chromatographic analyses were done in a manner similar to that described in.[1]

Acknowledgment. We are grateful to Prof. Manfred Weidenbruch of the Technical University of Aachen F.R.G. (presently at the University of Oldenburg) for providing us with a sample of *t*-Bu_3SiH. We also express gratitude to Dr. Jerzy Chruściel and Prof. Zygmunt Lasocki from Politechnika Lódzka for the gift of samples of $PhMe_2SiD$ and Et_3SiD. This was Research Project CPBP 01.13.

Registry No. $Ph_3C^+SbF_6^-$, 437-18-3; $Ph_3C^+AsF_6^-$, 437-15-0; $Ph_3C^+PF_6^-$, 437-17-2; $Ph_3C^+BF_4^-$, 341-02-6; $Ph_3C^+SbCl_6^-$, 1586-91-0; $Ph_3C^+FeCl_4^-$, 34690-18-1; $C_7H_7^+SbF_6^-$, 29630-12-4; $C_7H_7^+PF_6^-$, 29663-54-5; $C_7H_7^+BF_4^-$, 27081-10-3; Et_3SiH, 617-86-7; Et_3GeH, 1188-14-3; Me_3SiH, 993-07-7; *n*-Pr_3SiH, 998-29-8; *n*-Bu_3SiH, 998-41-4; *n*-Hex_3SiH, 2929-52-4; $PhMe_2SiH$, 766-77-8; $PhMe_2SiD$, 22034-19-1; Et_3SiD, 1631-33-0; $(CH_2)_3Si(Me)H$, 765-33-3; $EtMe_2SiH$, 758-21-4; $(CH_2)_4Si(Me)H$, 765-41-3; Et_2MeSiH, 760-32-7.

1,3-Nitrogen Shift Reaction in Sulfur–Nitrogen Chemistry. Preparation and Interconversion of *exo*- and *endo*-Trithiatetrazocines

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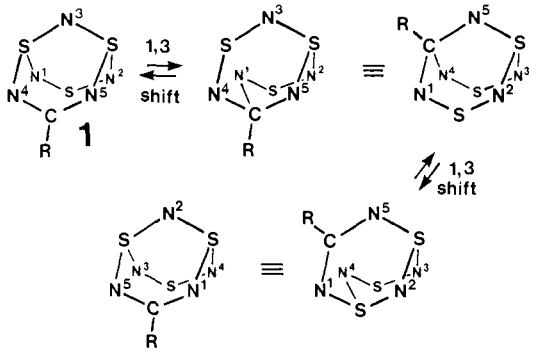
Contribution from The Guelph Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and the Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701. *Received May 20, 1987*

Abstract: The reaction of the 1,3-NSN-bridged 5-phenyl-1,3,2,4,6-dithiatriazine $PhCN_5S_3$ with tertiary phosphines [PPh_3, PCy_3, PPh_2Me, P(*o*-tol)$_3$] and triphenylarsine has been studied by ^{31}P and ^{15}N NMR spectroscopy. The mechanism of formation of the final product, the *endo*-3-imino-5-phenyl-1,3,5,2,4,6,8-trithiatetrazocines $PhCN_4S_3(NER_3)$ (E = P, As), involves the intermediacy of a rapidly formed 1-substituted 5-phenyl-1,3,2,4,6-dithiatriazine, which then transforms to either the *exo*- or *endo*-$PhCN_4S_3(NER_3)$ derivative. The exo isomer is kinetically preferred but slowly converts at room temperature to the thermodynamically more stable endo modification. The interconversion of the two isomers is suggested to occur in a stepwise process involving ring contraction (1,3-shift), ligand rotation, and ring expansion (1,3-shift). The importance of the 1,3-nitrogen shift reaction as a pathway for structural rearrangements in cyclic sulfur nitrogen systems is discussed.

Recent developments in the chemistry of heterocyclic thiazenes have provided a much clearer picture of the electronic factors that control the basic reactivity patterns of molecules containing conjugated —S=N— units.[2] Recognition of the electronic similarities between unsaturated cyclothiazenes and organic π-systems has been particularly useful and has led to the identification of several mechanistic parallels. Simple frontier orbital models, for example, successfully account for the rates and regiochemistries of olefin cycloadditions[3] and also provide insight into the stereochemistries of oxidative addition reactions.[4,5]

There remains, however, a vast array of chemistry whose mechanistic interpretation has never received any systematic analysis. Notable within this latter category are the reactions of S_4N_4 with nucleophiles (e.g., cyanide, azide, and sulfide ions, amines, phosphines, phosphinimines, diazomethanes),[6-9] which all result in cleavage of the S_4N_4 unit. Depending on the reagent involved, open-chain, cyclic, and cage species can be formed; usually a mixture of products is generated and, in the absence of any convenient and fast spectroscopic probe, the observation and characterization of the reaction intermediates represents a difficult if not impossible task.

Scheme I



In order to address these important mechanistic issues we are examining the reactivity of heterocyclic thiazenes with nucleophiles. The advantages are several. First, the mixed organic/inorganic rings are generally more kinetically stable than their purely binary sulfur–nitrogen counterparts, reacting more specifically and more slowly with nucleophiles. Second, many of these compounds can be prepared with ^{15}N labels at specific sites, a feature that allows the use of ^{15}N NMR spectroscopy as an analytical tool. The bicyclic derivative $PhCN_5S_3$ (**1**;[10,11] iso-

(1) (a) University of Guelph. (b) University of Arkansas.
(2) Oakley, R. T. *Prog. Inorg. Chem.*, in press.
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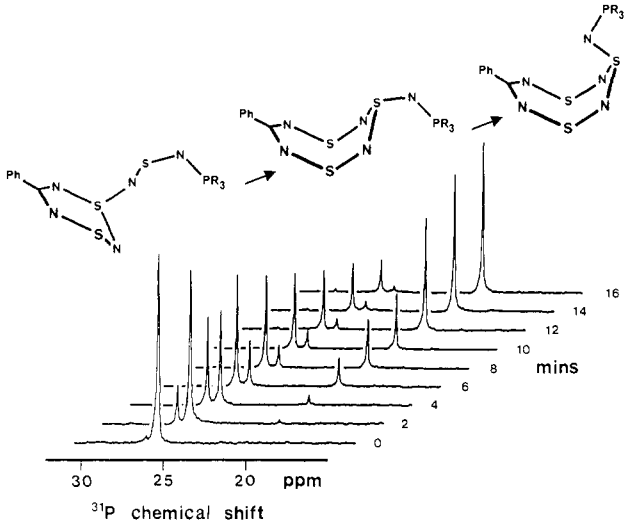
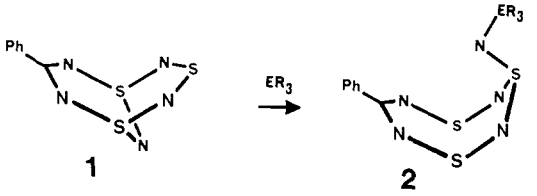


Figure 1. ^{31}P NMR spectrum (at room temperature, $CDCl_3$) of the reaction of **1** and PPh_3, showing the stepwise formation of **6a**, **3a**, and **2a** (R = phenyl).

electronic with $S_4N_5^+$)[12] represents an important example of such a system. Recently we were able to demonstrate, by using ^{15}N NMR spectroscopy on a specifically labeled sample of **1**, that the bicyclic structure is fluxional; i.e., the skeletal nitrogen atoms are exchanged in a scrambling reaction involving a series of pseudodegenerate 1,3-nitrogen shifts between two sulfur centers (Scheme I).[13]

In the present paper we focus attention on the reactions of **1** with nucleophiles, in particular tertiary arsines and phosphines R_3E (E = P, As). In contrast to the reactions of S_4N_4 with phosphines and arsines, which give rise to a complex mixture of products whose relative proportions vary with the nature of the solvent and the reaction temperature,[7] the reactions of **1** with R_3E are extremely specific, affording the corresponding 3-endo-substituted 1,3,5,2,4,6,8-trithiatetrazocines **2** (eq 1) as the sole



(1)

products.[14,15] In the hope of gaining some mechanistic insight into the overall transformation of **1** to **2**, we have carried out a detailed spectroscopic (^{15}N and ^{31}P NMR) and kinetic analysis of these reactions, the intention being to characterize the intermediates formed en route to the final product.

Results and Discussion

Reactions of 1 with Triphenylphosphine and Triphenylarsine. When carried out at room temperature, the reaction of **1** with triphenylphosphine in toluene is rapid. The color of the solution turns to red almost immediately and then slowly fades over a matter of hours to pale yellow. A yellow precipitate of the 5-endo-substituted trithiatetrazocine **2a** ($R_3E = Ph_3P$) is also formed after several minutes. X-ray crystallographic analysis of this compound has established the endo disposition of the Ph_3PN ligand and the folded conformation of the eight-membered CS_3N_4 ring.[14]

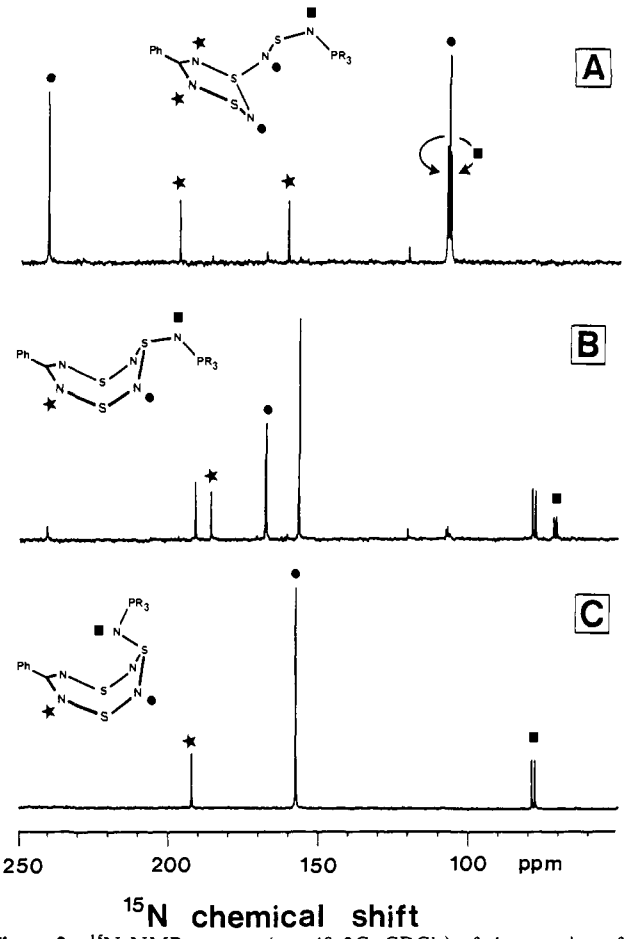
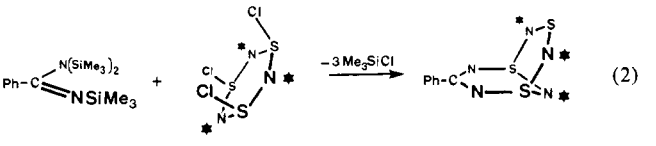


Figure 2. ^{15}N NMR spectra (at −40 °C, $CDCl_3$) of the reaction of ^{15}N-labeled **1** and PPh_3 as a function of time. Spectrum A shows pure **6a**, spectrum B a mixture of **2a** and **3a**, the spectrum C a sample of pure **2a**. For detailed assignments see Table I.

The final (isolated) yield of **2a** is extremely high. ^{31}P NMR analysis shows the reaction to be essentially quantitative; no Ph_3PS is formed when the reaction is performed at or below room temperature. However, two intermediate species can be detected in the early stages in the reaction. The growth and subsequent decay of these two intermediates are illustrated in Figure 1. The first is generated rapidly and quantitatively upon mixing the reagents at −40 °C, and at this temperature it is stable for several hours. When the solution is warmed to room temperature, another signal, corresponding to the second intermediate, slowly grows in at the expense of the first (see Figure 1). This latter species is also unstable at ambient temperatures; it converts to the final product **2a** over a matter of minutes.

Elucidation of the structures of the two intermediates has relied heavily on ^{15}N NMR spectroscopic analysis but also benefited from the serendipitous isolation of two crystalline products from the reaction of **1** with triphenylarsine.[15] Manual separation of the two types of crystals, and subsequent X-ray analysis of each, established them as the endo and exo isomers **2b** and **3b** of 3-(triphenylarsinimino)-7-phenyl-1,3,5,2,4,6,8-trithiatetrazocine.[15] The latter was readily converted into the former by warming it in acetonitrile solution. The ^{15}N NMR work was performed with **1** partially enriched with ^{15}N; this material was prepared by allowing $PhC(NSiMe_3)N(SiMe_3)_2$ to react with 99% ^{15}N-enriched $S_3N_3Cl_3$ (eq 2). The specifically labeled $PhCN_2S_3{}^*N_3$ (*N =



(2)

99% ^{15}N) so obtained was then allowed to scramble according

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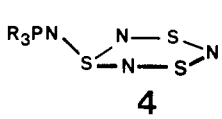
Table I. ^{15}N and ^{31}P NMR Data for **2**, **3**, and **6**[a]

		ER_3				
		PPh_3	PCy_3	PPh_2Me	$P(o\text{-tol})_3$	$AsPh_3$
6	$\delta(^{31}P)$	26.3	47.0	29.4	30.6	
	E*NS	106.8	99.9	108.2	110.0	*b*
	$^1J_{PN}$	53	55	55	57	
	C*NS	196.5	*b*	193.9	192.4	*b*
		160.3	*b*	159.8	160.5	*b*
	S*NS	106.7	99.5	106.4	103.3	*b*
		240.3	242.5	237.8	239.4	*b*
3	$\delta(^{31}P)$	27.0	48.1	29.1	32.3	
	E*NS	70.7	57.4	63.3	73.6	73.5
	$^1J_{PN}$	44	45	46	42	
	C*NS	185.7	186.2	184.8	185.4[c]	187.5
					186.0[c]	
	S*NS	167.4	168.5	169.3	167.2[d]	177.0
2	$\delta(^{31}P)$	20.9	40.7	20.1	25.8	
	E*NS	78.1	61.1	76.1	78.1	90.4
	$^1J_{PN}$	45.1	49	46	49	
	C*NS	192.3	191.7	191.3	190.2[e]	194.5
					192.6[e]	
	S*NS	157.5	158.0	156.5	158.5[f]	161.4
					154.6[f]	

[a] ^{15}N chemical shifts (at −40 °C in $CDCl_3$) in ppm, relative to $NH_3(l)$ at 25 °C. ^{31}P chemical shifts (at 22 °C in $CDCl_3$) in ppm, relative to 85% H_3PO_4. Coupling constants in hertz. [b] Too weak to be observed. [c] Barely resolved. [d] Broad line ($w_{1/2}$ = 40 Hz). [e] One sharp line at 192.3 ppm at +14 °C. [f] One sharp line at 156.9 ppm at +14 °C.

to eq 2 before being quenched by removal of the solvent. The extent of the scrambling was controlled so that the enrichment of the carbon-bound nitrogen sites was significantly less than that of the other nitrogen sites. This inhomogeneity of the ^{15}N distribution facilitated the later spectroscopic assignment of resonances belonging to carbon-bound nitrogens.

The limiting ($t = \infty$) ^{15}N NMR spectra obtained from the reactions of labeled **1** with triphenylphosphine and triphenylarsine show the same basic features (see Table I and Figure 2C). Three signals are observed, corresponding to the three distinct nitrogen environments of **2**; in the case of **2a**, assignment of the upfield signal to the exocyclic nitrogen is facilitated by the observation of a large (ca. 50-Hz) one-bond coupling to phosphorus, cf. $^1J_{PN}$ = 48.9 Hz in $Ph_3PNS_3N_3$ **4** and $^1J_{PN}$ = 43.9, 47.6 Hz in $(Ph_3PN)_2S_4N_4$ **5**).[16] The remaining two signals can be assigned



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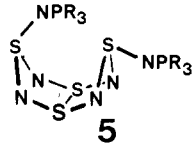
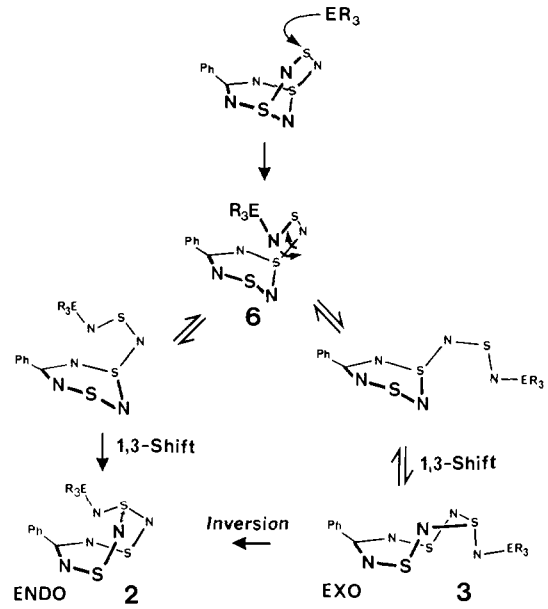


5

on the basis of their intensities; the downfield signal, whose intensity is diminished relative to the central peak, is assigned to the carbon-bound nitrogen sites.

^{15}N NMR spectra obtained from mixtures **1** and PPh_3 quenched (by freezing to −40 °C) at an earlier stage in the reaction show the presence of a new set of three signals similar in position to those of the endo isomer **2a**. These we assign, using reasoning similar to that outlined above, to the exo isomer **3a**, heretofore referred to as the second intermediate. The first intermediate, formed rapidly and specifically at −40 °C, exhibits a more complicated spectrum than either **2a** or **3a**. There are now five signals, indicative of five different nitrogen environments. We interpret this observation in terms of the six-membered dithiatriazine structure **6a**; accordingly the loss of C_s symmetry, present in **2a** and **3a**, renders the two carbon-bound nitrogens in **6a** chemically and magnetically distinct. The remaining endocyclic nitrogen and the first exocyclic nitrogen are likewise easily distinguished (although we cannot differentiate between them individually). The signal of the phosphorus- (or arsenic-) bound nitrogen appears in the region now characteristic of its environment.

Scheme II



On the basis of the above evidence, the course of the reaction between **1** and R_3E can be envisaged as shown in Scheme II. Nucleophilic attack of the phosphine (or arsine) occurs at the LUMO of the bridging NSN unit that, by analogy with the isoelectronic $S_4N_5^+$ cation, is a π^*-distribution spread over the bridging NSN fragment.[17] Following the mechanism established for the reaction of sulfur diimides with phosphines,[18] rapid migration of phosphorus from sulfur to nitrogen produces the dithiatriazine **6**. The critical step in the reaction is the subsequent ring expansion. This rearrangement, which involves a 1,3-shift of the endocyclic nitrogen between two sulfur atoms, can give rise to two stereoisomers for the final trithiatetrazocine, the exo isomer **3** or the endo isomer **2**. The kinetic preference for the formation of the exo isomer **3** vs the endo isomer **2** perhaps reflects the stereochemically less crowded conformation of **6** in which the bulky $NSNPPh_3$ ligand swings away from the six-membered ring. By contrast, formation of the endo isomer **2** requires that the $NSNPPh_3$ moiety of **6** lie above the CN_3S_2 ring.

Reactions of 1 with PR_3 (R = PPh_2Me, Cy, *o*-Tol, Mes). In order to investigate the dependence of the rates of the various steps of Scheme II on the steric bulk of the phosphine, we examined the reactions of **1** with methyldiphenylphosphine (PPh_2Me), tricyclohexylphosphine (PCy_3), tri-*o*-tolylphosphine [$P(o\text{-tol})_3$], and trimesitylphosphine [$P(Mes)_3$]. The results of this survey establish that the nucleophilic attack of phosphine on **1** is very sensitive to the steric bulk of the phosphine. Thus, PPh_2Me reacts at a rate similar to that of PPh_3, while the reactions involving PCy_3 and $P(o\text{-tol})_3$ are noticeably slower. Trimesitylphosphine fails to react at all at room temperature and causes decomposition after prolonged reflux in acetonitrile.

As a consequence of the variations in the first step of the reaction, high concentrations of **6** could only be obtained with PPh_3 and PPh_2Me. For the less reactive phosphines PCy_3 and $P(o\text{-tol})_3$, the subsequent rearrangements removed **6** almost as fast as it was formed. The exo isomer **3** could be generated in high abundance in solution with PPh_2Me and PCy_3 (70–80% and 95%, respectively), while for $P(o\text{-tol})_3$ and PPh_3 the rate of formation of the endo isomer **2** was too great to develop a reasonable concentration of **3** at any point in the reaction. ^{15}N and ^{31}P NMR data for the intermediates and final products of these reactions are given in Table I.[19]

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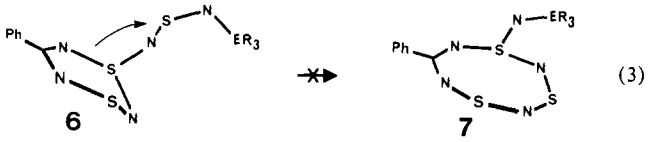
(18) Kresze, G. In *Organic Sulphur Chemistry*; Stirling, C. J. M., Ed.; Butterworths: London, 1975; p 65.

Isomerization of *exo*-$PhCN_4S_3(NPCy_3)$ (3c) to *endo*-$PhCN_4S_3(NPCy_3)$ (2c). The thermodynamic preference of trithiatetrazocines described herein for the endo geometry parallels the behavior of the corresponding 3-Cl-7-NMe_2 and 3-Cl-7-*t*-Bu derivatives[20,21] and perhaps reflects some subtle long-range interaction between the endo ligand and the transannular carbon. However, our concern in the present context is not so much the reason for the absolute preference of one structure over another as it is the mechanism by which the two isomers interconvert.

There are several pathways by which such a isomerization might proceed. One obvious possibility is an inversion process involving either the ring, the substituted sulfur atom, or a combination of both. Estimates of the activation barrier for either "pure" pathway are limited; although the potential for puckering of 10π-electron dithia- and trithiatetrazocine rings from planarity is well understood in terms of a second-order Jahn–Teller effect,[2] which repartitions electron density between the σ- and π-systems of the planar geometry, the magnitude of the effect (which defines the barrier to ring inversion) in the present system is not known. The pure sulfur inversion route is likely to be quite restrictive, at least on the basis of the (MNDO) estimated barriers (>45 kcal mol^{-1}) for sulfur inversion in S_4N_5F[17] and a variety of $S_4N_4R_2$ structures.[4]

The more plausible isomerization pathway involves a series of 1,3-shift steps and the intermediacy of **6** (Scheme II). The process begins with a 1,3-nitrogen shift, which causes a ring contraction of the exo isomer **3** to its dithiatriazine precursor **6**. Rotation of the exocyclic $NSNPR_3$ ligand of **6** and subsequent ring expansion via another 1,3-nitrogen shift then generate the endo isomer **2**. In order to gain some quantitative insight into this rearrangement, we carried out a kinetic study of the conversion of exo to endo for R = Cy, i.e., **3c** to **2c**. As indicated above, the rate of formation of exo was sufficiently fast, and its rate of isomerization sufficiently slow, to allow its isolation in a pure form. When this material was dissolved in $CDCl_3$ at temperatures ranging from 293 to 333 K, an equilibrium between the exo isomer and the ring-contracted intermediate **6c** was rapidly established (within seconds of dissolution). Generation of the endo isomer occurred far more slowly, and its rate of formation, along with the rate of decay of the exo isomer **3c** and dithiatriazine **6c**, could easily be monitored by ^{31}P NMR spectroscopy. Eyring analysis of the temperature dependence of the first-order rate constant for the conversion of **6c** to **2c** afforded activation parameters of $\Delta H^{\ddagger}$ = 16 (±1) kcal mol^{-1} and $\Delta S^{\ddagger}$ = 27 (±5) cal mol^{-1} $°C^{-1}$.[22]

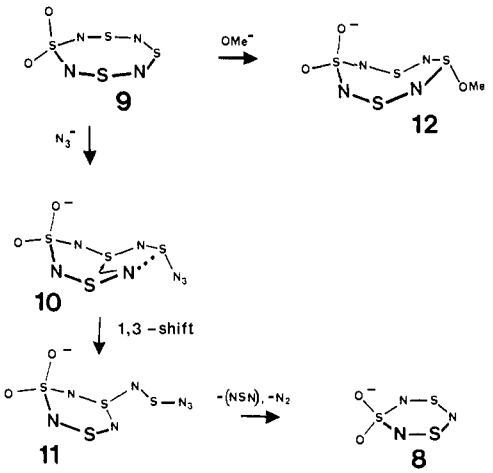
We note that ring expansion of **6** proceeds specifically to the two observed trithiatetrazocines **2** and **3** rather than the other potential structure isomer **7**. Presumably the kinetic barrier for the 1,3-shift necessary to form **7** (eq 3) is prohibitively large or, more likely, the product itself is thermodynamically less stable than either **2** or **3**.



(3)

Chemical Implications of the 1,3-Shift Mechanism. The preceding analysis of the reaction of **1** with tertiary phosphines and arsines illustrates the rapidity of interconversion of **6** to **3** via an intramolecular 1,3-nitrogen shift reaction and indicates how such a mechanism can facilitate an otherwise energetically costly configurational isomerization. This latter observation has parallels elsewhere. The fluxional behavior observed for $S_4N_4Cl_2$,[4] for example, may well be caused by a series of rapid ring expansion and contraction steps that interconvert the (thermodynamically more stable) exo–endo isomer with the (less stable) endo–endo and exo–exo structures.

Scheme III



In a broader context the 1,3-shift mechanism provides an explanation for the some of the structural changes that occur following the treatment of other sulfur nitrogen derivatives with nucleophiles. The formation of $S_3N_3O_2^-$ **8** from the reaction of $S_4N_4O_2$ **9** with azide ion (Scheme III) provides a good example.[23,24] Accordingly, the reaction can be viewed as being initiated by the attack of azide at sulfur to produce the tetrazocine derivative **10** (isoelectronic with **2** and **3**). A 1,3-nitrogen shift step then leads to the ring-contracted species **11** (cf. **6**), which spontaneously eliminates NSN[25] and dinitrogen to afford $S_3N_3O_2^-$ **8**. While there is no direct evidence for either **10** or **11**, the isolation of **12** from the reaction of $S_4N_4O_2$ with methoxide ion provides strong support for the intermediacy of **10**.[22] A similar mechanism can be invoked for the conversion of S_4N_4 to $S_3N_3^-$ in the presence of azide ion.[6]

Summary and Conclusion

The complexity of the reactions of cyclic and heterocyclic sulfur nitrogen derivatives has always provided an effective barrier to the development of a mechanism understanding of their chemistry. The results of the present study establish the 1,3-shift nitrogen shift as one important pathway by which intramolecular rearrangements can be easily effected. While considerably more experimental work needs to be done in this area, some good theoretical (quantum mechanical) calculations are also required to characterize the geometries, electronic features, and energies of the transition states for 1,3-shift reactions proposed here. It remains to be seen what qualitative analogies can be drawn between these bond migrations and the sigmatropic rearrangements observed in organic chemistry.

Experimental Section

Starting Materials and General Procedures. Triphenylphosphine (PPh_3), tri-*o*-tolylphosphine ($P(o\text{-tol})_3$), methyldiphenylphosphine (PPh_2Me), tricyclohexylphosphine (PCy_3), trimesitylphosphine ($PMes_3$), and triphenylarsine ($AsPh_3$) were obtained commercially (Aldrich) and all, save PPh_2Me, recrystallized from ethanol before use. 99% ^{15}N-labeled NH_4Cl was obtained from Merck Sharpe and Dohme. $PhCN_5S_3$ **1** was prepared as described previously from the reaction of PhC-

(19) In the case of **2e** and **3e** the two endocyclic C*NS nitrogens were heterotropic at −40 °C. We interpret this inequivalence in terms of the steric bulk of the exocyclic ligand and the consequent rotational isomerism. Similar effects have been documented in $S_4N_4(NMe_2)_2$: Roesky, H. W.; Pelz, C.; Gieren, A.; Hädicke, E. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1981**, *36B*, 1437. The data in Table I also allow a tentative assignment of the resonances in **5**. Thus, the low-field Ph_3PN signal in **5** belongs to the endo ligand; similarly, the ring nitrogens of the endo "half" of the molecule are expected to be high field of the others.

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(22) If one assumes a direct pathway for isomerization, i.e., one in which **6c** is a side equilibrium, the observed rate data provide the following activation parameters: $\Delta H^{\ddagger}$ = 12 (±1) kcal mol^{-1} and $\Delta S^{\ddagger}$ = 18 (±5) cal mol^{-1} $°C^{-1}$. Such a low barrier is inconsistent with that expected for an inversion process.

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$(NSiMe_3)N(SiMe_3)_2$[26] with $S_3N_3Cl_3$.[27] ^{15}N-Labeled material was generated from $S_3{}^*N_3Cl_3$ (*N = 99% ^{15}N), the latter being prepared as described previously;[16] the $PhCN_2{}^*N_3S_3$ so obtained was dissolved in CH_2Cl_2 and left for 30 min at room temperature in order to effect partial exchange of ^{14}N and ^{15}N nuclei. The scrambling process was halted by solvent removal. Methylene chloride was dried by distillation from P_2O_5, toluene by distillation from sodium, and acetonitrile by double distillation from P_2O_5 and CaH_2. All reactions were performed under an atmosphere of nitrogen. In the solid state the trithiatetrazocines **2** and **3** are perfectly air stable but are slowly hydrolyzed upon exposure to moisture in organic solvents. ^1H, ^{31}P, and ^{15}N NMR spectra were recorded on a Bruker WH-400 spectrometer; for the ^{15}N NMR work, 30-s pulse delays and 33-μs pulse widths were employed. Mass spectra (70 eV, EI) were obtained with a VG 7070 EF mass spectrometer, samples being admitted through conventional inlet systems. Infrared spectra were recorded on Nujol mulls (with CsI cells) with a Perkin-Elmer 1330 grating spectrophotometer. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

Preparation of *endo*-$PhCN_4S_3(NPPh_3)$ (2a, $ER_3 = PPh_3$). Triphenylphosphine (2.05 g, 7.82 mmol) and $PhCN_5S_3$ (**1**; 2.00 g, 7.83 mmol) were slurried together in 80 mL of toluene. The two reagents rapidly dissolved to produce a red solution, which slowly faded over several hours to pale yellow. The pale yellow precipitate formed during this time was filtered (in air), washed with toluene, and suction-dried to yield 3.67 g (7.1 mmol, 91%) of **2a**, recrystallized from CH_2Cl_2/CH_3CN (50/50) as yellow crystalline blocks: mp 194–196 °C; mass spectrum, *m/e* 457 (M^+, 3), 322 ($[Ph_3PNSN]^+$, 7), 308 ($[Ph_3PNS]^+$, 4), 276 ($[Ph_3PN]^+$, 100); IR (1600–250-cm^{-1} region) 1454 (s), 1457 (s), 1369 (vs), 1339 (s), 1290 (m), 1169 (m), 1148 (w), 1117 (vs), 1080 (vs), 1025 (w), 995 (w), 932 (vs), 924 (vs), 880 (m), 815 (w), 787 (vs), 766 (s), 727 (s), 723 (s), 690 (s), 665 (w), 630 (m), 604 (m), 534 (s), 527 (s), 484 (s), 450 (w), 445 (w), 435 (w). Anal. Calcd for $C_{25}H_{20}N_5PS_3$: C, 58.01; H, 3.89; N, 13.53; P, 5.98. Found: C, 57.93; H, 3.93; N, 13.52; P, 6.09.

Preparation of *endo*-$PhCN_4S_3(NPPh_2Me)$ (2d, $ER_3 = PPh_2Me$). This compound was prepared as described above, and recrystallized from CH_2Cl_2/CH_3CN (20/80): dec >165 °C; ^1H NMR ($CDCl_3$) δ 7.0–8.2 (m, aromatic, 15 H), 1.93 (d, CH_3, 3 H), $^2J_{PN}$ = 13 Hz. Anal. Calcd for $C_{20}H_{18}N_5PS_3$: C, 52.73; H, 3.98; N, 15.37; P, 6.80. Found: C, 52.81; H, 4.00; N, 15.40; P, 6.66.

Preparation of *endo*-$PhCN_4S_3(NPCy_3)$ (2c, $ER_3 = PCy_3$). This compound was prepared as described above, save that the two reagents were heated together under gentle reflux in acetonitrile. The endo isomer **2c** separated as yellow blocks on cooling the solution to room temperature; it was recrystallized from CH_2Cl_2/CH_3CN (20/80), dec >188 °C. Anal. Calcd for $C_{25}H_{38}N_5PS_3$: C, 56.05; H, 7.15; N, 13.07; P, 5.78. Found: C, 56.08; H, 7.01; N, 13.05; P, 5.83.

Preparation of *exo*-$PhCN_4S_3(NPCy_3)$ (3c, $ER_3 = PCy_3$). This isomer was prepared by mixing the reagents at room temperature in toluene. After 5 min, the red solution was placed in a freezer at −30 °C. The organge crystalline flakes so obtained were suction-filtered, washed with hexanes, and air-dried. ^{31}P NMR analysis (at −40 °C) of this solid confirmed it to be the exo isomer **3c**, dec >188 °C. Anal. Calcd for $C_{25}H_{38}N_5PS_3$: C, 56.05; H, 7.15; N, 13.07; S, 18.11. Found: C, 56.20, H, 7.11; N, 13.00; S, 18.11. When this isomer was recrystallized from CH_2Cl_2/CH_3CN (50/50), yellow blocks of the endo isomer **2** ($ER_3 = PCy_3$) were obtained.

Preparation of *endo*-$PhCN_4S_3(NP(o\text{-tol})_3)$ (2e, $ER_3 = P(o\text{-tol})_3$). Tri-*o*-tolylphosphine (0.50 g, 1.64 mmol) and $PhCN_5S_3$ (**1**; 0.42 g, 1.64 mmol) were added to 15 mL of CH_3CN, and the mixture was heated to reflux for 2 h. The mixture was then cooled to 30 °C. The dark orange blocks so obtained were suction-filtered, washed with CH_3CN, and air-dried to give 0.74 g (1.32 mmol, 80%) of **2e** ($ER_3 = P(o\text{-tol})_3$). Recrystallization from CH_2Cl_2/CH_3CN (50/50) afforded yellow blocks, dec >175 °C. Anal. Calcd for $C_{28}H_{26}N_5PS_3$: C, 60.09; H, 4.68; N, 12.51; P, 5.53. Found: C, 60.04; H, 4.59; N, 12.55; P, 5.49.

Preparation of *endo*-$PhCN_4S_3(NAsPh_3)$ (2b, $ER_3 = AsPh_3$). Triphenylarsine (2.39 g, 7.82 mmol) and $PhCN_5S_3$ (2.00 g, 7.82 mmol) were added to 10 mL of CH_3CN, and the resulting mixture was heated to reflux for 1 h. Yellow crystals of *endo*-$PhCN_4S_3(NAsPh_3)$ (**2b**; 3.81 g, 6.80 mmol, 87%), dec >163 °C, separated from the solution upon cooling to room temperature.

Preparation of *exo*-$PhCN_4S_3(NAsPh_3)$ (3b, $ER_3 = AsPh_3$). When a similar scale reaction to that described above for *endo*-$PhCN_4S_3NAsPh_3$ was carried out in 10 mL of toluene at room temperature, a mixture of orange [λ_{max} (CH_2Cl_2) 422 nm] crystals of *exo*-$PhCN_4S_3(NAsPh_3)$ (**3b**) and yellow crystals of *endo*-$PhCN_4S_3(NAsPh_3)$ (**2b**) were obtained. The former, which actually contained 1 mol of toluene as solvate, were characterized crystallographically.[15] When crystals of the exo isomer were dissolved in warm acetonitrile, they rapidly converted into the endo form, which crystallized as yellow blocks on cooling the solution to room temperature. This latter isomer was also characterized by X-ray crystallography.[15]

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Registry No. 1, 98990-56-8; **2a**, 103768-11-2; **2b**, 110798-36-2; **2c**, 110798-33-9; **2d**, 110798-34-0; **2e**, 110798-35-1; **6a**, 110798-37-3; **6c**, 110798-38-4; **6d**, 110798-39-5; **6e**, 110825-96-2; PPh_3, 603-35-0; PCy_3, 2622-14-2; PPh_2Me, 1486-28-8; $P(o\text{-tol})_3$, 6163-58-2; $AsPh_3$, 603-32-7.

Supplementary Material Available: Table S1 summarizing the kinetic data used to derive the activation parameters for the isomerization of **3c** to **2c** (1 page). Ordering information is given on any masthead page.

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