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An Easy Access to Hydrazinocarbonyl Carbamic Acid Ethyl Esters

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Summary. The reaction of carboisocyanatidic acid ethyl ester with hydrazines and 3,5-dioxo-1,2,4-triazolidine is reported. The thermal cyclization of the products to 1-substituted 3,5-dioxo-1,2,4-triazolidines and to [1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,3,5,7-tetraone was investigated.

Keywords. Hydrazinocarbonyl carbamic acid ethyl esters; 3,5-Dioxo-1,2,4-triazolidine; [1,2,4]Triazolo[1,2-*a*][1,2,4]triazole-1,3,5,7-tetraone.

Eine einfache Darstellung von Hydrazinocarbonyl-carbaminsäureethylestern

Zusammenfassung. Die Reaktion von Ethoxycarbonylisocyanat mit Hydrazinen und 3,5-Dioxo-1,2,4-triazolidin und die thermische Zyklisierung dieser Produkte unter Bildung von 1-substituierten 3,5-Dioxo-1,2,4-triazolidinen und [1,2,4-]Triazolo[1,2-*a*][1,2,4]triazolo-1,3,5,7-tetraon wurde untersucht.

Introduction

The thermal cyclization of 1-phenyl-4-carbethoxysemicarbazide has been shown to result in the formation of 1-phenyl-1,2,4-triazolidine-3,5-dione [1]. The nucleophilic addition of *Lewis* bases with carboisocyanatidic acid ethyl ester (**1**) is well known since 1908 [2]. However, the reaction of **1** with hydrazines has not been investigated until now. Comparable reactions of hydrazine carboxylic acid ethyl ester with **1** [3] and of carboisocyanatidic acid phenyl ester with hydrazine compounds [4] have already been described. In this paper, the preparation of substituted semicarbazides from carboisocyanatidic acid ethyl ester and hydrazine compounds as well as the thermal reactions of these compounds are described.

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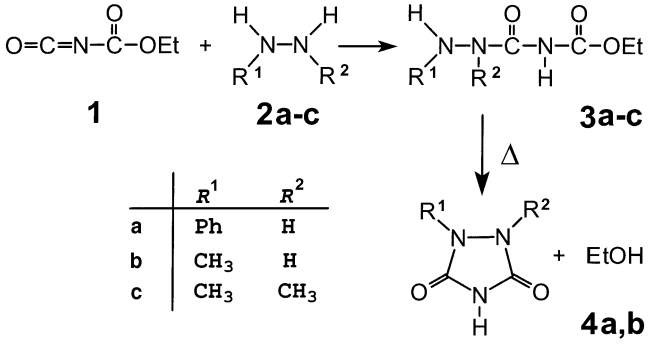
Results and Discussion

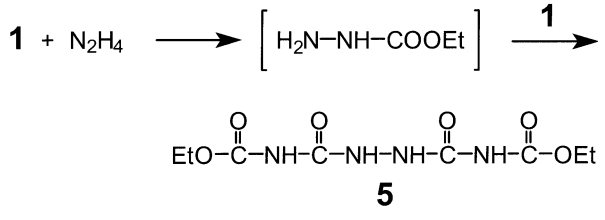
We found that treatment of **1** with substituted hydrazines **2a–c** leads to the corresponding hydrazinocabonyl carbamic acid ethyl esters **3a–c** in high yields.

The thermal cyclization of **3a** and **3b** affords the triazolidines **4a**,**b** which could be obtained by direct reaction of **1** and the corresponding hydrazines. The ^{1}H NMR spectra of **3b** and comparison of the IR spectra of **3a** and **3b** confirm the structure of **3b**. Attempts to cyclize **3c** to 3,5-dioxo-1,2-dimethyl-1,2,4-triazolidine failed. Thermal analysis of **3c** indicates complete decomposition starting at 121°C without formation of 3,5-dioxo-1,2-dimethyl-1,2,4-triazolidine.



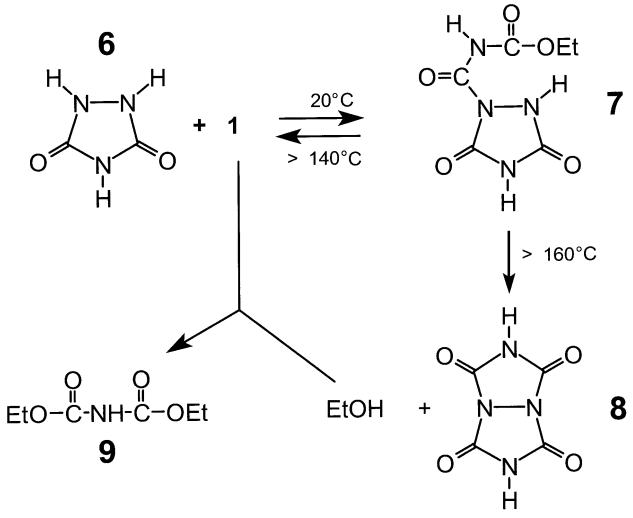
	R^1	R^2
a	Ph	H
b	CH_3	H
c	CH_3	CH_3

In the reaction of **1** with hydrazine hydrochloride, the formation of hydrazine-N,N′-di-(carboxylic acid carbamic acid ethyl ester) (**5**) is observed. Therefore, the addition of **1** to the intermediate hydrazinocarbonyl carbamic acid ethyl ester is preferred over the addition of the almost insoluble hydrazine hydrochloride.



In former work we have described the multistage preparation of [1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,3,5,7-tetraone **8** [5]. In the reaction of 1,2,4-triazole-3,5-dione (**6**) with **1**, a quantitative yield of (3,5-dioxo[1,2,4]triazolidine-1-carbonyl)-carbamic acid ethyl ester (**7**) is obtained. Cyclization of **7** at 160°C affords **8** with 35% yield only. In the starting period of the reaction, a precipitation of **6** could be observed at 140°C. This can be explained by the reverse reaction of **7** to **6** and **1** at temperatures above 140°C, followed by the reaction of ethanol and **1** to imidodicarbonic acid diethyl ester (**9**) [1]. Due to this behaviour, **8** could be prepared in 85% yield if the resulting ethanol was trapped with tetrachlorosilane to prevent the formation of **9**. In an analogous manner, 3,5-dioxo-1,2,4-triazolidine (**6**) was be prepared in 75% yield by treatment of equimolar amounts of **1** and

hydrazine hydrochloride in the presence of tetrachlorosilane.



Experimental

IR: Perkin-Elmer 882; ^{1}H and ^{13}C NMR (*DMSO*-d_6, *TMS*): Bruker MSL 300; MS: Carlo-Erba QDM-1000 (70 eV); melting points: Mettler FP61 (capillary); decomposition point onset: Perkin-Elmer TGA7 (scan rate: 2°C/min, purge gas: N_2(2 l/h), sample weight; 10 mg). The elemental analyses (C,H,N) compared with the calculated values. Carboisocyanatidic acid ethyl ester (**1**) was prepared according to Ref. [6].

(3-Phenyl-hydrazinocarbonyl)-carbamic acid ethyl ester (**3a**; $C_{10}H_{13}N_3O_3$)

To a stirred solution of 8.0 g (74 mmol) phenylhydrazine in 40 ml *THF*, a solution of 8.5 g (74 mmol) **1** in 30 ml *THF* was added dropwise at 20°C. The mixture was refluxed for 2 h. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to yield 14.1 g (85%) white crystals.

Decomp. (loss of EtOH): 172°C (Ref. [1]: 176°C); IR (KBr): ν(N–H) = 3274, 3244 cm^{-1}, ν(C=O) = 1718, 1696 cm^{-1}; ^{1}H NMR: δ = 10.25 (s, 1H, NH), 9.18 (s, NH), 7.81 (s, 1H, NH), 7.22–6.73 (m, 5H, phenyl), 4.19 (q, 2H, CH_2), 1.27 (t, 3H, CH_3) ppm; ^{13}C NMR: δ = 153.8, 149.5, 129.1, 119.06, 112.36, 61.81, 14.5 ppm; MS: *m/z* (%) = 223 (12, M^+), 177(23), 134(13), 105(35), 91(19), 17(100), 70(56), 51(35), 44(32), 29(93).

(3-Methyl-hydrazinocarbonyl)-carbamic acid ethyl ester (**3b**; $C_5H_{11}N_3O_3$)

To a stirred solution of 3.7 g (80 mmol) methylhydrazine in 50 ml *THF*, a solution of 9.2 g (80 mmol) **1** in 100 ml *THF* was added dropwise at 0°C. The mixture was refluxed for 2 h and filtered hot to remove approx. 4 g of **4b**. The *THF* solution was concentrated to 40 ml, cooled, and filtered. The white product was recrystallized from ethanol to yield 6.4 g (49%) white crystals.

Decomp. (loss of EtOH): 139°C; IR (KBr): ν(N–H) = 3288, 3241 cm^{-1}, ν(C=O) = 1718, 1696 cm^{-1}; ^{1}H NMR: δ = 10.1 (s, 1H, NH), 8.77 (s, 1H, NH), 4.8 (s, 1H, NH), 4.13 (q, 2H, CH_2-ethyl), 2.49 (s, 3H, N–CH_3), 1.23 (t, 3H, CH_3-ethyl) ppm; ^{13}C NMR: δ = 155.33, 154.63, 61.62, 38.7, 14.49 ppm; MS: *m/z* (%) = 161 (13, M^+), 115(46), 90(40), 72(26), 62(68), 46(92), 29(100).

(2,3-Dimethyl-hydrazinocarbonyl)-carbamic acid ethyl ester (**3b**; $C_6H_{13}N_3O_3$)

To a stirred solution of 4.3 g (72 mmol) N,N′-dimethylhydrazine in 80 ml *THF*, a solution of 8.25 g (72 mmol) **1** in 50 ml *THF* was added dropwise at 0°C. The mixture was stirred for 2 h at 20°C. The solvent was removed under reduced pressure, and the residue was recrystallized from heptane to yield 11.2 g (89%) white crystals.

M.p.: 76.1°C; decomp.: 121°C; IR (KBr): ν(N–H) = 3287 cm^{-1}, ν(C=O) = 1719, 1707 cm^{-1}; ^1H NMR: δ = 9.95 (s, 1H, NH), 8.54 (s, 1H, NH), 4.13 (q, 2H, CH_2-ethyl), 2.45 (s, 6H, 2xN–CH_3), 1.23 (t, 3H, CH_3-ethyl) ppm; ^{13}C NMR: δ = 151.51, 151.3, 61.54, 47.6, 47.0, 14.46 ppm; MS: *m/z* (%) = 175 (25, M^+), 133(48), 105(17), 86(28), 59(100), 43(64), 29(68).

3,5-Dioxo-1-phenyl-1,2,4-triazolidine (**4a**, $C_8H_7N_3O_2$)

To a stirred solution of 6.6 g (61 mmol) phenylhydrazine in 30 ml diglyme, 7.0 g **1** (61 mmol) in 20 ml diglyme were added dropwise, and the mixture was refluxed for 2 h. To the cooled solution, 100 ml heptane was added. The precipitate was filtered and recrystallized from ethanol to yield 8.2 g (76%) white flakes; m.p.: 269°C (Ref. [7]: 269°C).

3,5-Dioxo-1-methyl-1,2,4-triazolidine (**4b**, $C_3H_5N_3O_2$)

To a stirred solution of 2.0 g (43.5 mmol) methylhydrazine in 30 ml diglyme, a solution of 5.0 g (43.5 mmol) **1** in 20 ml diglyme was added dropwise at 0°C. The mixture was refluxed for 4 h, cooled, filtered, and recrystallized from water to yield 3.9 g (78%) white crystals; m.p.: 242°C (Ref. [4]: 243°C).

3,5-Dioxo-[1,2,4]triazolidine-1-carbonyl-carbamic acid ethyl ester (**7**; $C_6H_8N_4O_5$)

To a stirred solution of 5.05 g (50 mmol) **6** in 40 ml *THF*, a solution of 5.75 g (50 mmol) **1** in 50 ml *THF* was added dropwise at 20°C. The mixture was refluxed for 4 h, the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to yield 10.2 g (94%) white crystals.

Decomp.: 156°C; IR (KBr): ν(N–H) = 3220 cm^{-1}, ν(C=O) = 1800, 1755, 1700 cm^{-1}; ^1H NMR: δ = 10.05 (s, 1H, NH), 8.54 (s, 1H, NH), 4.20 (q, 2H, CH_2-ethyl), 1.27 (t, 3H, CH_3-ethyl) ppm; ^{13}C NMR: δ = 151.57, 151.45, 149.90, 143.25, 62.26, 14.32 ppm.

Hydrazine-N,N′-di(carboxylic acid carbamic acid ethyl ester) (**5**; $C_8H_{14}N_4O_6$)

7.0 g (0.103 mol) hydrazine hydrochloride and 11.5 g (0.1 mol) **1** in 50 ml toluene were refluxed for 5 h. The mixture was cooled and filtered. The white precipitate was washed with acetone to remove toluene and twice with 50 ml water to yield 12.5 g (95%) white powder.

Decomp.: 203°C; IR (KBr): ν(N–H) = 3322 cm^{-1}, ν(C=O) = 1722 (sh) 1714, 1698 cm^{-1}; ^1H NMR: δ = 10.39 (s, 2H, 2xNH), 9.21 (s, 2H, 2xNH), 4.18 (q, 4H, 2xCH_2), 1.26 (t, 6H, 2xCH_3) ppm; ^{13}C NMR: δ = 154.2, 153.17, 61.93, 14.49 ppm.

[1,2,4]Triazolo[1,2-a][1,2,4]triazole-1,3,5,7-tetraone (**8**)

6.1 g (60 mmol) 3,5-dioxo-1,2,4-triazolidine, 6.95 g (60 mmol) **1**, and 4 g (23.5 mmol) $SiCl_4$ were refluxed in 50 ml diglyme for 6 h. The solution was cooled to 0°C, and the precipitate was filtered and washed with dichloromethane to yield 8.5 g (85%) white crystals; m.p.: 341°C (Ref. [5]: 340°C).

3,5-Dioxo-1,2,4-triazolidine (**6**)

A mixture of 9.5 g **1** (82 mmol), 6 g (87.6 mmol) hydrazine hydrochlorid, and 5 g (29 mmol) $SiCl_4$ in 90 ml diglyme was refluxed for 20 h. The solvent was removed under reduced pressure, and the residue was recrystallized from water to yield 6.1 g (75.5%) white needles; m.p.: 251°C (Ref. [8]: 250°C).

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