calcd for $C_{17}H_{14}BF_2NO_5$: C, 56.54; H, 3.91; N, 3.88; Found: C, 56.55; H, 3.96; N, 3.92.

5-[Difluoroboroxy(4-nitrophenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**2f**). Purification by flash column chromatography on neutral aluminium oxide (EtOAc-toluene, 1:7); mp 154–156 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.89 (s, 12 H), 7.69–7.74 (d, *J* = 9.1 Hz, 4 H), 8.30–8.35 (d, *J* = 9.1 Hz, 4 H), 11.32 (brs, 2 H). ^{13}C NMR (50 MHz, acetone-d_6): δ 26.1, 76.3, 111.1, 125.3, 126.1, 141.0, 147.4, 162.2, 166.8, 173.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ = −142.77. Anal. Calcd for $C_{13}H_{11}BF_2N_2O_7$: C, 43.85; H, 3.11; N, 7.87; Found: C, 44.15; H, 3.07; N, 8.16.

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[22] X-ray crystal data for **2a**: $C_{13}H_{12}BF_2NO_5$, $M = 311.05$, monoclinic, space group $P2_1/c$, $a = 15.5284(2)$, $b = 5.547(8)$, $c = 16.278(3)$ Å, $\beta = 99.190(15)^\circ$, $V = 1362.6(3)$ Å^3, $T = 298(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.132 mm^{-1}, Dc = 1.516 g cm^{-3}, 4714 reflections measured, 2645 unique ($R_{int} = 0.0695$), 880 observed [$I > 2\sigma(I)$]. The final R_1 and $wR_2(F^2)$ were 0.0588 [$I > 2\sigma(I)$] and 0.1197, respectively. Further details of the X-ray structure can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC 87 0688).