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A Ring Expansion Reaction of $(Me_2NCN)(NSCl)_2$ with Me_3SiNSO: Preparation of the Bicyclic Compounds $R_2NCS_3N_5$ (R = Me, Et, *i*-Pr) and X-ray Crystal Structure of the Folded Eight-Membered Ring 1,5-$Me_2NC(NSN)_2SCl$

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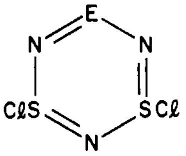
The reaction of the six-membered rings $(R_2NCN)(NSCl)_2$ (R = Me, Et, *i*-Pr) with $Me_3SiNSNSiMe_3$ or Me_3SiNSO produces the bicyclic compounds $R_2NCS_3N_5$. The latter reagent yields an additional minor product, 1,5-$Me_2NCN(NSN)_2SCl$, shown by X-ray crystallography to be a folded eight-membered ring with a transannular S–S bond, d(S–S) = 2.432 (3) Å. The crystals are monoclinic and belong to the space group $P2_1/n$, with a = 8.938 (2) Å, b = 11.947 (1) Å, c = 8.485 (1) Å, β = 91.387 (8)°, V = 905.7 (2) Å^3, and Z = 4. The final R and R_w values were 0.045 and 0.041, respectively.

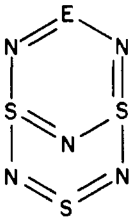
Introduction

The mixed thiazyl–cyanuric ring $(Me_2NCN)(NSCl)_2$ (**1a**) was first prepared in 7% yield by Roesky et al. via the cyclocondensation reaction of dimethylguanidine hydrochloride with $S_3N_2Cl_2$.[1] Recently, we obtained **1a–c** in much improved yields (65–90%) by the cycloaddition reaction of the appropriate dialkylcyanamide with NSCl units generated from $(NSCl)_3$ in carbon tetrachloride at ca. 65 °C,[2] thus facilitating investigations of the reactions of this bifunctional heterocycle.

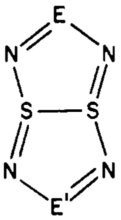
We describe here the preparation of the bicyclic derivatives **2a–c** obtained when compounds **1a–c** are treated with $Me_3SiNSNSiMe_3$. The reaction of **1a** with Me_3SiNSO also produces the bicyclic ring **2a**. In addition, however, a minor product, shown by X-ray crystallography to be the folded eight-membered ring **3a**, was isolated.[3] The structure of **3a** is compared with those of the symmetrical analogues **3b**[4] and **3c**,[5] and the mechanism of this unusual ring expansion reaction is discussed.



1a, E = Me_2NC
b, E = Et_2NC
c, E = *i*-Pr_2NC
d, E = R_2P



2a, E = Me_2NC
b, E = Et_2NC
c, E = *i*-Pr_2NC
d, E = R_2P



3a, E = Me_2NC,
E′ = SCl
b, E = E′ = Me_2NC
c, E = E′ = SCl
d, E = E′ = R_2P

Experimental Section

Reagents and General Procedures. Solvents were dried [carbon tetrachloride (P_2O_5), *n*-pentane and *n*-hexane (CaH_2), acetonitrile (CaH_2 and P_2O_5)] and freshly distilled before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen (99.99% purity). The progress of reactions with trimethylsilyl reagents was monitored by ^{1}H NMR spectroscopy. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary, and by MHW Laboratories, Phoenix, AZ.

The following reagents were prepared by literature procedures: $(R_2NCN)(NSCl)_2$ (R = Me, Et, *i*-Pr),[2] $(NSCl)_3$,[6] Me_3SiNSO,[7] and $Me_3SiNSNSiMe_3$.[8]

Instrumentation. Infrared spectra were recorded as Nujol mulls (CsI windows) on a Nicolet 5DX FT-IR spectrometer. NMR spectra were recorded on Hitachi Perkin-Elmer R-24B (routine ^{1}H) and Bruker WH-90 or Varian XL-200 (^{1}H or ^{13}C) instruments. Chemical shifts are reported in ppm downfield from Me_4Si. Mass spectra were obtained on a Kratos MS80RFA instrument (EI/70 eV).

Preparation of $Me_2NCS_3N_5$ (2a). A mixture of $(Me_2NCN)(NSCl)_2$ (1.75 g, 7.50 mmol) and $Me_3SiNSNSiMe_3$ (1.55 g, 7.50 mmol) in carbon tetrachloride (60 mL) was stirred at 23 °C. The reaction was monitored by ^{1}H NMR spectroscopy and shown to be complete after 15 h. Removal of the solvent in vacuo gave an orange solid (1.3 g), which was recrystallized from acetonitrile (25 mL) at −25 °C to give $Me_2NCS_3N_5$. Anal. Calcd for $C_3H_6N_6S_3$: C, 16.19; H, 2.69; N, 37.82. Found: C, 16.34; H, 2.67; N, 38.16. MS, *m/e* (relative intensity): 222 (0.5, M$^+$), 162 (42, $M - N_2S)^+$), 148 (49), 116 (31), 102 (37), 92 (27), 78 (60), 70 (44), 69 (75), 46 (100). NMR data are summarized in Table IV.

Preparation of $Et_2NCS_3N_5$ (2b). A mixture of $(Et_2NCN)(NSCl)_2$ (1.27 g, 4.86 mmol) and $Me_3SiNSNSiMe_3$ (1.00 g, 4.86 mmol) in carbon tetrachloride (50 mL) was stirred at 23 °C for 24 h. The red-orange solution was filtered, reduced in volume to ca. 5 mL, and treated with *n*-pentane (60 mL). After 16 h at −20 °C orange crystals of $Et_2NCS_3N_5$ (0.50 g, 2.00 mmol) were isolated by filtration. Anal. Calcd for $C_5H_{10}N_6S_3$: C, 23.93; H, 3.99; N, 33.58; S, 38.44. Found: C, 24.14; H, 4.07; N, 32.70; S, 37.29. MS, *m/e* (relative intensity): 250 (1.5, M$^+$), 190 (32, $(M - N_2S)^+$), 176 (42), 98 (32), 78 (62), 72 (61), 64 (38), 46 (100). NMR data are summarized in Table IV.

Preparation of *i*-$Pr_2NCS_3N_5$ (2c). A mixture of (*i*-$Pr_2NCN)(NSCl)_2$ (0.50 g, 1.73 mmol) and $Me_3SiNSNSiMe_3$ (0.36 g, 1.73 mmol) in *n*-pentane (50 mL) was stirred at 23 °C for 24 h. The solution was filtered and reduced in volume to ca. 10 mL. After 72 h at −20 °C orange crystals of *i*-$Pr_2NCS_3N_5$ (0.20 g, 0.72 mmol) were isolated by filtration. Anal. Calcd for $C_7H_{14}N_6S_3$: C, 30.19; H, 5.03; N, 30.20. Found: C, 31.09; H, 5.37; N, 30.05. MS, *m/e* (relative intensity): 278 (65, M$^+$), 218 (73, $(M - N_2S)^+$), 204 (100), 189 (52), 172 (18), 147 (63), 126 (57), 100 (76), 78 (70), 43 (97). NMR data are summarized in Table IV.

Reaction of $(Me_2NCN)(NSCl)_2$ with Me_3SiNSO. A mixture of $(Me_2NCN)(NSCl)_2$ (0.30 g, 1.28 mmol) and Me_3SiNSO (0.35 g, 2.56 mmol) in CCl_4 (50 mL) was stirred at 23 °C. The progress of the reaction was monitored by ^{1}H NMR spectroscopy over a period of 27 days. The resonances at 3.25 [$(Me_2NCN)(NSCl)_2$] and 0.33 ppm (Me_3SiNSO) gradually decreased, while signals at 3.03 ($Me_2NCS_3N_5$) and 0.40 ppm (Me_3SiCl) correspondingly increased in intensity. Three weaker signals at 3.17, 1.90, and 0.03 ppm ($Me_3SiNSNSiMe_3$) were also observed prior to the workup. The signal at 1.90 ppm was due to an unidentified volatile product since it disappeared on removal of solvent in vacuo from the reaction mixture. The solid residue was extracted with acetonitrile (10 mL) and cooled at −30 °C for 3 days to give yellow crystals identified as 1,5-$Me_2NC(NSN)_2SCl$ (0.10 g, 0.41 mmol) by X-ray crystallography (vide infra). IR: 1590 vs, 1408 s, 1309 s, 1244 vs, 940 vs, 893 vs, 800 m, 780 s, 690 s, 680 s, 575 m, 550 s, 485 s, 455 vs, 371 m, 344 m, and 320 s cm^{-1}. ^{1}H NMR (in $CDCl_3$): δ 3.20.

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Table I. X-ray Experimental Data for 1,5-$Me_2NC(NSN)_2SCl$

mol formula: $C_3H_6ClN_5S_3$
mol wt: 243.76
cryst system: monoclinic
space gp: $P2_1/n$ (alternate setting of $P2_1/c$, No. 14)
cell dimens
$a = 8.938\ (2)$ Å
$b = 11.947\ (1)$ Å
$c = 8.485\ (1)$ Å
$\beta = 91.387\ (8)°$
$V = 905.7\ (2)$ Å^3
$Z = 4$
$D_c = 1.79$ g cm^{-3}
radiation: Mo Kα ($\lambda = 0.71069$ Å)
monochromator: graphite
temp: 21 (1) °C
max θ: 25°
scan range, $\Delta\omega$: $1.5(0.80 + 0.347 \tan \theta)$
scan speed: 4.2–20.1° min^{-1}
octants collcd: $+h,+k,\pm l$
μ(Mo Kα): 10.34 cm^{-1}
no. of unique data: 1591
no. of obsd. data ($I > 3\sigma(I)$): 834
no. of data used in final cycle: 834
no. variables in final cycle: 110
max Δ/σ: 0.02
GOF: 0.85
residual electron density: 0.6 e Å^{-3}
isotropic extinction parameter: $5.4\ (9) \times 10^{-4}$
R, R_w:[a] 0.045, 0.041

[a] $R = \sum(||F_o| - F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Reaction of $Me_2NCS_3N_5$ with $(NSCl)_3$. A solution of $Me_2NCS_3N_5$ (0.13 g, 0.58 mmol) in carbon tetrachloride (10 mL) was added dropwise to a solution of $(NSCl)_3$ (0.14 g, 0.58 mmol) in carbon tetrachloride (15 mL) at 65 °C. After 30 min, the ^1H NMR spectrum of the reaction mixture showed a peak at δ 3.26 due to $(Me_2NCN)(NSCl)_2$ and a weaker signal at δ 2.98 attributed to unreacted $Me_2NCS_3N_5$. Removal of solvent in vacuo gave a brown solid (0.17 g) identified as $(Me_2NCN)(NSCl)_2$[1,2] containing some S_4N_4 (IR spectrum).

X-ray Analysis of 1,5-$Me_2NCN(NSN)_2SCl$. A suitable sample of approximate dimensions 0.2 × 0.3 × 0.4 mm was cut from a much longer rectangular plate and sealed under nitrogen in a glass capillary. Data were collected on an Enraf-Nonius CAD4F automated diffractometer. All experimental parameters and conditions are listed in Table I.

Space group determination and data collection procedures were as described previously.[9] The intensities of three standard reflections ($15\bar{2}$,214,$31\bar{3}$), which were measured every 1200 s of X-ray exposure time, showed a steady decrease of 10.6%. The data were corrected for this decrease by using a smoothing function.[10] Lorentz and polarization corrections were applied, but an absorption correction was not made due to the decomposition of the crystal. The structure was solved by MULTAN 78[11] followed by Fourier and least-squares techniques. The final full-matrix least-squares cycle was based on F and minimized the function $\sum w(|F_o| - |F_c|)^2$, where the weight w was defined as $[\sigma^2(F_o) + 0.0001 \cdot (F_o{}^2)]^{-1}$. H atoms were located on a difference Fourier map and included in idealized positions (sp^3, C–H = 1.00 Å) with thermal parameters set to 1.1 × B_{eq} of the C atom to which they are bonded, but not refined.

All computations were done using the XRAY-76 system of programs[10] implemented on the Honeywell computer at the University of Calgary. Atomic scattering factors used for non-hydrogen atoms were those of Cromer and Mann[12] and those for H atoms were from ref 13. Real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[14] The final atomic coordinates of the non-hydrogen atoms are given in Table II.

Table II. Positional Parameters (×10^4) and B_{eq} (×10) for the Non-Hydrogen Atoms of 1,5-$Me_2NC(NSN)_2SCl$[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2
Cl	867 (2)	2283 (2)	−380 (2)	42 (1)
S(1)	3368 (2)	4252 (2)	2025 (2)	34 (1)
S(2)	2442 (2)	2048 (2)	1675 (2)	34 (1)
S(3)	4920 (2)	3082 (2)	385 (2)	35 (1)
N(1)	2385 (6)	3187 (4)	2602 (6)	33 (3)
N(2)	4028 (6)	1942 (4)	892 (6)	32 (3)
N(3)	4220 (6)	3676 (5)	−1113 (6)	30 (3)
N(4)	2712 (6)	4829 (4)	492 (6)	30 (3)
N(5)	2305 (6)	4740 (4)	−2193 (6)	29 (3)
C(1)	3034 (8)	4381 (5)	−940 (8)	28 (3)
C(2)	2664 (8)	4342 (6)	−3745 (8)	37 (4)
C(3)	1111 (8)	5562 (6)	−2092 (8)	44 (4)

[a] Esd's are given in parentheses.

Table III. Selected IR Data for $(R_2NCN)(NSCl)_2$ and $R_2NCS_3N_5$ (cm^{-1})

	$(R_2NCN)(NSCl)_2$		$R_2NCS_3N_5$	
R	$\nu(CN_2)$	ν(S—Cl)	$\nu(CN_2)$	ν(–N=S=N–)
Me	1572 s	438 s	1537 s	1032 m 1015 m, 547 s
Et	1550 s	425 s	1514 vs	1030 s, 548 vs
i-Pr	1536 s	445 s	1496 s	1017 m, 545 s

Results and Discussion

Preparation of $R_2NCS_3N_5$ (R = Me, Et, *i*-Pr). The metathetical reaction between **1d** and $Me_3SiNSNSiMe_3$ has been successfully employed in the synthesis of bicyclic compounds of type **2d**,[15] and the structure of **2** (E = PF_2) has been established by X-ray crystallography.[16] In view of the isolobal[17] and isoelectronic relationship between RC and R_2P groups as substituents in cyclothiazenes, we set out to prepare **2a–c** from **1a–c** in an analogous manner. The reaction of **1a** with $Me_3SiNSNSiMe_3$ was monitored by ^1H NMR spectroscopy, which indicated that the expected methathesis had occurred. After 15 h at 23 °C, only two signals at 3.03 and 0.40 ppm, attributable to **2a** and Me_3SiCl, respectively, were apparent. The product **2a** was isolated in excellent yield. Compounds **2b** and **2c** were prepared in good yields in a similar manner. The products **2a–c** are formulated as bicyclic compounds on the basis of the method of synthesis, elemental analyses, and spectroscopic data (infrared, mass, and NMR spectra).

Spectroscopic Characterization of $R_2NCS_3N_5$ (R = Me, Et, *i*-Pr). As indicated in Table III the strong bands at 425–445 cm^{-1} in the IR spectra of **1a–c**,[2] attributed to ν(S–Cl), are replaced by bands at 1020–1030 (m) and ca. 545 (s) cm^{-1} in **2a–c**, which appear to be characteristic of the –N=S=N– bridge. In all three derivatives, the strong band at 1535–1570 cm^{-1}, assigned to a ring vibration $\nu(CN_2)$, is lowered in frequency by 35–40 cm^{-1} in going from **1** to **2**.

The parent ions in the mass spectra of **2a** and **2b** are weak (ca. 1%), but the isopropyl derivative, **2c**, shows a much stronger parent ion peak (65%). The loss of N_2S from the parent ions to give $R_2NCS_2N_3{}^+$ (M − 60) represents a major fragmentation pathway for **2a–c**. The same ion is also prominent in the mass spectra of **1a–c** $(M - Cl_2)^+$.[2] However, an additional strong peak corresponding to $R_2NCS_2N_2{}^+$, observed for the bicyclic derivatives **2a–c**, is not found in the mass spectra of **1a–c**. These observations indicate that the $R_2NCS_2N_2{}^+$ ion is not formed by loss of N from $R_2NCS_2N_3{}^+$. Thus it appears that the bicyclic compounds **2a–c**

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Table IV. ^1H and ^{13}C NMR Data for $(R_2NCN)(NSCl)_2$ and $R_2NCS_3N_5$ (R = Me, Et, *i*-Pr)

	^1H: δ, m, J^a			^{13}C: $\delta^{a,b}$			
	CH_3	CH_2	CH	CH_3	CH_2	CH	C(ring)^c
$(Me_2NCN)(NSCl)_2$	3.25, s			36.65			152.25
$Me_2NCS_3N_5$	3.03, s			35.87			154.87
$(Et_2NCN)(NSCl)_2$	1.28, t, 7.2	3.63, q, 7.3		13.31	42.76		151.49
$Et_2NCS_3N_5$	1.16, t, 6.6	3.47, q, 6.6		13.11	41.13		153.78
$(i\text{-}Pr_2NCN)(NSCl)_2$	1.39, d, 7.2		4.41, sep, 6.8	20.51		48.46	151.67
$i\text{-}Pr_2NCS_3N_5$	1.26, d, 7.2		4.25, sep, 7.2	20.50		45.92	153.81

^{a} δ values are in ppm downfield from Me_4Si. m, multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; sep, septet. *J* values are in Hz. ^{b} The ^{13}C chemical shifts were referenced with respect to $CDCl_3$ (δ($CDCl_3$) = δ(Me_4Si) + 77.0). ^{c} T_1 delay times of 20 s were necessary in order to observe the signal for the ring carbon atoms.

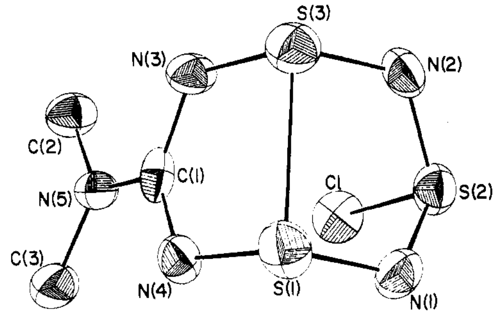

Figure 1. ORTEP plot (50% probability ellipsoids) for 1,5-$Me_2NC(NSN)_2SCl$ showing the atomic numbering scheme.

fragment by two pathways to give either five- or six-membered rings, $R_2NCS_2N_2^+$ or $R_2NCS_2N_3^+$, respectively.

The ^1H and ^{13}C NMR data for **2a–c** are compared with the corresponding parameters for **1a–c** in Table IV. The replacement of the Cl substituents on sulfur by an –N=S=N– bridge results in small upshield shifts of both the ^{13}C and ^1H signals of the dialkylamino substituents. As expected, this effect is most pronounced for the α-carbon and -hydrogen atoms. In contrast, the signal for the ring carbon atom at 150–155 ppm is deshielded by 2–3 ppm in the bicyclic derivatives compared to that in **1a–c**.

Reaction of $(Me_2NCN)(NSCl)_2$ with Me_3SiNSO. Several examples of the formation of an –N=S=N– bridge via the elimination of SO_2 from two juxtaposed thionylimino (NSO) groups have been reported.[19-22] By analogy, the reaction of **1a** with 2 molar equiv of Me_3SiNSO could provide an alternative synthesis of **2a**. This reaction proceeded very slowly at 23 °C in CCl_4. After 3 days, the ^1H NMR spectrum exhibited signals due to **2a** and Me_3SiCl that were much smaller than those attributable to **1a** and Me_3SiNSO. After 13 days the signals corresponding to **1a** and **2a**, and those due to Me_3SiNSO and Me_3SiCl, were of approximately equal intensity and an additional very weak signal appeared at +3.17 ppm. After 27 days, the ^1H NMR spectrum showed the major product to be **2a** with a smaller amount of the +3.17 ppm species. This minor product was isolated as yellow, moisture-sensitive crystals, and the structure was determined by X-ray crystallography.

Crystal and Molecular Structure of 1,5-$Me_2NC(NSN)_2SCl$. An ORTEP drawing of the molecules is shown in Figure 1. Table V contains the bond lengths and bond angles for non-hydrogen atoms in 1,5-$Me_2NC(NSN)_2SCl$. The molecule is an eight-membered ring and can be considered as a hybrid of 1,5-$Me_2NC(NSN)_2CNMe_2$ (**3b**)[4] and 1,5-$ClS(NSN)_2SCl$ (**3c**).[5] It has a similar folded structure with a cross-ring S–S distance of 2.432 (3) Å (cf. *d*(S–S) = 2.428 (5) Å in **3b** and 2.484 (1) Å in **3c**). The chlorine atom occupies an endo position with *d*(S–Cl) = 2.233 (2) Å (cf. 2.181 (1) Å in **3c**[5]). The planar geometry at C(1) and N(5) and the short C(1)–N(5) distance (1.31 (1) Å) indicate strong π-bonding between the exocyclic nitrogen and C(1). The

Table V. Bond Lengths (Å) and Angles (deg) for 1,5-$Me_2NC(NSN)_2SCl^a$

	Distances		
S(1)–S(3)	2.432 (3)	S(3)–N(3)	1.573 (5)
S(1)–N(1)	1.629 (6)	C(1)–N(3)	1.366 (9)
S(1)–N(4)	1.574 (5)	C(1)–N(4)	1.366 (8)
S(2)–Cl	2.233 (2)	C(1)–N(5)	1.305 (8)
S(2)–N(1)	1.574 (5)	N(5)–C(2)	1.445 (8)
S(2)–N(2)	1.586 (6)	N(5)–C(3)	1.455 (9)
S(3)–N(2)	1.642 (6)		
	Angles		
N(4)–S(1)–N(1)	113.5 (3)	N(2)–S(3)–S(1)	92.3 (2)
N(4)–S(1)–S(3)	89.1 (2)	N(3)–S(3)–S(1)	89.0 (2)
N(1)–S(1)–S(3)	92.4 (2)	S(3)–N(3)–C(1)	119.1 (4)
S(1)–N(1)–S(2)	120.1 (3)	N(3)–C(1)–N(4)	121.2 (6)
N(1)–S(2)–N(2)	108.6 (3)	N(3)–C(1)–N(5)	119.2 (6)
N(1)–S(2)–Cl	104.7 (2)	N(4)–C(1)–N(5)	119.0 (6)
N(2)–S(2)–Cl	103.6 (2)	C(1)–N(5)–C(2)	121.2 (6)
S(2)–N(2)–S(3)	119.2 (3)	C(1)–N(5)–C(3)	121.7 (5)
N(2)–S(3)–N(3)	113.6 (3)	C(2)–N(5)–C(3)	117.1 (5)

^{a} Esd's are given in parentheses.

five-membered CS_2N_2 ring is almost planar, the largest deviation being 0.09 Å for the carbon atom. Larger deviations from planarity are observed for the S_3N_2 ring with S(2) being 0.17 Å above and N(1) and N(3) 0.13 Å below the plane. The variation in S–N bond distances is consistent with some localization of positive charge on S(2) (cf. S_4N_5Cl[23]), but the average of 1.60 Å is similar to those found for **3b** and **3c**, 1.60[4] and 1.59 Å,[5] respectively.

Theoretical calculations at the simple Hückel,[18,24] MNDO,[25,26] and ab initio[25,27] levels have shown that there is a delicate balance between folded and planar structures (e.g. $S_4N_4^{2+}$,[28] **3** (E = E′ = CPh)[4]) for π-electron eight-membered cyclothiazenes. Electron-donating substituents favor the former. The isoelectronic cation $(CF_3CN)(SN)_3^+$ has been obtained recently by Mews et al. and found to have a planar structure.[17] It would, therefore, be of interest to determine whether planarity is retained in $(Me_2NCN)(SN)_3^+$. This cation should be readily obtained from **3a**, but it will be necessary to develop an alternative synthesis of this precursor in view of the prolonged reaction time and low yields found for the formation of **3a** from **1a** and Me_3SiNSO.

Mechanism of Formation of 1,5-$Me_2NC(NSN)_2SCl$. The major product of the reaction of **1a** with 2 mol of Me_3SiNSO is the bicyclic compound **2a**, presumably formed by the spontaneous *intramolecular* elimination of SO_2 from $(Me_2NCN)(NSNSO)_2$, the bis(thionylimino) derivative of **1a**. The creation of the minor product, **3a**, formally involves a six- to eight-membered-ring expansion reaction. We considered that **3a** might be formed by the insertion reaction of NSCl monomer with the six-membered ring,

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$(Me_2NCN)(SN)_2$, generated in situ from **2a**. To test this possibility we added a solution of **2a** in CCl_4 to a green solution of $(NSCl)_3$ in CCl_4 at 60 °C.[29] However, this reaction resulted in the dechlorination of $(NSCl)_3$ by **2a** to give S_4N_4 and **1a**. An alternative mechanism for the production of **3a** involves the formation of the monosubstituted derivative of **1a**, $(Me_2NCN)(NSCl)(NSNSO)$, which undergoes *intermolecular* elimination of SO_2 to give $RN{=}S{=}NR$ (where $R = (Me_2NCN)(NSCl)(NS)$). When $R = (Ph_2PN)_2(SN)$, this type of compound readily undergoes a six- to eight-membered-ring expansion to give a spirocyclic compound, which forms a monocyclic eight-membered ring on thermal decomposition.[30] A similar sequence of transformations could account for the formation of **3a**.[31]

Conclusions

The metathetical reaction of **1a–c** with $Me_3SiNSNSiMe_3$ gives good yields of the corresponding bicyclic derivatives, **2a–c**.[32] The same compound **2a** is formed when **1a** is treated with 2 mol of Me_3SiNSO. In the latter reaction a ring expansion to give the eight-membered ring $1,5\text{-}Me_2NC(NSN)_2SCl$ also occurs. Although the synthetic applications of this transformation are limited by the low yield and long reaction time, it may provide an initial approach to novel, ring-expanded heterocyclothiazenes from heterocyclothiazyl chlorides. The compounds **2a–c** are potential sources of the eight-π-electron six-membered rings $R_2NCS_2N_3$ via loss of N_2S on thermolysis, but the mass spectra indicate that the fragmentation of the bicyclic rings may involve more than one pathway.

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Registry No. **1a**, 85869-54-1; **1b**, 99618-21-0; **1c**, 99618-22-1; **2a**, 99618-23-2; **2b**, 99618-24-3; **2c**, 99618-25-4; **3a**, 99618-26-5; $Me_3SiNSNSiMe_3$, 18156-25-7; Me_3SiNSO, 7522-26-1; $(NSCl)_3$, 5964-00-1.

Supplementary Material Available: Tables containing anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, best planes, and observed and calculated structure factors for $1,5\text{-}Me_2NC(NSN)_2SCl$ and IR data for compounds **2a–c** (11 pages). Ordering information is given on any current masthead page.

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Gas-Phase Structures of Bis(pentafluorothio)difluoromethane and Tetrafluoro-1,3-dithietane Octafluoride

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The structures of $(SF_5)_2CF_2$ and $(SF_4CF_2)_2$ have been studied by gas electron diffraction. Very long S–C bonds (1.908 (7) Å) and a large SCS bond angle (124.3 (7)°) have been determined for $(SF_5)_2CF_2$. These results are compared to the skeletal parameters of $(SF_5)_2O$ and $(SF_5)_2NF$. A simple bonding model based on polar effects is proposed. For the cyclic $(SF_4CF_2)_2$ the SCSC four-membered ring is planar with S–C = 1.886 (4) Å, SCS = 96.2 (3)°, and CSC = 83.8 (3)°. The effects of ring formation are discussed in connection with those for the analogous oxygen and nitrogen compounds.

Introduction

Bis(pentafluorothio)difluoromethane was synthesized 30 years ago by electrochemical fluorination of carbon disulfide.[2] Recently a simple procedure, which is based on direct fluorination of CS_2 and which is suitable for high-yield preparation, was reported by Waterfeld et al.[3] From the structural point of view the skeletal parameters of $(SF_5)_2CF_2$ are interesting in comparison with those of the isoelectronic analogues, $(SF_5)_2O$ and $(SF_5)_2NF$, whose gas-phase structures have been determined previously.[4,5] Such a comparison provides information on the structural effects and steric requirements of SF_5 groups. Tetrafluoro-1,3-dithietane octafluoride has been synthesized by direct room-temperature fluorination of tetrafluoro-1,3-dithietane with chlorine monofluoride.[6] The comparison of the sulfur–carbon skeleton in the unstrained $(SF_5)_2CF_2$ with the SCSC four-membered ring in $(SF_4CF_2)_2$ provides information on the effects of ring formation. These effects can be compared to those for the nitrogen analogues $(SF_5)_2NF$ vs. $(SF_4NCl)_2$ and for the oxygen compounds $(SeF_5)_2O$ vs. $(SeF_4O)_2$. Furthermore, the structure of $(SF_4CF_2)_2$ is interesting in relation to those of other four-membered sulfur–carbon ring systems where sulfur is found in different oxidation states and with different coordination numbers.

Experimental Section

Bis(pentafluorothio)difluoromethane. $(SF_5)_2CF_2$ was prepared according to the published method.[3] It was separated from byproducts (SF_6, CF_3SF_5) by fractional condensation (−70, −100, −196 °C) under vacuum. The pure compound remained in the trap at −100 °C. The purity was checked by IR and NMR spectroscopy. The compound is stable at room temperature and inert toward acids and bases.

Tetrafluoro-1,3-dithietane Octafluoride.[6] A reaction mixture of 0.33 g (2.0 mmol) of tetrafluoro-1,3-dithietane and 22.0 mmol of ClF in a 75-mL stainless-steel bomb was held at −20 °C for 2 h. Then it was warmed to 25 °C and held there overnight. Initial separation was conducted by passing the mixture through a trap held at −40 °C. Further

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