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THE PREPARATION OF N^1-ALKOXYCARBONYL-N^2-(METHYLTHIO)THIOCARBONYL-GUANIDINES VIA Δ^4-1,2,4-THIADIAZOLINE DERIVATIVES[1)]

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The reaction of potassium methyl cyanoiminodithiocarbonate (1) with N-chlorocarbamates (2) gave 2-alkoxycarbonyl-3-imino-5-methylthio-Δ^4-1,2,4-thiadiazolines (3). The reduction of (3) with hydrogen sulfide gave N^1-alkoxycarbonyl-N^2-(methylthio)thiocarbonylguanidines (4) quantitatively.

In our previous work,[2-5)] it was found that Δ^4-1,2,4-thiadiazolines (TDZ) could easily be prepared by the reaction of N-chloroamidino compounds with (1) and potassium alkoxythiocarbonylcyanamide and that TDZ was readily cleft at the N-S link by reduction with hydrogen sulfide and recyclized to s-triazines.

In this communication, we wish to report the preparation of new TDZ (3) from N-chlorocarbamates (2) and (1) together with a novel method for preparation of N^1-alkoxycarbonyl-N^2-(methylthio)thiocarbonylguanidines (4) via (3) as shown in the scheme. The compound (4) is an entirely new type of guanidine derivatives and would be useful starting material for organic synthesis.

3-Imino-2-methoxycarbonyl-5-methylthio-Δ^4-1,2,4-thiadiazoline (3a) was prepared by the following procedure. To a stirred suspension of (1) (50 mmol) in dichloromethane (45 ml) was gradually added dropwise a solution of methyl N-chlorocarbamate[6)] (2a), 50 mmol) in dichloromethane (10 ml). The temperature was maintained below 10°C during the reaction. After stirring 1 h, the reaction mixture was mixed with water (20 ml). After the insoluble material[7)] (5a, 4.68 g) had been filtered off, the organic layer of the filtrate was separated, and then was evaporated under reduced pressure. The residual oily material was combined with (5a) and was dissolved in methanol (100 ml) and 2N hydrochloric acid (15 ml). After stirring the solution for 1 h at room temperature, the solution was neutralized with 2N sodium hydroxide. TDZ (3a) was precipitated by evaporating methanol (7.2 g, 70%).

Recrystallization from aq. methanol gave pure (3a).

N^1-Methoxycarbonyl-N^2-(methylthio)thiocarbonylguanidine (4a) was prepared quantitatively by the reduction of (3a) with hydrogen sulfide. Hydrogen sulfide was passed through a solution of (3a) (3 mmol) in methanol (15 ml). The solution was left at room temperature for several minutes. The precipitated sulfur was removed by filtration, and then the filtrate was evaporated to dryness. The recrystallization of the residual material from aq. methanol gave pure (4a). The structures of (3a) and (4a) were confirmed by elemental analyses and various spectral data as shown in Table 1.

In a similar manner as described above, the corresponding TDZ and guanidine, (3b) and (4b), were prepared from ethyl N-chlorocarbamate (2b).

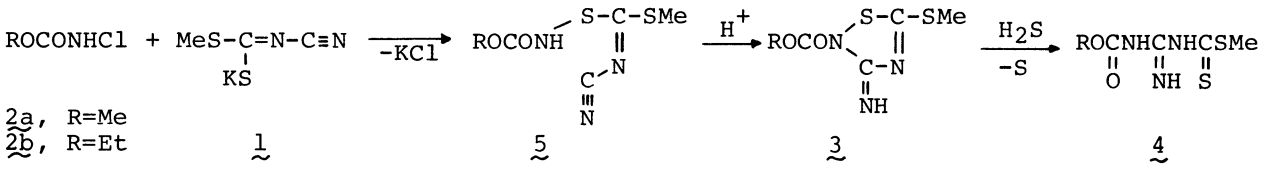

Table 1. Preparation of (3) and (4)

Compd	R	Yield (%)	Mp (°C)	IR (cm^{-1}) ν C=O	NMR[a] (δ ppm) R	MeS	NH	MS (m/e)
3a	Me	70	116-118	1760	3.80(s)	2.67(s)	8.93(s)	205(M^+)
3b	Et	53	82-84	1750	1.33(t),4.30(q)	2.70(s)	8.58(s)	219(M^+)
4a	Me	98	128-129	1700 1740	3.80(s)	2.50(s)	8.7-9.6[b]	207(M^+)
4b	Et	95	98	1740	1.33(t),4.30(q)	2.53(s)	8.8[b]	221(M^+)

[a] Measured in $CDCl_3$. [b] 3H, broad.

References and Notes

1) Organic N-Halogenocompounds. Part 13.
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5) T. Fuchigami, T. Nonaka, and K. Odo, Bull. Chem. Soc. Jpn, 49, 3170 (1976).
6) Methyl N-chlorocarbamate was prepared according to the method of Lessard et al. C. Bachand, H. Driguez, J. M. Paton, D. Touchard, and J. Lessard, J. Org. Chem., 39, 3136 (1974).
7) It showed a strong absorption of a nitrile group at 2200 cm^{-1} in the IR spectrum. MS, m/e 205 (M^+).

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