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## Rearrangement of $\alpha$ -Chloroaldimines: Synthesis of 2-Imidazolidinethiones<sup>1</sup>

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1-Substituted 4-methoxy-5,5-dimethyl-2-imidazolidinethiones have been prepared by reaction of *N*-1-(2-chloro-2-methylpropylidene)amines with potassium thiocyanate in methanol under reflux. The 1-substituted 4-methoxy-5,5-dimethyl-2-imidazolidinethiones were conveniently converted into the corresponding 1-substituted 5,5-dimethyl-2-imidazolidinethiones by lithium aluminum hydride treatment in ethereal medium. The structure elucidation was based on NMR, IR, and mass spectrometry next to x-ray crystallographic analysis. The formation of the heterocyclic five-membered rings was explained by a mechanism involving an aziridine intermediate, which underwent competitive opening.

*N*-1-(2-Chloro-2-methylpropylidene)amines (**1**), easily obtained from isobutyraldimines and *N*-chlorosuccinimide, are a new class of simple bifunctional compounds which have been used recently as synthetic blocks in organic synthesis.<sup>3,4</sup> An entry into the heterocyclic chemistry is presented here.

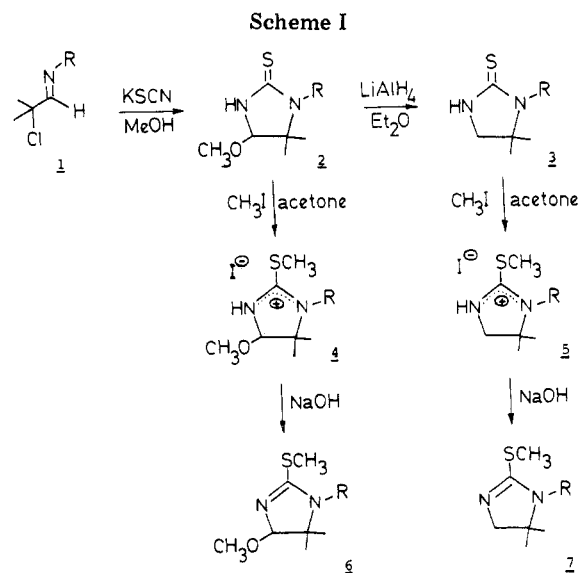
### Results and Discussion

In continuation of work on the reactivity of  $\alpha$ -halogenated imino compounds, the reaction of  $\alpha$ -chloroaldimines **1** with KSCN in methanol has been found to provide a convenient preparation of 1-substituted 4-methoxy-5,5-dimethyl-2-imidazolidinethiones (**2**) (Table I).

Treatment of compounds **2** with methyl iodide in dry acetone afforded imidazoline hydriodides **4**, which were converted into the 2-methylthioimidazolines **6** by alkali treatment (Scheme I). The structure of these products, which involved rearrangement of the imino nitrogen, was established by x-ray crystallographic analysis of 1-cyclohexyl-4-methoxy-5,5-dimethyl-2-methylthioimidazoline hydriodide (**4b**).

The molecular structure of compound **4b** as determined by the x-ray analysis is shown in Figure 1 together with the atom labeling system used. The final coordinates, standard deviations, and bond distances are listed in Tables II and III, included in the microfilm edition of this journal. The experimental conditions for the x-ray crystallographic analysis are further given in the Experimental Section.

A further support of the presence of a CH<sub>3</sub>OCHN moiety in the heterocycles described here was provided by the conversion of **2** into the nonmethoxylated compounds **3**, i.e., 1-substituted 5,5-dimethyl-2-imidazolidinethiones, by reaction



**Table I. Synthesis and Spectrometric Properties of 1-Substituted 4-Methoxy-5,5-dimethyl-2-imidazolidinethiones 2, 1-Substituted 5,5-Dimethyl-2-imidazolidinethiones 3, and 1-Substituted 4-Alkoxy-5,5-dimethyl-2-imidazolidinethiones 24**

Compd <sup>a</sup>	R	Yield, %	Mp, °C	NMR, $\delta$ (CDCl <sub>3</sub> )					IR (KBr), <sup>c</sup> cm <sup>-1</sup>	Mass spec- trum, <sup>a,e</sup> $m/e$ (rel intensity)	
				$\delta_{(\text{CH}_3)_2}$	$\delta_{\text{NCHO}}$	$\delta_{\text{NCH}_2}$	$\delta_{\text{OCH}_3}$	$\delta_{\text{NH}}^b$			$\delta_{\text{R}}$
2a	<i>t</i> -Bu	50	176	1.44 (s, 3) 1.51 (s, 3)	4.25 (d, $J = 1.0$ Hz)		3.40 (s)	7.50	1.76 (s, 9, <i>t</i> -Bu)	3220 ( $\nu_{\text{NH}}$ )	216 (M <sup>+</sup> , 24); 184 (M <sup>+</sup> - MeOH, 48); 60 (100)
2b	Cyclo- hexyl	78	184	1.30 (s, 3) 1.36 (s, 3)	4.38 (d, $J = 1.0$ Hz)		3.38 (s)	7.65	1-2 [m, 10, (CH <sub>2</sub> ) <sub>5</sub> ]; 2.5 (m, 1, NCH)	3220 ( $\nu_{\text{NH}}$ )	242 (M <sup>+</sup> , 27); 210 (M <sup>+</sup> - MeOH, 60); 86 (100)
2c	<i>n</i> -Bu	22	110	1.22 (s, 3) 1.30 (s, 3)	4.41 (d, $J = 1.0$ Hz)		3.36 (s)	7.78	0.94 (t, 3, CH <sub>3</sub> ) 1.1-2 [m, 4, (CH <sub>2</sub> ) <sub>2</sub> ]; 3.4 (m, 2, NCH <sub>2</sub> )	3220 ( $\nu_{\text{NH}}$ )	216 (M <sup>+</sup> , 27); 184 (M <sup>+</sup> - MeOH, 53); 86 (100)
2d	<i>i</i> -Pr	73	126	1.30 (s, 3) 1.35 (s, 3)	4.36 (d, $J = 1.0$ Hz)		3.36 (s)	7.69	1.52 [d, $J = 7$ Hz, 6, (CH <sub>3</sub> ) <sub>2</sub> ]; 4.13 (septet, $J = 7$ Hz, 1, CHMe <sub>2</sub> )	3220 ( $\nu_{\text{NH}}$ )	202 (M <sup>+</sup> , 19); 170 (M <sup>+</sup> - MeOH, 15); 86 (100)
2e	CH <sub>2</sub> - C <sub>6</sub> H <sub>5</sub>	64	126	1.08 (s, 3) 1.17 (s, 3)	4.46 (d, $J = 0.8$ Hz)		3.35 (s)	7.97	4.77 and 4.87 (AB, $J = 15.6$ Hz, NCH <sub>2</sub> ); 7.1-7.6 (m, 5, C <sub>6</sub> H <sub>5</sub> )	3220 ( $\nu_{\text{NH}}$ )	250 (M <sup>+</sup> , 26); 218 (M <sup>+</sup> - MeOH, 20); 86 (100)
3a	<i>t</i> -Bu	75	180	1.50 (s, 6)		3.23 (d, 1.0 Hz)		6.65	1.76 (s, 9, <i>t</i> -Bu)	3180 ( $\nu_{\text{NH}}$ )	186 (M <sup>+</sup> , 3); 41 (100)
3b	Cyclo- hexyl	89	164	1.37 (s, 6)		3.35 (d, 0.8 Hz)		7.08	1-2 [m, 10, (CH <sub>2</sub> ) <sub>5</sub> ]; 2.6 (m, 1, NCH)	3100- 3220 ( $\nu_{\text{NH}}$ )	212 (M <sup>+</sup> , 78); 55 (100)
3c	<i>n</i> -Bu	85	70	1.30 (s, 6)		3.35 (d, 1.0 Hz)		7.23	0.95 (t, 3, CH <sub>3</sub> ); 1.2-1.9 [m, 4, (CH <sub>2</sub> ) <sub>2</sub> ]; 3.4 (covered, NCH <sub>2</sub> )	3260 ( $\nu_{\text{NH}}$ )	186 (M <sup>+</sup> , 100)
3d	<i>i</i> -Pr	91	181	1.37 (s, 6)		3.33 (d, 1.0 Hz)		6.85	1.56 [d, $J = 7$ Hz, 6, (CH <sub>3</sub> ) <sub>2</sub> ]; 4.04 (1, H, septet, 1, CHMe <sub>2</sub> )	3180 ( $\nu_{\text{NH}}$ )	172 (M <sup>+</sup> , 100)
3e	CH <sub>2</sub> - C <sub>6</sub> H <sub>5</sub>	86	128	1.16 (s, 6)		3.33 (d, 1.0 Hz)		see $\delta_{\text{R}}$	4.77 (s br, 2, NCH <sub>2</sub> ); 6.9 (m, 6, C <sub>6</sub> H <sub>5</sub> + NH)	3100- 3200 ( $\nu_{\text{NH}}$ )	220 (M <sup>+</sup> , 96); 91 (100)
24b (R' = Et)	Cyclo- hexyl	85	124	1.30 (s, 3) 1.34 (s, 3)	4.46 (d, $J = 1$ Hz)		$\delta_{\text{OEt}}$ (see $\delta_{\text{R}}$ entry)	7.86	1-2 [m, 10, (CH <sub>2</sub> ) <sub>5</sub> ]; ~2.5 (m, 1, NCH); 1.19 (t, $J = 7$ Hz, 3 CH <sub>3</sub> CO); 3.2-4 (m, 2, OCH <sub>2</sub> )	3200 ( $\nu_{\text{NH}}$ )	no M <sup>+</sup> ; 184 (M <sup>+</sup> - EtOH, 70); 57 (100)
24a (R' = Et)	<i>t</i> -Bu	34		1.40 (s, 3) 1.47 (s, 3)	4.26 (d, $J = 1$ Hz)		$\delta_{\text{OEt}}$ (see $\delta_{\text{R}}$ entry)	7.50	1.75 (s, 9, <i>t</i> -Bu); 1.19 (t, $J = 7$ Hz, 3, CH <sub>3</sub> CO); 3.5 (m, 2, OCH <sub>2</sub> )	3200 ( $\nu_{\text{NH}}$ )	no M <sup>+</sup> ; 184 (M <sup>+</sup> - EtOH, 70); 57 (100)
24a (R' = <i>i</i> -Pr)	<i>t</i> -Bu	50		1.40 (s, 6)	4.33 (d, $J = 1$ Hz)		$\delta_{\text{O-}i\text{-Pr}}$ (see $\delta_{\text{R}}$ entry)	7.80	1.71 (s, 9, <i>t</i> -Bu); 1.15 and 1.22 (2 d, $J = 6$ Hz, 6 H, Me <sub>2</sub> CO); 3.80 (m, 1, CHO)	3200 ( $\nu_{\text{NH}}$ )	244 (M <sup>+</sup> , 33); 184 (M <sup>+</sup> - <i>i</i> -PrOH, 20); 91 (100)

<sup>a</sup> Elemental analyses of compounds 2 and 3 are tabulated in the microfilm edition (Tables IV and V). <sup>b</sup> Broad signal. <sup>c</sup> Full IR data will appear in the microfilm edition of this journal (Table VI). <sup>d</sup> Mass spectra of compounds 2 were recorded with a A.E.I. MS 30 mass spectrometer, while mass spectra of compounds 3 were measured with a A.E.I. MS 20 mass spectrometer coupled with a gas chromatograph (GC-MS). <sup>e</sup> Full mass spectral data will appear in the microfilm edition of this journal (Table VI).

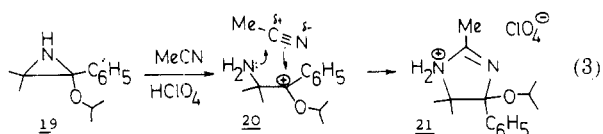
with mixed metal hydrides, such as lithium aluminum hydride in diethyl ether (for R = *t*-Bu, cyclohexyl, *n*-Bu, *i*-Pr, benzyl), and sodium bis(2-methoxyethoxy)aluminum hydride in benzene (for R = cyclohexyl). Sodium borohydride in meth-

anol did not react. Physical and spectrometrical data of compounds 3 are given in Table I.

This nucleophilic substitution by hydride is analogous to the reactions of mixed metal hydrides with *N*-( $\alpha$ -alkoxy-



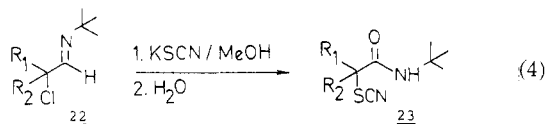
analogously, as was proposed for the thiocyanate anion. As shown in eq 3 aziridine **19** and  $\text{CH}_3\text{CN}/\text{HClO}_4$  gave rise to



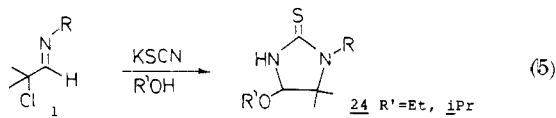
imidazolium perchlorate **21**. Less activated aziridines such as 1,1,2,2-tetramethylaziridinium perchlorate reacted in similar manner to imidazolium salts,<sup>18</sup> while the corresponding oxygen analogues, i.e., epoxides, showed comparable ring expansions to oxazolium salts with nitriles.<sup>19,20</sup>

Therefore we carried out the reaction of **1a** with  $\text{KSCN}/\text{CH}_3\text{OH}$  in the presence of acetonitrile in order to trap the intermediate methoxyaziridine **14**. The exclusive product, however, was 1-*tert*-butyl-4-methoxy-5,5-dimethyl-2-imidazolidinethione (**2a**).

The scope of the reaction of  $\alpha$ -chloroaldimines with  $\text{KSCN}$  is limited to the  $\alpha$ -chloroisobutyraldimines **1** (or **22**;  $\text{R}_1 = \text{R}_2 = \text{CH}_3$ ), since higher substituted derivatives **22** ( $\text{R}_1, \text{R}_2 \neq \text{CH}_3$ ) yielded no heterocyclic compounds. In this manner, *N*-1-(2-chloro-2-ethylbutylidene)-*tert*-butylamine (**22**,  $\text{R}_1 = \text{R}_2 = \text{Et}$ ) reacted with  $\text{KSCN}$  in methanol for 48 h under reflux to afford a reaction mixture from which only 19% *N*-*tert*-butyl-2-ethyl-2-thiocyanobutanamide (**23**;  $\text{R}_1 = \text{R}_2 = \text{Et}$ ) was isolated by crystallization (mp 126–127 °C) (eq 4). Ac-



cordingly, no 2-imidazolidinethione was formed by reaction of *N*-(1'-chlorocyclohexylmethylidene)-*tert*-butylamine [**22**;  $\text{R}_1, \text{R}_2 = (\text{CH}_2)_5$ ] with  $\text{KSCN}$  in methanol. Even carefully dried and purified reagents did not afford any five-membered ring. These limitations are in accordance with the observation that the reaction of higher substituted compounds **22** ( $\text{R}_1, \text{R}_2 \neq \text{CH}_3$ ) with methanol produced only a minor amount of the rearranged  $\beta$ -amino acetals besides the corresponding *N*-alkyl- $\alpha$ -chloroamides. However, an extension of the reaction outlined in Scheme I was the use of other alcohols than methanol. It was possible to obtain 1-alkyl-4-alkoxy-5,5-dimethyl-2-imidazolidinethiones **24** by carrying out the reaction of **1** with  $\text{KSCN}$  in ethanol or 2-propanol (eq 5).



The reaction with ethanol proceeded readily, while several days of reflux were required for the reactions with 2-propanol. The reaction in 2-methyl-2-propanol did not give heterocycles at all. In conclusion, the reaction of  $\alpha$ -chloroisobutyraldimines **1** with  $\text{KSCN}$  in alcoholic medium presents a versatile one-step synthesis of functionalized and otherwise not accessible 2-imidazolidinethiones **2**. The final products were formed by a rearrangement of the  $\alpha$ -chloroaldimines **1** involving an aziridine intermediate.

### Experimental Section

Nuclear magnetic resonance spectra were recorded with a Varian T-60 NMR spectrometer. Infrared spectra were measured with a Perkin-Elmer Model 257 spectrophotometer. Mass spectra were obtained from A.E.I. MS 20 or A.E.I. MS 30 mass spectrometers (70 eV). Melting points were measured with a Kofler hot stage and are uncorrected.

*N*-1-(2-chloro-2-methylpropylidene)amines **1** were prepared by condensing isobutyraldehyde with a primary amine, followed by chlorination of the resulting aldimine with *N*-chlorosuccinimide according to a method described previously.<sup>3</sup>

**Preparation of 1-Substituted 4-Methoxy-5,5-dimethyl-2-imidazolidinethiones (2).** In a typical experiment, 15.0 g (0.080 mol) of *N*-1-(2-chloro-2-methylpropylidene)cyclohexylamine (**1b**) was dissolved in 150 mL of dry methanol and treated with 23.3 g (0.24 mol) of  $\text{KSCN}$ . The mixture was refluxed overnight, half evaporated, and poured into 500 mL of vigorously stirred distilled water. The resulting precipitate was collected by filtration and washed with cold methanol/water, 25/75. 1-Cyclohexyl-4-methoxy-5,5-dimethyl-2-imidazolidinethione (**2b**) was dried in the desiccator, yield 15.1 g (78%), mp 184 °C. The product could be recrystallized from diethyl ether. Physical and spectral data of compounds **2** are given in Table I.

When other alcohols than methanol and ethanol were used, the following isolation procedure was applied as illustrated for 1-*tert*-butyl-4-isopropoxy-5,5-dimethyl-2-imidazolidinethione (**24a**;  $\text{R}' = i\text{-Pr}$ ). The reaction mixture, obtained as above, was poured into distilled water. The liquid which separated was taken up in ether, and the water layer was extracted twice with ether. After drying ( $\text{MgSO}_4$ ), evaporation of the solvent left an oil which was purified by passing it through a silica gel column (elution with ether). Compound **24a** ( $\text{R}' = i\text{-Pr}$ ) was sufficiently pure (>95% as revealed by NMR), but the purity could not be checked by gas chromatography due to decomposition, probably in the injector (see data in Table I).

### Synthesis of 1-Substituted 5,5-Dimethyl-2-imidazolidinethiones 3. (A) Reaction of 2 with $\text{LiAlH}_4$ in Diethyl Ether.

In a typical experiment, a suspension of 380 mg (0.01 mol) of lithium aluminum hydride and 10 mL of dry diethyl ether (distilled over lithium aluminum hydride) was cooled in an ice bath. A solution of 1.21 g (0.005 mol) of 1-cyclohexyl-4-methoxy-5,5-dimethyl-2-imidazolidinethione (**2b**) in 30 mL of dry diethyl ether was added dropwise over a period of 15 min. The suspension was further stirred for 1 h and then poured into a vigorously stirred mixture of ether and water. The ether layer was separated and the water layer was extracted twice with ether. The combined extracts were dried ( $\text{MgSO}_4$ ), and evaporation of the solvent in vacuo yielded 890 mg of pure 1-cyclohexyl-4,4-dimethyl-2-imidazolidinethione (**3b**) as white crystals, yield 80%. Recrystallization was performed with ether/pentane.

**(B) Reaction of  $\text{Na}(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_2\text{AlH}_2$  in Benzene.** To a solution of 1.0 g (0.0041 mol) of 1-cyclohexyl-4-methoxy-5,5-dimethyl-2-imidazolidinethione (**2b**) in 20 cm<sup>3</sup> of dry benzene was added dropwise with stirring 2.37 mL of a 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene (= Red-Al, purchased from the Aldrich Chemical Co.). After stirring for 2 h at ambient temperature, the homogenous yellow benzene solution was treated with moistened ether and poured into a mixture of ether and water. The ether layer was separated and the water layer twice extracted with ether. After drying the combined extracts ( $\text{MgSO}_4$ ), evaporation of the solvent yielded 780 mg of pure 1-cyclohexyl-5,5-dimethyl-2-imidazolidinethione (**3b**), yield 89%. Physical and spectral data of compounds **3** are given in Table I.

The structural assignment of compounds **3** was also supported by the <sup>13</sup>C NMR spectrum (Varian XL-100). The  $\delta$  values (ppm) of 1-isopropyl-5,5-dimethyl-2-imidazolidinethione (**3d**) in  $\text{CDCl}_3$  solution are given below (noise decoupled): 21.1 (q), 26.3 (q), 47.1 (d), 56.5 (t), 65.5 (s). The signal corresponding with the thione function was not visible. The multiplicities are derived from the partially decoupled spectrum.

**Synthesis of 2-Amino-1-isopropylamino-2-methylpropane (11).** Condensation of isopropylamine, formaldehyde, and 2-nitropropane afforded *N*-isopropyl-2-methyl-2-nitropropylamine (**10**), which was reduced by catalytic hydrogenation to 2-amino-1-isopropylamino-2-methylpropane (**11**) as previously described.<sup>13</sup>

**Preparation of 1-Isopropyl-4,4-dimethyl-2-imidazolidinethione (12).** A solution of 13.0 g (0.1 mol) of 2-amino-1-isopropylamino-2-methylpropane (**11**) in 20 mL of  $\text{H}_2\text{O}$  and 20 mL of 95% ethanol was thoroughly stirred and treated dropwise with 8.4 g (0.11 mol) of carbon disulfide over a period of 15 min. The reaction mixture was then heated under reflux in an oil bath (110 °C). After cooling in the refrigerator for 1 h, the solid material was collected by filtration, washed with a little cold acetone and dried, yielding 11.2 g of 1-isopropyl-4,4-dimethyl-2-imidazolidinethione (**12**): mp 192 °C; yield, 73%; NMR ( $\text{CDCl}_3$ )  $\delta$  1.17 [d,  $J = 7$  Hz, 6,  $(\text{CH}_3)_2\text{CH}$ ], 1.33 [s, 6,  $(\text{CH}_3)_2$ ], 3.31 (s, 2,  $\text{CH}_2\text{N}$ ), 4.83 (septet,  $J = 7$  Hz, 1,  $\text{NCHMe}_2$ ), 6.80 (s br, 1, NH); IR (KBr) 3200 ( $\nu_{\text{NH}}$ ), 1510–1450 (br, strong), 1370, 1320, 1286, 1235, 1195, 1165, 1129, 1063  $\text{cm}^{-1}$ ; mass spectrum  $m/e$  (rel abundance) 172 (M, 78), 171 (12), 157 (12), 139 (4), 130 (4), 129 (4), 115 (18), 112 (7), 100 (8), 98 (12), 83 (41), 72 (30), 58 (100), 57 (26), 56 (12), 55 (17), 43 (15), 42 (25), 41 (21).

**Reaction of 2-Imidazolidinethiones 2 and 3 with Methyl Iodide.**<sup>21,22,23</sup> In a typical experiment, 1.21 g (0.005 mol) of 1-cyclohexyl-4-methoxy-5,5-dimethyl-2-imidazolidinethione (**2b**), dissolved

in a minimum of dry acetone, was treated with 750 mg (1.05 equiv) of methyl iodide. After standing overnight at ambient temperature 1.8 g of colorless well-formed crystals of **4b** were separated by filtration, yield 93%. If little or no crystals were formed, the acetone was treated with dry diethyl ether, after which evaporation yielded hydriodides **4** or **5** in pure form. The crystals were isolated by filtration and washed with ether (see data in the microfilm edition).

**Conversion of Hydriodides 4 and 5 into Imidazolines 6 and 7.** To a mixture of 60 mL of 1 N NaOH and 50 mL of ether was added 1.0 g of hydriodide **4b**. After shaking for 2 min the ether layer was separated and the water layer twice extracted with ether. Drying of the ether (MgSO<sub>4</sub>) and evaporation in vacuo left 550 mg of a colorless oil. The purity of 1-cyclohexyl-4-methoxy-5,5-dimethyl-2-methylthioimidazoline (**6b**) was higher than 98% as revealed by NMR and VPC (see data in the microfilm edition).

**Reaction of N-1-(2-Chloro-2-ethylbutylidene)-tert-butylamine (22; R<sub>1</sub> = R<sub>2</sub> = Et) and KSCN/CH<sub>3</sub>OH.** Compound **22** (R<sub>1</sub> = R<sub>2</sub> = Et) was treated with KSCN in methanol, as described for  $\alpha$ -chloroisobutyraldimines **1**. After pouring the reaction mixture in water, extraction with ether, drying (MgSO<sub>4</sub>), and evaporation yielded a residue from which N-tert-butyl-2-ethyl-2-thiocyanobutanamide (**23**; R<sub>1</sub> = R<sub>2</sub> = Et) was isolated as a solid compound by trituration with ether/hexane: mp 126–127 °C; yield 19%; NMR (CDCl<sub>3</sub>)  $\delta$  0.87 (t, *J* = 6.2 Hz, 6, 2 CH<sub>3</sub>), 1.34 (s, 9, *t*-Bu), 1.56 (m, 4, 2 CH<sub>2</sub>), 5.49 (s br, 1, NH); IR (KBr) 3305 ( $\nu_{\text{NH}}$ ), 2065 (SCN), 1650 cm<sup>-1</sup> ( $\nu_{\text{C}=\text{O}}$ ); mass spectrum *m/e* (rel abundance) no M<sup>+</sup>, 170 (29), 156 (6), 143 (53), 142 (10), 128 (9), 116 (55), 100 (8), 99 (15), 87 (10), 86 (13), 72 (12), 71 (26), 58 (100), 57 (86), 56 (17), 55 (9), 43 (21), 41 (15).

Anal. Calcd: C, 57.86; H, 8.83; N, 12.27. Found: C, 57.99; H, 8.95; N, 12.16.

**X-Ray Crystallographic Analysis.** Well-formed colorless crystals of **4b**, obtained by recrystallization from acetone, were used for the x-ray work. Crystal data: C<sub>13</sub>H<sub>26</sub>N<sub>2</sub>OSI, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 20.462 (10), *b* = 8.659 (4), *c* = 9.847 (3) Å,  $\beta$  = 99.20 (3)°, *Z* = 4. Experimental conditions: source CuK $\alpha$ ;  $\lambda$  1.5418 Å; *w*- $2\theta$  scan;  $\theta_{\text{max}}$  = 55°; confidence level 2.5; total number of independent reflections, 2167; total observed, 1892.

The data were collected on a Syntex *P*2<sub>1</sub> diffractometer. The experimental conditions during the measurement of the intensities were given above. The structure was determined by direct methods using the MULTAN 74 program<sup>24</sup> and refined by block-diagonal least-squares calculations with the programs written by Ahmed et al.<sup>25</sup> A structure-factor calculation resulted in  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.078$  for all observed reflections. The scattering factors used are those given in the international Tables for X-Ray Crystallography.<sup>26</sup>

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**Supplementary Material Available:** positional and thermal parameters of compound **4b** (x-ray) (Table II); intramolecular bond distances and angles of compound **4b** (x-ray) (Table III); elemental analyses of 2-imidazolidinethiones **2** (Table IV); elemental analyses of 2-imidazolidinethiones **3** (Table V); full IR and MS data of 2-imidazolidinethiones **2**, **3**, and **24** (Table VI); synthesis and spectrometric

properties (IR and NMR) of compounds **4** and **5** (Table VII); synthesis and spectrometric properties (IR, NMR, and MS) of compounds **6** and **7** (Table VIII) (10 pages). Ordering information is given on any current masthead page.

**Registry No.**—**1a**, 56990-50-2; **1b**, 63364-31-8; **1c**, 63547-66-0; **1d**, 63364-30-7; **1e**, 63547-67-1; **2a**, 63547-68-2; **2b**, 63547-69-3; **2c**, 63547-70-6; **2d**, 63547-71-7; **2e**, 63547-72-8; **3a**, 63547-73-9; **3b**, 63547-74-0; **3c**, 63547-75-1; **3d**, 63547-76-2; **3e**, 63547-77-3; **4b**, 63547-78-4; **4c**, 63547-79-5; **4e**, 63547-80-8; **5d**, 63547-81-9; **5e**, 63547-82-0; **6b**, 63588-59-0; **6c**, 63547-83-1; **6e**, 63547-84-2; **7d**, 63547-85-3; **7e**, 63547-86-4; **11**, 5448-29-3; **12**, 31596-21-1; **22** (R<sub>1</sub> = R<sub>2</sub> = Et), 63364-33-0; **23** (R<sub>1</sub> = R<sub>2</sub> = Et), 63547-87-5; **24a** (R<sub>1</sub> = Et), 63547-88-6; **24a** (R<sub>1</sub> = *i*-Pr), 63547-89-7; **24b** (R<sub>1</sub> = Et), 63547-90-0; KSCN, 333-20-0; ethanol, 64-17-5; isopropyl alcohol, 67-63-0; methyl iodide, 74-88-4.

## References and Notes

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