monochromatized Mo Kα radiation (λ = 0.71073 Å). A total of 2861 reflections was collected up to 2θ = 50°, among which 2373 were observed reflections.

The crystal structure was solved by the direct method (MULTAN)[24] and refined by the full-matrix least-squares method to the R_w index of 0.065.

The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were made ride at fixed C–H bond distances (0.95 Å) with fixed thermal parameters.

All the computations were performed on a PDP 11/34 computer by using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants therein tabulated,[25] with ORTEP[26] being used for drawings.

(24) MULTAN, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (Germain, G.; Main, P.; Woolfson, M. M., *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368).

(25) SDP Plus, Version 1.0, from Enraf-Nonius, Delft, Holland, 1980.

(26) A Fortran thermal-ellipsoid-plot program for crystal-structure illustrations (Johnson, C. K. ORTEP; Oak Ridge National Laboratory: Oak Ridge, TN, 1971).

Registry No. **1a**, 115942-17-1; **1b**, 110668-29-6; **2a**, 96528-90-4; **2b**, 96528-89-1; **3**, 72358-83-9; **4**, 80639-61-8; **5**, 80639-62-9; **6**, 115942-18-2; **7**, 96563-15-4; **8**, 96563-14-3; **9a**, 607-81-8; **9b**, 41433-81-2; **10a**, 2612-30-8; **10b**, 91662-77-0; **11a**, 86103-46-0; **11b**, 96563-16-5; **12a**, 96563-18-7; **12b**, 96563-17-6; **13a**, 96563-20-1; **13b**, 96563-19-8; [Li ⊂ **1a**]$^+ClO_4^-$, 115942-20-6; [K ⊂ **1a**]$^+PF_6^-$, 115960-11-7; [Na ⊂ **1a**]$^+I^-$, 96528-95-9; [Na ⊂ **1a**]$^+Br^-$, 116003-24-8; [Na ⊂ **1a**]$^+Cl^-$, 96528-96-0; [Na ⊂ **1a**]$^+PF_6^-$, 116003-25-9; Li^+, 17341-24-1; Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8; Cs, 18459-37-5; 2-(2-chloroethoxy)ethanol, 628-89-7; *p*-toluenesulfonamide, 70-55-3; diethyl malonate, 105-53-3; hexadecyl bromide, 112-82-3; diethylene glycol bis(*p*-toluenesulfonate), 7460-82-4; benzylamine, 100-46-9; diphenylmethane, 101-81-5.

Supplementary Material Available: The fractional atomic coordinates (Table V), the anisotropic thermal factors (Table VI), and the computed positions of the hydrogen atoms for the structure of **2a** (Table VII) (6 pages). Ordering information is given on any current masthead page.

Reactions of Trimethylsilyl Isocyanate and Isothiocyanate with 3-(Dialkylamino)-2*H*-azirines. A Facile Synthesis of 1-Unsubstituted 4-(Dialkylamino)imidazolin-2-ones and 4-(Dialkylamino)imidazoline-2-thiones[1]

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Received February 9, 1988

The reaction of azirines **3a,b,d,e** with trimethylsilyl isocyanate (**4**) or isothiocyanate (**5**) gives imidazolinones **6a,b,e** and thiones **7a,b,d,e**, respectively. However, in an alternate reaction course, azirine **3c** leads to amidinium salts **9**. The potential of the products for chemical modification is shown by hydrolysis of **7a** to give **12** and by the oxidative desulfurization of **7a,d** to furnish **6a,d**.

Introduction

A variety of synthetic approaches to hydantoins and related compounds have been devised.[2] Because of the therapeutic value of some 5,5-diarylhydantoins[3] and the 2-thio analogues,[4] we report here a new approach to some 5-substituted hydantoin derivatives using the cycloadditon of 3-(dialkylamino)-2*H*-azirines **3** with trimethylsilyl isocyanate (**4**) and isothiocyanate (**5**). Previous investigations on the reaction of the highly nucleophilic azirines **3** with alkyl,[5] phenyl,[6] or tosyl isocyanate[7] or with isothiocyanates[8] had provided a host of heterocyclic systems, resulting from opening of either the 1,2- or the 1,3-bond in **3**.

(1) Part 9 in the series "Heterocyclic Ring-Closure Reactions." Part 8: Khattak, I.; Ketcham, R.; Schaumann, E.; Adiwidjaja, G.; *J. Org. Chem.* **1985**, *50*, 3431.

(2) Lopez, C. A.; Trigo, G. G. *Adv. Heterocycl. Chem.* **1985**, *38*, 177.

(3) Isaacson, E. I.; Delgado, J. N. In *Burger's Medicinal Chemistry, 4th ed.*; Wolff, M. E., Ed.; Wiley: New York; 1981; Part III.

(4) Tomkins, J. E. *J. Med. Chem.* **1986**, *29*, 855.

(5) Schaumann, E.; Grabley, S.; Adiwidjaja, G. *Justus Liebigs Ann. Chem.* **1981**, 264.

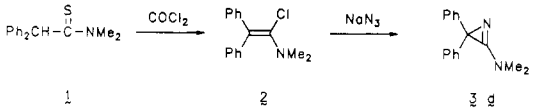
(6) Mukherjee-Müller, G.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta* **1979**, *62*, 1429.

(7) Schaumann, E.; Grabley, S. *Chem. Ber.* **1980**, *113*, 934.

(8) Schmid, U.; Heimgartner, H.; Schmid, H.; Oberhänsli, W. E.; *Helv. Chim. Acta* **1976**, *59*, 2768. Schaumann, E.; Kausch, E.; Walter, W. *Chem. Ber.* **1977**, *110*, 820.

Results and Discussion

Azirines **3a–d** were prepared from the chloro enamines and sodium azide according to the method of Ghosez.[9] The carbamoyl azirine **3e** was prepared by the photolysis of the isoxazole following Viehe's method.[10,11] Only the diphenyl azirine **3d** had not been previously reported and was prepared from thioamide **1** via the chloro enamine **2** by the following reaction sequence.



1 2 3 d

In contrast to other chloro enamines **2** and 2,2-disubstituted azirines **3** the diphenyl compounds **2**, **3d** were both solids. Azirine **3d** gave the typical IR band at 1775 cm^{-1} associated with the amidine moiety.[9] Because of its reactivity and sensitivity to moisture, the chloro enamine was not fully characterized but was reacted after distillation with sodium azide to give the azirine **3d**.

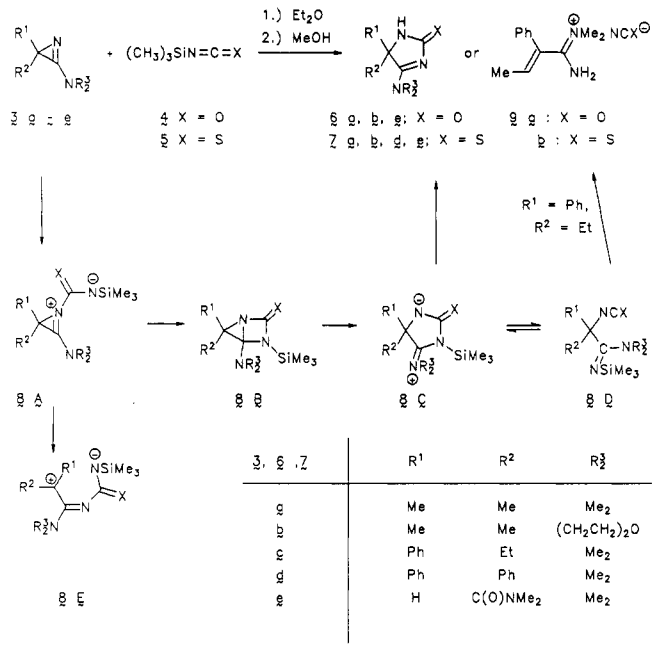
(9) Rens, M.; Ghosez, L. *Tetrahedron Lett.* **1970**, 3765. Rens, M. Dissertation, University of Louvain, 1973.

(10) De Voghel, G. J.; Eggerichs, T. L.; Clamot, B.; Viehe, H. G. *Chimia* **1976**, *30*, 191.

(11) Seybold, G.; Heibl, Ch. *Chem. Ber.* **1977**, *110*, 1225.

0022-3263/88/1953-5298$01.50/0

Scheme I



3, 6, 7	R^1	R^2	R^3_2
a	Me	Me	Me_2
b	Me	Me	$(CH_2CH_2)_2O$
c	Ph	Et	Me_2
d	Ph	Ph	Me_2
e	H	C(O)NMe_2	Me_2

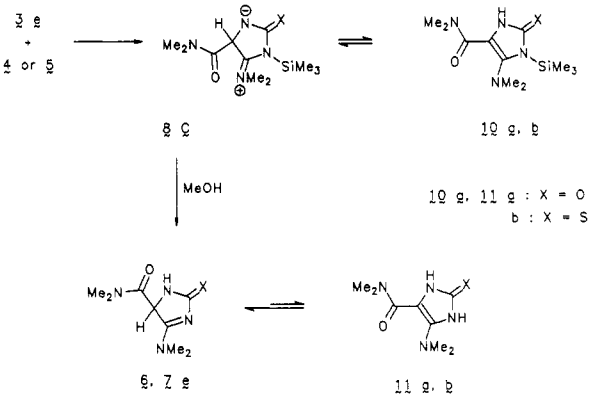
Initial experiments, using the azirines **3a,b** and the heterocumulenes **4**, **5** in the absence of a proton source, gave low yields of the expected hydrolysis products **6**, **7**, thus indicating that silylated derivatives would be difficult to isolate. For better yields, reactions of the azirine **3** with heterocumulenes were followed by methanolysis to remove the silyl group. This sequence leads to products equivalent to the reaction of **3** with isocyanic or isothiocyanic acid, which are not effective electrophiles.[12]

Trimethylsilyl isocyanate (**4**) and isothiocyanate (**5**) react rapidly with the azirines **3a,b** in ether or acetonitrile. On the basis of spectroscopic evidence and elementary analyses, the structures **6**, **7** of 4-(dialkylamino)-3-imidazoline derivatives are assigned to the products. By analogy with the reaction of **3** with phenyl[6] and tosyl isocyanate[7] or isothiocyanates,[8] zwitterion **8C** appears to be a reasonable precursor, which is solvolyzed with methanol to give products **6a,b** and **7a,b** (Scheme I). However, it should be noted that without labeling one nitrogen a mechanism involving formation of **6**, **7** via opening of the original azirine 1,2 bond in **8A** and recyclization of the resulting 1,5 dipole **8E** cannot be rigorously excluded.

In the case of 2-monosubstituted **3e**, the initial dipolar products **8C** from the cyclization should be capable of tautomerism to **10a,b**. This appears not to occur since the desilylated products obtained from methanolysis have the structure **6e**, **7e** corresponding to the desilylated **8C**, rather than the structure **11** with the potential for aromatic type resonance (Scheme II). This is evident from the ^1H NMR and ^{13}C NMR spectra of these substances (cf. Experimental Section).

It was of interest to see if the 2-aryl substituted azirine **3c** would give normal products **6**, **7** or whether as with other heterocumulenes,[13] the aryl substituent would lead to open chain compounds derived from a proton transfer in an intermediate **8E**. Isothiocyanate **5** and azirine **3c**

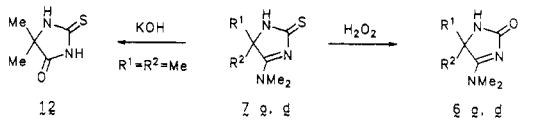
Scheme II



gave the thiocyanate salt of the open-chain crotonic acid amidine **9b**, possibly via elimination of the thiocyanic acid from the open-chain intermediate **8D** or by initial silylation of **3c** on the ring nitrogen followed by ring opening to an intermediate of type **8E** and finally desilylation and proton transfer. The reaction of isocyanate **4** with **3c** furnished the corresponding salt **9a** as indicated by the spectroscopic data.

Having made these observations regarding the effect of the phenyl substituent, it was of even greater interest to study the reactions of **4**, **5** with 2,2-diphenylazirine **3d** since it has no β proton that can be lost, although formation of an intermediate carbocation of type **8E** should be greatly facilitated. 2,2-Diphenyl-3-(dimethylamino)azirine **3d** reacted normally, though more slowly, with **5** to give the expected cyclization product **7c**. However, **3d** failed to react with isocyanate **4** under the usual reaction conditions.

The cyclization products **6a,b,e** and **7a,b,d,e**, are seen as amidino derivatives of hydantions and their 2-thio analogues. As such they are of potential interest as prodrugs or structural analogues as well as sources of hydantoins or their thio analogues by hydrolysis. Alkaline or acid hydrolysis of **7a** provided the hydantoin **12** in good yield, and the thione group of **7a** was oxidized to the carbonyl analogue **6a** with hydrogen peroxide. The same approach using **7d** allowed synthesis of **6d**, which had been inaccessible by the direct reaction of isocyanate **4** with **3d**.



Experimental Section

General Methods. Reactions were carried out at the 5–10-mmol range, and products were weighed to the closest 10 mg. Yields are given of isolated, recrystallized products. ^1H NMR spectra were taken on Bruker WP 80-FT, Varian T60, FT-80A, or EM 360 instruments in $CDCl_3$ unless otherwise indicated, and ^{13}C NMR spectra were taken on a Bruker WM 400 spectrometer. IR spectra were recorded on a Perkin-Elmer 399 spectrometer. Melting points were taken on a Seitz-Koeffler hot stage and are uncorrected. Electron impact mass spectra (70 eV) were recorded on a Varian CH7 instrument. The high-resolution mass spectrum was taken on a Kratos MS9 instrument.

2,2-Diphenyl-3-(dimethylamino)-2*H*-azirine (3d). *N,N*-Dimethyl-2,2-diphenylthioacetamide (**1**) was treated with an excess of phosgene in CH_2Cl_2 for 8 days.[9] The chloro enamine **2** was obtained as a crystalline solid in 80% yield after distillation, bp 130 °C (0.001 Torr). Reaction of the chloro enamine with NaN_3 in DMF gave **3d** in 50% yield, mp 66–68 °C: ^1H NMR δ 3.13 [s, 6 H, $N(CH_3)_2$], 7.45 (s, 10 H, C_6H_5); IR 1775 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.15; H, 6.96; N, 11.18.

(12) Schaumann, E.; Kausch, E.; Walter, W. *Chem. Ber.* **1975**, *108*, 2500.

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Reactions of 3-(Dialkylamino)-2*H*-azirines 3 with Trimethylsilyl Isocyanate (4) and Isothiocyanate (5). To a stirred solution of the azirine **3**, usually in ether, was added an etheral solution of 1 equiv of the isocyanate **4** or the isothiocyanate **5**. A small amount of oil or precipitate was formed. After the mixture was stirred for a few minutes, methanol in ether was added slowly so that the sometimes vigorous reaction progressed slowly. The crude product was collected and washed with ether.

4-(Dimethylamino)-5,5-dimethyl-3-imidazolin-2-one (6a) was recrystallized from 2-propanol: yield 78%; mp 281–285 °C; ^{1}H NMR δ 1.05 [s, 6 H, $C(CH_3)_2$], 2.98 [s, 6 H, $N(CH_3)_2$]; IR 3150 (NH), 2950, 1685 (CO), 1580 (C=N), 1300, 900 cm^{-1}. Anal. Calcd for $C_7H_{13}N_3O$: C, 54.17; H, 8.44; N, 27.07. Found: C, 54.48; H, 8.47; N, 26.70.

5,5-Dimethyl-4-(*N*-morpholino)-3-imidazolin-2-one (6b). The crude product was stirred with hot acetone followed by crystallization from butanol: mp 300–304 °C; yield 86%; ^{1}H NMR (DMSO-d_6) δ 1.50 [s, 6 H, $C(CH_3)_2$], 3.71 [s, 8 H, $(CH_2CH_2)_2$], 7.40 (s, 1 H, NH); IR 3300 (NH), 1690 (C=O), 1570 (C=N), 880 cm^{-1}. Anal. Calcd for $C_9H_{15}N_3O_2$: C, 54.81; H, 7.67; N, 21.30. Found: C, 54.98; H, 7.50; N, 21.05.

4-(Dimethylamino)-5-(dimethylcarbamoyl)-3-imidazolin-2-one (6e). Reaction of the azirine **3e** in acetonitrile at 0 °C with **4** gave **6e** in 30% yield after recrystallization from acetonitrile–ethyl ether: mp 226–228 °C; ^{1}H NMR (DMSO-d_6) δ 2.79, 3.03, 3.22, 3.39, [4 s, 12 H, 2 $N(CH_3)_2$] 5.68 (s, 1 H, CH); IR 3140 (NH), 1684 (CO), 1630, 1590 (CO) cm^{-1}; ^{13}C NMR (DMSO-d_6, assignments supported by broad-band decoupled DEPT) δ 176.23, 170.37, 165.88 (CO, C=N), 57.74 (CH), 37.86, 37.54, 37.08, 35.37 [$N(CH_3)_2$]. Anal. Calcd for $C_8H_{14}N_4O_2$: C, 48.47; H, 7.12; N, 28.27. Found: C, 48.51; H, 7.14; N, 28.34.

4-(Dimethylamino)-5,5-dimethyl-3-imidazoline-2-thione (7a) was crystallized from ethanol: yield 80%; mp 277–284 °C (lit.[14] mp 267–268 °C); ^{1}H NMR δ 9.4 (s, 1 H, NH), 3.12 [s, 6 H, $N(CH_3)_2$], 1.48 [s, 6 H, $C(CH_3)_2$]; IR (KBr) 3150 (NH), 1620 (C=N), 1495 (C—N), 1470, 1400, 1310, 1230, 1155 (C=S), 910, 890 cm^{-1}; ^{13}C NMR (100.62 MHz, DMSO, broad-band decoupled DEPT) δ 192.54 (C-2), 181.62 (C-4), 65.17 (C-5), 39.6 and 38.3 [$N(CH_3)_2$], 23.29 [$C(CH_3)_2$]; mass spectrum, *m/e* (relative intensity) 171 (M^+, 100), 156 ($M^+ - 15$, 29), 115 [$M^+ - (CH_3)_2CN$, 37], 99 [$(CH_3)_2CCHN(CH_3)_2$, 40], 71 (25).

5,5-Dimethyl-4-(*N*-morpholino)-3-imidazoline-2-thione (7b) was crystallized from ethanol: yield 69%; mp 284–289 °C; ^{1}H NMR (DMSO) δ 1.46 [s, 6 H, $C(CH_3)_2$], 3.68 [s, 8 H, $(CH_2CH_2)_2$], 9.50 (br s, 1 H, NH); ^{13}C NMR (DMSO, 60 °C) δ 192.62 (C-2), 180.68 (C-4), 65.91 (OCH_2), 64.99 (C-5), 64.67 (NCH_2), 23.45 (CH_3); IR 3130 (NH), 1572 (C=N), 1440, 1220, 1145 (C=S), 890 cm^{-1}. Anal. Calcd for $C_9H_{15}N_3OS$: C, 50.67; H, 7.09; N, 19.70; S, 15.03. Found: C, 50.87; H, 7.14; N, 19.68; S, 14.83.

4-(Dimethylamino)-5,5-diphenyl-3-imidazoline-2-thione (7d) was isolated in 26% yield after recrystallization from ethanol: mp 304 °C; ^{1}H NMR (Me_2SO-d_6) δ 2.67 and 3.20 [2 s, 3 H each, $N(CH_3)_2$], 7.22–7.29 and 7.40–7.49 (2 m, 10 H, C_6H_5); IR 3150 (NH), 1615 cm^{-1} (C=N). Anal. Calcd for $C_{17}H_{17}N_3S$: C, 68.65; H, 6.44; N, 14.13; S, 10.78. Found: C, 68.67; H, 6.02; N, 14.03; S, 10.67.

5-(Dimethylcarbamoyl)-4-(dimethylamino)-3-imidazoline-2-thione (7e). Reaction of the azirine **3e** in acetonitrile with **5** gave **7e** in 42% yield after recrystallization from acetonitrile–petroleum ether (60–70 °C): mp 220–230 °C; ^{1}H NMR (DMSO-d_6) δ 2.90, 3.09, 3.15, 3.38 [4 s, 3 H each, 2 $N(CH_3)_2$], 6.45 (s, 1 H, CH); IR 3200 (NH), 1620 (CO), 1450, 1395, 1180 cm^{-1} (C=S); ^{13}C NMR (DMSO-d_6, assignments supported by broad-band decoupled DEPT), δ 181.58 (C=S), 178.18, 163.64, (C=O, C=N), 54.10 (CH), 41.75, 40.30, 37.78, 35.59 [$N(CH_3)_2$]; mass spectrum, *m/e* (relative intensity) 214 (M^+, 100), 169 (23), 142 (46), 72 (Me_2NC=O, 83). Anal. Calcd for $C_8H_{14}N_4OS$: C, 44.84; H, 6.59; N, 26.15; S, 14.96. Found: C, 44.98; H, 6.67; N, 26.27; S, 14.95.

Reaction of 3-(Dimethylamino)-2-ethyl-2-phenyl-2*H*-azirine (3c) with 5 To Give *N,N*-Dimethyl-2-phenylcrotonamidinium Thiocyanate (9b). The product was obtained in 74% yield, mp 116.5–117.5 °C (from CH_2Cl_2). An aqueous solution gave a positive test for SCN^- with $FeCl_3$: ^{1}H NMR δ 8.35 (s, 2 H, NH_2), 7.20 (s, 5 H, C_6H_5), 6.40 (q, J = 7, 1 H, HC=), 2.90 and 3.27 [2 s, 3 H each, $N(CH_3)_2$], 1.80 (d, J = 7, 3 H, =CCH_3); ^{13}C NMR δ 163.98 (C=N), 134.04 (=*C*Ph), 133.49 (SCN^-), 132.09, 130.97, 129.12, 128.53, 125.10 (aromatic C), 40.86 and 30.07 [$N(CH_3)_2$], 15.77 (CCH_3); IR (KBr) 3320 (NH), 2080 (SCN^-), 1670 (C=C), 1620 (C=N) cm^{-1}; mass spectrum, *m/e* (relative intensity) 189 [M^+, 5.6], 188 ($M^+ - 1$, 34); 187 (25); 173 ($M^+ - NH_2$, 100), 117 (38), 115 (41), 59 (45), 44 (58). Anal. Calcd for $C_{13}H_{17}N_3S$; C, 63.12; H, 6.93; N, 16.99; S, 12.96. Found: C, 63.42; H, 6.92; N, 17.05; S, 12.78. The analogous reaction of **3c** with isocyanate **4** gave 23% of unstable cyanate **9a** (mp 176 °C dec) as indicated by the spectroscopic data: IR (KBr) 3100 (NH), 2150 (OCN^-), 1680 (sh, C=C), 1620 (C=N) cm^{-1}; ^{1}H NMR δ 7.32 (s, 5 H, C_6H_5), 6.25 (q, J = 7 Hz, 1 H, HC=), 3.05 [br s, 6 H, $N(CH_3)_2$], 1.88 (d, J = 7 Hz, 3 H, CCH_3).

4-(Dimethylamino)-5,5-dimethyl-3-imidazolin-2-one (6a) from 4-(Dimethylamino)-5,5-dimethyl-3-imidazoline-2-thione (7a). The thio compound **7a** (72 mg, 0.4 mmol) dissolved in 2 N ethanolic NaOH (0.4 mL) at 50 °C was treated with 30% H_2O_2 (0.42 mL) and stirred at 50 °C for 1 h. Dilution with water, extraction with CH_2Cl_2, and concentration followed by recrystallization from CH_2Cl_2 gave 25% of **4a**, mp 256–258 °C, identical (from IR, NMR, MS) with the product derived from **3a** and the isocyanate **4**.

The same procedure converted **7d** into **4-(dimethylamino)-5,5-diphenyl-3-imidazolin-2-one (6d)** in 30% yield (from CH_2Cl_2/ethyl acetate): mp 247–250 °C; ^{1}H NMR δ 7.37 (s, 10 H, C_6H_5), 6.72 (s, 1 H, NH exchanges with D_2O) 3.25 and 2.68 [2 s, 3 H each, $N(CH_3)_2$]; IR 3180 (NH), 1690 (CO), 1585 (C=N), 1290, 895, 700 cm^{-1}; high-resolution MS, *m/e* (relative intensity, formula) 279.1368 (12, calculated for $C_{17}H_{17}N_3O$: 279.1371), 209.0844 (60, $C_{14}H_{11}NO$), 180.0817 (100, $C_{13}H_{10}N$), 165.0702 (32, $C_{13}H_9$), 104.0501 (48, C_7H_6N). Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 72.64; H, 6.11; N, 14.96.

5,5-Dimethyl-2-thiohydantoin (12). The amino thione **7a** was hydrolyzed with methanolic KOH for 2.5 days under reflux. The acidified (HCl) reaction mixture was saturated with NaCl and extracted several times with CH_2Cl_2. Evaporation gave 51% of **12**, mp 179 °C (lit.[15] mp 178–179 °C). Hydrolysis of **7a** with 2 N HCl for 2 h under reflux gave 62% of **12**.

Acknowledgment. We gratefully acknowledge support from Fonds der Chemischen Industrie and a NATO travel grant (Grant No. 12G 83/0836). The HRMS was provided by the Mass Spectrometry Facility, University of California, San Francisco, supported by the NIH, Division of Research Resources, Grant RR 01614.

Registry No. 1, 54191-80-9; **2**, 116437-56-0; **3a**, 54856-83-6; **3b**, 66721-67-3; **3c**, 64276-78-4; **3d**, 77767-35-2; **3e**, 59566-40-4; **4**, 1118-02-1; **5**, 2290-65-5; **6a**, 73766-15-1; **6b**, 116437-57-1; **6d**, 116437-58-2; **6e**, 116437-59-3; **7a**, 61796-07-4; **7b**, 66721-76-4; **7d**, 116437-60-6; **7e**, 116466-12-7; **9a**, 116437-62-8; **9b**, 116437-63-9; **12**, 15998-93-3.

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