

## Synthetical Application of Alkyl 2-isothiocyanatocarboxylates. A Simple Synthesis of 5-Substituted-3-amino-2-thioxo-4-imidazolidinones (3-Amino-2-thiohydantoins)

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**Abstract:** The title 3-amino-2-thiohydantoins **3** has been prepared in very good yields by the reaction of alkyl isothiocyanatocarboxylates **1** with hydrazine hydrate. The synthesis of starting isothiocyanates as well as spectral data of 3-aminothiohydantoins and alkyl isothiocyanatocarboxylates has been presented.

**Keywords:** thiohydantoin, isothiocyanate, thiosemicarbazide, agrochemicals.

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### Introduction

In the last twenty years, much interest has been focused on the synthesis of N-aminoheterocycles, since this class of compounds has interesting biological properties. Numerous heterocyclic compounds having a thiourea or a thiosemicarbazide moiety have been found to be active as agrochemicals [1-3]. As a part of our research in the synthesis of novel heterocycles derived from  $\alpha$ -aminoacids we have found a very simple way leading to the 3-aminothiohydantoins.

The title compounds of the general formula **3** are novel, except for **3b** (R=H), which has been pos-



ether) failed. Compound **3c** crystallized with difficulties and a prolonged standing upon crystallization from ethanol-diethyl ether was necessary.

The physicochemical data 3-aminothiohydantoins **3** are summarized in the Table 2 and Table 3. Structural assignment of isothiocyanates **1** and 3-aminothiohydantoins **3** is based on spectroscopic data (IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, mass spectrometry ) (Tables 1-3).

In summary, we have synthesized in novel and facile way 3-aminothiohydantoins **3** and a new isothiocyanate **1d**.

## Experimental

Hydrazine hydrate, thiophosgene, glycine, L- $\alpha$ -alanine, DL-tert-leucine, L-aspartic acid, L-glutamic acid, DL-phenylglycine, DL-phenylalanine, L-tyrosine were purchased from Fluka. Solvents were purified, dried and distilled. Melting points (uncorrected) were determined on a Boetius hot plate. Chromatography: TLC: Silica gel 60 F<sub>254</sub> (Merck). Column chromatography: Silica gel 60, mesh size 0.04 - 0.0630 mm (Merck). Elemental analyses were obtained using Carlo Erba CHNS-OEA 1108 - Elemental Analyzer. Optical rotation values were measured on a Perkin Elmer P 241 polarimeter. IR spectra were recorded using a Philips FTIR PU 9800 spectrometer, with only selected peaks reported. UV spectra were measured in MeOH solution and were recorded on a Specord UV-VIS M-40 (Zeiss Jena) instrument. Mass spectra were recorded on a AEI MS 902 S electron ionization spectrometer (EI = 70eV).  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) spectra were recorded on a Varian VXR 300. Spectra were internally referenced to TMS. Peaks are reported in ppm down field of TMS.  $^{13}\text{C}$  NMR peak assignments were made by DEPT editing of the spectra.

### General method for preparation of isothiocyanates **1b-i**

A solution of the requisite amino ester hydrochloride (1g) in water (10ml) was mixed with chloroform (10ml) and a stock solution of thiophosgene (1.05 mol-equivalent) was added under stirring with simultaneous addition of a reagent neutralizing the hydrogen chloride, liberated during the reaction ( $\text{NaHCO}_3$ ). The addition was carried out at such rate as to maintain the coloration of the reaction mixture due to an excess of thiophosgene. After the carbon dioxide evolution had ceased, the chloroform layer was separated, washed successively with 0.1M-HCl ( $2 \times 10$  ml) and water ( $3 \times 10$ ml), dried over sodium sulphate and taken down at 25°C. The oily residue was distilled under diminished pressure, or, alternatively, the solid compound was crystallized from a suitable solvent [11] (Tab.1).

### *Ethoxycarbonylmethylthiosemicarbazide (2b)*

Yield 95%, mp. 172°-174° C, lit.[5] 171° C, Elemental anal. for  $\text{C}_5\text{H}_{11}\text{N}_3\text{O}_2\text{S}$  (M 177.24), calc. / found %C 33,88 / 33,76, %H 6.26 / 6.31, %N 23.71 / 23.67, %S 18.09 / 18.07 .

MS (70eV) m/z (%): 177 ( $\text{M}^+$ , 96), 132 (13), 131 (100), 118 (10), 115 (6), 104 (30), 103 (47), 102 (5), 90 (12), 75 (26), 74 (41), 73 (14), 72 (81), 70 (5), 62 (7), 60 (28), 59 (15), 56 (5), 55 (17), 46 (22),

45 (44), 44 (38), 43 (37), 42 (22), 41 (13).

IR (KBr,  $\text{cm}^{-1}$ ): 3351, 3312, 3271, 3215, 1750, 1632, 1545, 1497, 1398, 1206, 1375, 1341, 1296, 1240, 1208.

$^1\text{H-NMR}$  (DMSO- $d_6$  / TMS): 1.18 (t,  $J = 7.1$ , 3H,  $\text{CH}_3$ ), 3.27 (s, 4.07 (q,  $J = 7.1$ , 2H,  $\text{OCH}_2$ ), 4.21 (d,  $J = 3.0$ , 2H,  $\underline{\text{CH}_2\text{NH}}$ ), 4.48 (br, 2H,  $\text{NH}_2$ ), 8.11 (t,  $J = 3.0$ , 1H,  $\underline{\text{NH-CH}_2}$ ), 8.89 (s, 1H,  $\text{NH-N}$ ).

$^{13}\text{C-NMR}$  (DMSO- $d_6$  / TMS): 14.1 ( $\text{CH}_3$ ), 44.7 ( $\text{CH}_2\text{NH}$ ), 60.2 ( $\text{CH}_2\text{O}$ ), 169.8 (C=O), 181.9 (C=S).

#### Methoxycarbonyl-*t*-butylmethylthiosemicarbazide (2d)

Yield 60%, m.p. 108° - 111°C,

MS (70eV)  $m/z$  (%): 219 ( $\text{M}^+$ , 54), 188 (14), 187 (24), 184 (10), 160 (12), 159 (12), 146 (8), 144 (10), 131 (24), 128 (18), 115 (20), 112 (10), 99 (14), 90 (12), 89 (18), 88 (28), 86 (74), 84 (28), 73 (20), 72 (42), 69 (36), 58 (44), 57 (64), 56 (32), 55 (28), 41 (60), 37 (42), 35 (100), 32 (100). IR (KBr,  $\text{cm}^{-1}$ ): 3368, 3316, 3295, 2972, 2959, 1730  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  (DMSO- $d_6$  / TMS): 0.95 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 3.65 (s, 3H,  $\text{OCH}_3$ ), 4.70 (br, 2H,  $\text{NH}_2$ ), 4.79 (d, 1H,  $J = 9.3$ , CH), 7.91 (d, 1H,  $J = 9.3$ ,  $\underline{\text{NH-CH}}$ ), 9.05 (s, 1H,  $\text{NH-N}$ ).

$^{13}\text{C-NMR}$  (DMSO- $d_6$  / TMS): 26.53, 34.31, 51.55, 63.56, 171.5, 181.3

#### 3-Aminothiohydantoin (3b)

**Method A:** 0.44 g (3 mM) of **2b** is heated (160° C) under vacuum (0.1 mbar) for 0.5 hours. The dark solid afforded after recrystallization from ethanol (charcoal) 0.12 g (36%) of gray crystals, mp. 159-160° C, with satisfactory spectral data (Table 2).

**Method B:** 1.64g (9.2 mM) of **2b** was dissolved in ethanol (50 ml) under reflux, water solution of sodium hydroxide (0.1g in 2 ml  $\text{H}_2\text{O}$ ) was added, reaction mixture was after 1 minute cooled to 50° C, acidified by diluted HCl (1:10) to pH 6.5. Purification of the reaction mixture with active charcoal and crystallization afforded 0.4 g (33%) of **3b**, mp 156 -158° C. Recrystallisation from methanol gave sample with mp.159 -160° (TLC:  $\text{CHCl}_3$  / MeOH 9:1,  $R_f$  0.27) having satisfactory elemental analysis data and identical spectral data as the compound **3b** prepared by the method A.

#### 3-Aminothiohydantoins **3**; General procedure

A solution of hydrazin hydrate 80% (0.62 g, 11 mM) in MeOH or EtOH (3 mL) was added dropwise to an intensively stirred cooled solution (0° C) of the appropriate isothiocyanate **1b-i** (10 mM) in diethyl ether (20 mL). The mixture was stirred for 30 minutes at laboratory temperature (22°C) and then allowed to stand in refrigerator (4°C) for 2 hours. The precipitate was separated by suction filtration, and washed by  $\text{Et}_2\text{O}$ . Recrystallization from EtOH /  $\text{Et}_2\text{O}$  resulted in white crystals (Table 2, Table 3).

**Table 1.** Spectral Data of Isothiocyanates **1**.

Product	$[\alpha]^{22}$ (g/100ml) n - hexane	IR ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR ( $\text{CDCl}_3/\text{TMS}$ ) $\delta$ (ppm), $J$ (Hz)	$^{13}\text{C}$ NMR ( $\text{CDCl}_3/\text{TMS}$ ) $\delta$ (ppm)
<b>1d<sup>c</sup></b>	$\pm$	2081, 1750 <sup>b</sup>	1.06 (s, 9H, $(\text{CH}_3)_3\text{C}$ ), 3.81 (s, 3H, OCH <sub>3</sub> ), 3.96 (s, 1H, H-2)	26.5 (CH <sub>3</sub> ), 36.8 ( $\underline{\text{C}}(\text{CH}_3)_3$ ), 68.9 (OCH <sub>3</sub> ), 136.1 (NCS), 167.8 (C=O)
<b>1e</b>	-26.2° (0,29)	2054, 1740 <sup>a</sup>	2.98 (dd, $J = 11.2, 5.5$ , H-3a), 3.04 (dd, 1H, $J = 11.2, 5.5$ , H-3b), 3.75 (s, 3H, OCH <sub>3</sub> ), 3.85 (s, 3H, OCH <sub>3</sub> ), 4.75 (dd, 1H, $2 \times J = 4.9$ , H-2)	36.9 (C-3), 52.0, 53.2 (2xOCH <sub>3</sub> ), 55.1 (C-2), 139.0 (NCS), 167.4, 168.9 (2xC=O)
<b>1f</b>	-32.4° (0.37)	2085, 1740 <sup>b</sup>	2.16 (m, 1H, H-3a), 2.30 (m, 1H, H-3b), 2.53 (m, 2H, H-4), 3.71 (s, 3H, OCH <sub>3</sub> ), 3.83 (s, 3H, OCH <sub>3</sub> ), 4.44 (dd, 1H, $2 \times J = 4.9$ , H-2)	28.2 (C-4), 29.4 (C-3), 51.6, 53.0 (2xOCH <sub>3</sub> ), 58.2 (C-2), 137.8 (NCS), 166.2, 171.9 (2xC=O)
<b>1g</b>	$\pm$	2052, 1749	1.25 (t, 3H, $J = 7.1$ , OCH <sub>2</sub> CH <sub>3</sub> ), 4.21 (q, 2H, $J = 7.1$ , OCH <sub>2</sub> CH <sub>3</sub> ), 5.26 (s, 1H, H-2), 7.42-7.98 (m, 5H <sub>arom.</sub> )	14.0 (OCH <sub>2</sub> CH <sub>3</sub> ), 62.9 (OCH <sub>2</sub> ), 62.9 (C-2), 126.8, 129.1, 129.3 (C <sub>arom.</sub> ), 131.0 (C-1'arom.), 139.8 (NCS), 167.4 (C=O)
<b>1h</b>	$\pm$	2110, 2170, 1742, 1732 <sup>a</sup>	1.27 (t, 3H, $J = 7.2$ , OCH <sub>2</sub> CH <sub>3</sub> ), 3.23 (dd, 1H, $J = 4.8, 13.7$ , H-3a), 3.11 (dd, 1H, $J = 8.2, 13.7$ , H-3b), 4.22 (q, 2H, $J = 7.2$ , OCH <sub>2</sub> CH <sub>3</sub> ), 4.44 (dd, 1H, $2 \times J = 4.8$ , H-2), 7.21-7.35 (m, 5H, H <sub>arom.</sub> )	14.1 (OCH <sub>2</sub> CH <sub>3</sub> ), 39.7 (C-3), 60.9 (C-2), 62.6 (OCH <sub>2</sub> ), 127.6, 128.8, 129.4, (3xC <sub>arom.</sub> ), 135.1 (C-1'arom.), 138.0 (NCS), 167.9 (C=O)
<b>1i</b>	-35.3° (0.45)	2064, 1760, 1749 <sup>a</sup>	1.29 (t, 3H, $J = 7.2$ , OCH <sub>2</sub> CH <sub>3</sub> ), 3.07 (dd, 1H, $J = 7.8, 14.0$ , H-3a), 3.17 (dd, 1H, $J = 4.8, 14.0$ , H-3b), 4.21 (q, 2H, $2 \times J = 7.2$ , OCH <sub>2</sub> CH <sub>3</sub> ), 4.41 (dd, 1H, $2 \times J = 4.7$ , H-2), 6.79 (d, 2H, $J = 8.4$ , H <sub>arom.</sub> ), 7.09 (d, 2H, $J = 8.4$ , H <sub>arom.</sub> )	14.1 (OCH <sub>2</sub> CH <sub>3</sub> ), 38.9 (C-3), 61.1 (C-2), 62.7 (OCH <sub>2</sub> ), 115.7 (C-2',6'), 127.1 (C-1'), 130.7 (C-3',5'arom.), 137.9 (NCS), 155.1 (C-4'), 168.1 (C=O)

a-CHCl<sub>3</sub> solution

b-KBr disc/film

c-yield 21%, b.p.29°C/0.09 mbar

Table 2. Spectral data of 3-Aminothiohydantoins 3.

Product	[ $\alpha$ ] <sup>22</sup> (g / 100 ml)	UV (MeOH) $\lambda_m$ (nm)	IR (cm <sup>-1</sup> )	<sup>1</sup> H NMR (DMSO-d <sub>6</sub> /TMS) $\delta$ (ppm), <i>J</i> (Hz)	<sup>13</sup> C NMR (DMSO d <sub>6</sub> /TMS) $\delta$ (ppm)	
					C-2,4,5	others
<b>3b</b>	-	239.5 (3.84)	3283, 3179, 3135, 1742, 1514	4.08 (s, 2H, CH <sub>2</sub> ), 4.96 (s, 2H, NH <sub>2</sub> ), 10.06 (bs, 1H, NH)	183.55 169.42 46.99	-
<b>3c</b>	+3.7° (0.4) MeOH	234.0 (3.48) 264.0 (3.97)	3304, 3240, 3210, 1741, 1507	1.46 (d, 3H, <i>J</i> = 7.1, CH <sub>3</sub> ), 4.09 (dq, 1H, <i>J</i> = 7.1, 1.3, CH), 9.65 (bs, 1H, NH)	182.63 172.47 53.09	16.21
<b>3d</b>	±	-	-	0.94 (s, 9H, (CH <sub>3</sub> ) <sub>3</sub> C), 3.73 (s, 2H, NH <sub>2</sub> ), 3.89 (s, 1H, CH), 10.27 (bs, 1H, NH)	183.10 170.49 65.59	34.91 25.27
<b>3e</b>	- 25.4° (0.45) 4% HCl	235.8 (3.85) 264.8 (4.35)	3360, 3230, 1744, 1729	2.81 (d, 2H, <i>J</i> = 5.1, CH <sub>2</sub> ), 3.60 (s, 3H, OCH <sub>3</sub> ), 4.43 (dd, 1H, 2 x <i>J</i> = 5.4, CH), 4.98 (s, 2H, NH <sub>2</sub> ), 10.18 (bs, 1H, NH)	183.40 170.73 53.75	169.23 51.74 34.41
<b>3f</b>	- 25.3° (0.27) 4% HCl	235.8 (3.83) 264.6 (4.32)	3343, 3240, 3196, 1740, 1732, 1501	1.9 (m, 2H, CCH <sub>2</sub> ), 2.43 (m, 2H, CH <sub>2</sub> CO), 3.60 (s, 3 H, OCH <sub>3</sub> ), 4.23 (dd, 1H, 2 x <i>J</i> = 5.4, CH), 4.98 (s, 2H, NH <sub>2</sub> ), 10.29 (bs, 1H, NH)	183.0 172.25 56.29	171.35 51.44 28.46 26.04
<b>3g</b>	±	270.0 (4.17)	3324, 3248, 3162, 1757, 1518	5.08 (s, 2H, NH), 5.38 (s, 1H, CH), 7.45 - 7.26 (m, 5H, H <sub>arom.</sub> ), 10.70 (bs, 1H, NH)	183.30 170.22 60.59	134.40 128.76 127.57 126.88
<b>3h</b>	±	238.0 (3.78) 266.0 (4.25)	3308, 3235, 3179, 1736, 1510	3.05 (dd, 1H, <i>J</i> = 14.1, 6.1, CHH), 3.21 (dd, 1H, <i>J</i> = 14.3, 4.4, CHH), 3.30 (s, 2H, NH <sub>2</sub> ), 4.31 (dd, 1H, <i>J</i> = 6.1, 4.3, CH), 7.20-7.43 (m, 5H, H <sub>arom.</sub> ), 9.90 (bs, 1H, NH)	182.66 170.78 58.16	134.91 129.4 128.11 126.77 35.83
<b>3i</b>	+12.0° (0.14) 4% HCl	226.7 (4.04) 266.2 (4.26)	3435, 3299, 3237, 3177, 1724, 1514	2.47 (m, 2H, CH <sub>2</sub> ), 4.42 (m, 1H, CH), 4.83 (s, 1H, NH <sub>2</sub> ), 6.60 (d, 2H, <i>J</i> = 8.5, H <sub>arom.</sub> ), 6.92 (d, 2H, <i>J</i> = 8.4, H <sub>arom.</sub> ), 9.28 (s, 1H, OH), 10.25 (bs, 1H, NH)	182.61 170.90 58.48	156.09 130.42 124.80 114.96 35.02

**Table 3.** Physicochemical data and Mass spectra of 3-Aminothiohydantoin 3.

Product	mp (°C) Yield (%)	Molecular Formula <sup>a</sup> M.W.	MS m/z (%)
<b>3b</b>	159 - 160 80	C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> OS 131.15	131 (M <sup>+</sup> , 100), 103 (47), 74 (20), 73 (5), 72 (11), 60 (6), 55 (4), 47 (5), 45 (10), 43 (13), 34 (41), 33 (14)
<b>3c</b>	161 - 163 70	C <sub>4</sub> H <sub>7</sub> N <sub>3</sub> OS 145.18	145 (M <sup>+</sup> , 100), 117 (27), 86 (17), 74 (13), 60 (8), 44 (56)
<b>3e</b>	152 - 154 72	C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub> S 203.22	203 (M <sup>+</sup> , 100), 175 (13), 172 (14), 171 (6), 144 (20), 143 (16), 130 (11), 116 (5), 113 (30), 112 (9), 102 (96), 101 (25), 86 (22), 85 (29), 75 (24), 74 (39), 70 (39), 60 (26), 59 (42), 58 (8), 57 (16), 55 (34), 54 (5), 43 (46)
<b>3f</b>	160 - 61 75	C <sub>7</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S 217.34	217 (M <sup>+</sup> , 100), 186 (18), 185 (49), 158 (5), 144 (11), 143 (15), 126 (11), 116 (11), 114 (5), 102 (8), 98 (17), 84 (60), 75 (9), 74 (12), 59 (5), 56 (13), 55 (13)
<b>3g</b>	157 - 158 80	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> OS 207.25	207 (M <sup>+</sup> , 100), 205 (7), 179 (20), 148 (47), 147 (27), 118 (14), 106 (58), 104 (14), 102 (5), 91 (8), 90 (15), 89 (5), 79 (8), 77 (10), 74 (15), 51 (6)
<b>3h</b>	234 - 235 75	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> OS 221.28	221 (M <sup>+</sup> , 61), 193 (26), 163 (5), 162 (5), 131 (7), 130 (13), 128 (13), 121 (6), 120 (64), 119 (5), 118 (5), 117 (17), 116 (20), 106 (45), 104 (13), 103 (16), 102 (12), 92 (23), 91 (100), 89 (5), 86 (5), 78 (8), 77 (17), 75 (18), 65 (23), 63 (6), 51 (12), 50 (6)
<b>3i</b>	210 - 212 64	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> S 237.27	237 (M <sup>+</sup> , 12), 131 (10), 122 (9), 108 (9), 107 (100), 77 (5)

<sup>a</sup> Satisfactory microanalyses obtained: C± 0.3, H± 0.2, N±0.3, S± 0.4

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*Sample Availability:* Available from the authors.