Ring Cleavage of Cyclic Thioureas; A Synthesis of *N*-(Alkylthio-carbonyl)-*N'*-(alkylthio-thiocarbonyl)-alkanediamines and *N,N'*-Bis[alkylthio-thiocarbonyl]-alkanediamines

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Symmetrical metal *N,N'*-alkanediyl-bis-dithiocarbamates, which can be easily prepared from alkanediamines and carbon disulfide, are components of agricultural chemicals such as Maneb, Zineb, and Dithane Stenless. The corresponding esters **5**, i.e., symmetrical dialkyl *N,N'*-alkanediyl-bis-dithiocarbamates, can be easily prepared via the alkali metal salts. However, analogous unsymmetrical esters such as *N*-(methylthio-carbonyl)-*N'*-(alkylthio-thiocarbonyl)-alkanediamines **(3)** are not accessible in the same way and have hitherto not been described.

In our study of the synthesis of heterocycles from thioureas[1,2,3] we found that the unsymmetrical compounds **3** can be easily obtained from the ring cleavage of cyclic methyl *N*-(methylthio-thiocarbonyl)-carbamimidothioates (**2**, cyclic isothiourea derivatives) by acidic hydrolysis; compounds **3** are accompanied by the cyclic hydrolysis products **4** which can be easily separated from the solution containing **3**. The analogous reaction of **2** with hydrogen sulfide in dry ethanol affords the bis-dithiocarbamates **5** and the cyclic thioureas **6**.

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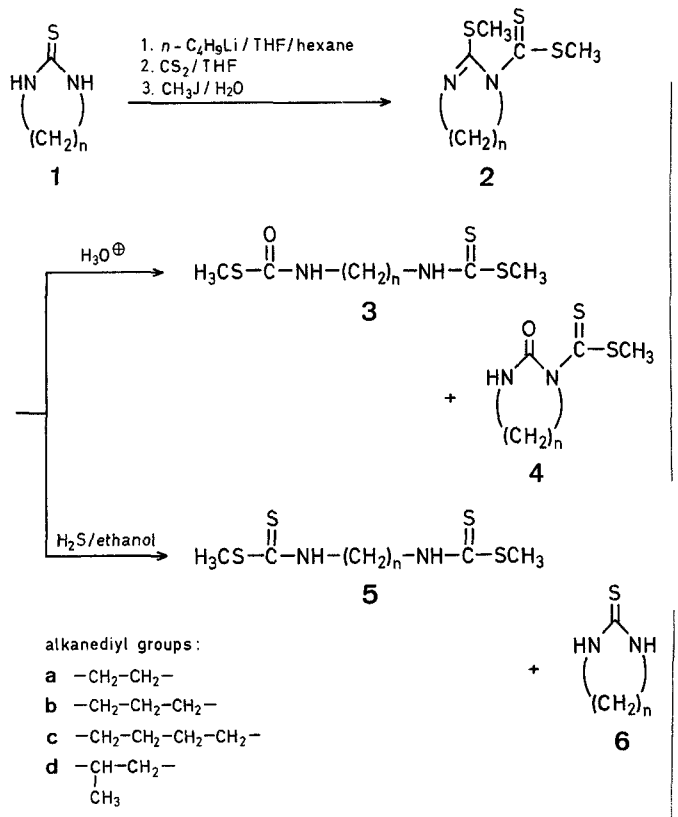
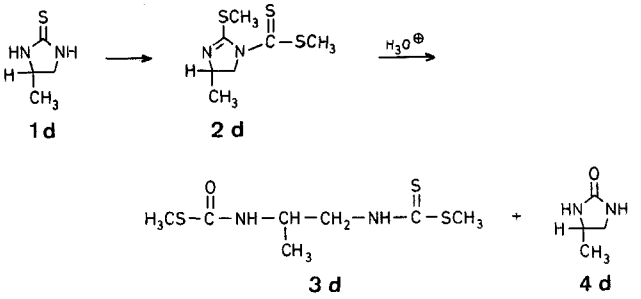


Application of the hydrolytic ring-cleavage method to compound **2d** derived from 4-methyl-2-thioxoimidazolidine (**1d**) affords the unsymmetrical N^2-(methylthio-carbonyl)-N^1-(methylthio-thiocarbonyl)-1,2-propanediamine **3d** together with **4d**. The structure of **3d** (and thereby also that of **2d**) was determined by the mass-fragmentation pattern which showed the ion $(H_3CSCONHCHCH_3)^+$.



In an attempt to extend the reaction to analogous systems, we found that treatment of 1-methoxycarbonyl-2-methylthio-4,5-dihydroimidazole (**7**) with dilute sulfuric acid or hydrogen sulfide in ethanol did not lead to ring cleavage. Instead, the 2-oxo- or 2-thioxo-imidazolidine derivatives **8** or **9**[5] were obtained in 64 and 99% yields, respectively.

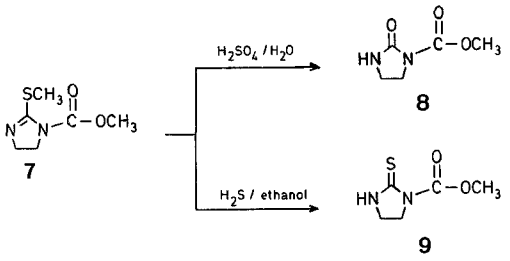


Table 1. 2-Methylthio-1-(methylthio-thiocarbonyl)-1,3-diaza-2-cycloalkenes (**2**)

2	Yield [%]	m.p. or b.p./torr [°C]	Molecular formula[a]
a	74	m.p. 90–91° (ethanol, orange needles)	$C_6H_{10}N_2S_3$ (206.2)
b	64	m.p. 59–60° (hexane, yellow needles)	$C_7H_{12}N_2S_3$ (220.2)
c	66	b.p. 160°/2 (yellow oil)	$C_8H_{14}N_2S_3$ (234.2)
d	67	m.p. 54–55° (hexane, yellow prisms)	$C_7H_{12}N_2S_3$ (220.2)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.23; H, ±0.20; N, ±0.24; S, ±0.30.

Table 3. Dimethyl *N,N'*-Alkanediyl-bis-dithiocarbamates (**5**)

5	Yield [%]	m.p. [°C]	Molecular formula or m.p. [°C] reported	Yield of **6** [%]
a	66	101–102° (ethanol, light yellow needles)	105–107°[4]	20
b	48	72–73° (hexane/ethanol, yellow prisms)	$C_7H_{14}N_2S_4$ (254.2)	47
d	57	yellow oil (dec. 160°)	$C_7H_{14}N_2S_4$ (254.2)	35

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.24; H, ±0.22; N, ±0.24; S, ±0.28.

Table 2. *N*-(Methylthio-carbonyl)-*N'*-(methylthio-thiocarbonyl)-alkanediamines (**3**) and 1-(Methylthio-thiocarbonyl)-2-oxo-1,3-diazacycloalkanes (**4**)

3, 4	Products **3**			Products **4**		
	Yield [%]	m.p. [°C]	Molecular formula[a]	Yield [%]	m.p. [°C]	Molecular formula[a]
a	39	103–104°[b] (colorless needles)	$C_6H_{12}N_2OS_3$ (224.2)	48	213–214°	$C_5H_8N_2OS_2$ (176.1)
b	40	84–85°[b] (colorless needles)	$C_7H_{14}N_2OS_3$ (238.2)	35	145–146°	$C_6H_{10}N_2OS_2$ (190.2)
c	33	77–78°[b] (colorless prisms)	$C_8H_{16}N_2OS_3$ (252.3)			
d	33	colorless oil (dec. 130°)	$C_7H_{14}N_2OS_3$ (238.2)	35	167–168°	$C_6H_{10}N_2OS_2$ (190.2)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.22; H, ±0.22; N, ±0.25; S, ±0.28.
[b] Recrystallized from ethanol.

Table 4. Spectral Data of Compounds **3**

3	M.S. *m/e*	I.R. (KBr) ν [cm^{-1}]	U.V. (ethanol) λ_{max} [nm] (ε)	^{1}H-N.M.R. (solvent/TMS) δ [ppm]
a	224	3230 (NH); 3000, 2925 (CH); 1645 (CO)	253 (15500), 272 (16000)	11.25 (s, 1H); 9.52 (s, 1H); 4.13 (t, 2H); 3.90 (t, 2H); 2.67 (s, 3H); 2.37 (s, 3H)[a]
b	238	3250 (NH); 3000, 2920 (CH); 1640 (CO)	252 (17000), 270 (16300)	8.17 (s, 1H); 6.30 (s, 1H); 3.90 (q, 2H); 2.70 (s, 3H); 2.40 (s, 3H); 1.93 (m, 2H)[b]
c	252	3230 (NH); 3000, 2910, 2850 (CH); 1640 (CO)	254 (13000), 270 (14000)	7.60 (s, 1H); 5.83 (s, 1H); 3.80 (m, 2H); 3.40 (m, 2H); 2.70 (s, 3H); 2.43 (s, 3H); 1.70 (m, 4H)[b]
d	238.0276	(neat) 3250 (NH); 2960, 2910 (CH); 1640 (CO)	253 (18000), 271 (18000)	8.17 (s, 1H); 5.73 (s, 1H); 4.17 (m, 1H); 3.83 (t, 2H); 2.68 (s, 3H); 2.43 (s, 3H); 1.33 (d, 3H)[b]

[a] Pyridine-d_5.
[b] Deuterochloroform.

2-Methylthio-1-(methylthio-thiocarbonyl)-4,5-dihydroimidazole (2a); Typical Procedure:

A solution of butyllithium (48 mmol) in hexane (30 ml) is added dropwise to a stirred suspension of 2-thioxoimidazolidine (**1**, *N,N'*-ethanediylthiourea; 2 g, 19.6 mmol) in tetrahydrofuran (40 ml) under nitrogen at 0 °C, and stirring is continued for 30 min. Then, a solution of carbon disulfide (8 ml) in tetrahydrofuran (40 ml) is added dropwise and the mixture stirred for an additional 30 min. The mixture is then vigorously shaken with methyl iodide (8 ml) and water (20 ml) for 30 min and kept in a refrigerator overnight. The organic layer is separated and rotary-evaporated and the residue is recrystallized from ethanol to give **2a** as orange needles; yield: 3.0 g (74%); m.p. 90–91 °C.

***N*-(Methylthio-carbonyl)-*N'*-(methylthio-thiocarbonyl)-1,2-ethanediamine (3a) and 1-(Methylthio-thiocarbonyl)-2-oxoimidazolidine (4a); Typical Procedure:**

A mixture of compound **2a** (1 g, 4.9 mmol), 2% sulfuric acid (1 ml), ethanol (5 ml), and water (1 ml) is refluxed for 4 h. The colorless crystalline product **4a** is isolated by suction and recrystallized from ethanol; yield: 0.41 g (48%); m.p. 203–204 °C. The filtrate is rotary-evaporated, the residual yellow oil triturated with water (5 ml), the resultant solid product **3a** isolated by suction, and recrystallized from ethanol; yield: 0.43 g (39%); m.p. 103–104 °C.

When 47% hydrobromic acid is used as the hydrolyzing agent in place of sulfuric acid a 2 h reaction time is sufficient for complete hydrolysis.

***N,N'*-Bis[methylthio-thiocarbonyl]-alkanediamines (5, Dimethyl *N,N'*-Alkanediyl-bis-dithiocarbamates); General Procedure:**

A solution of the cyclic isothiourea derivative **2** (4.9 mmol) in ethanol (20 ml) is refluxed for 90 min while dry hydrogen sulfide is bubbled through the solution (25–30 ml/min). The solution is then evaporated and the residue worked up by column chromatography on silica gel using ethyl acetate/benzene (1/1) as eluent. Compound **5** is eluted first.

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