to $CH_3Br$ was 152.5:1 and the Mg to Ar ratio was 1:($10^4$–$10^5$).

Before an experiment the background pressure was below $2 \times 10^{-6}$ torr, and during an experiment it was $2 \times 10^{-5}$ to $1.5 \times 10^{-5}$ torr. Vaporization periods were long, perhaps 14 h, but during spectroscopic observations a shutter covered the KBr cold window, thereby not allowing any Mg vapor or $Ar/CH_3Br$ to contact it. During the observation times the window was rotated 90° into the UV–visible source path and was rotated back during deposition periods.

During observation by UV–visible spectroscopy, a 5-mil KBr (25 mm × 5 mm) clean window served as a reference sample. A scan from 650 to 230 nm (usually 450–240 nm) was obtained at a scan speed of 0.25 nm/s. A black cloth was used to block out all room light around the entrance of the MI unit into the spectrometer. Peak areas were determined by using an Apple computer graphic tablet.

Direct comparisons of UV–visible spectra with IR spectra were attempted but were not successful due to the very low concentrations of magnesium species in the UV–visible experiments but rather high concentrations needed for IR studies. The UV–visible spectra were the highest quality when the matrix was almost completely clear and transparent whereas good IR spectra required a deep red to black matrix, which has also been reported by Ault.[22] Table I summarizes UV–visible data for the Mg and Ca systems.

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**Registry No.** Mg, 7439-95-4; $Mg_2$, 29904-79-8; $Mg_3$, 72673-77-9; $CH_3Br$, 74-83-9; $CH_3Mg_2Br$, 92055-49-7; $CH_3Mg_3Br$, 92055-50-0.

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Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

# Reactions of $S_4N_4$ with $Ph_2PCl$, $PhPCl_2$, and $PCl_3$: Preparation of the Six-Membered Rings $(Ph_2PN)_2(NSX)$ (X = Cl, Br, I, Ph, $NR_2$) and the Related Cation $[(Ph_2PN)_2(SN)]^+$

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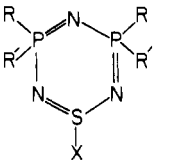
The reaction of $S_4N_4$ with $Ph_2PCl$ (1:3 molar ratio) in boiling acetonitrile produces the six-membered ring $(Ph_2PN)_2(NSCl)$ in excellent yield. The salt $[Ph_2P(Cl)N(Cl)PPh_2]^+Cl^-$ is the major product when the molar ratio is increased to 1:12. The reactions of $S_4N_4$ with $PCl_3$ or $PhPCl_2$ (1:3 molar ratio) also give heterocycles containing the $P_2SN_3$ ring. Derivatives of the type $(Ph_2PN)_2(NSX)$ (X = I, Ph, $NR_2$ (R = Me, Et, $-(CH_2)_5-$)) are obtained by treatment of $(Ph_2PN)_2(NSCl)$ with KI, $Ph_2Hg$, $Me_3SiNMe_2$, $Et_2NH$, or $C_5H_{10}NH$, respectively, in acetonitrile. The cation $[(Ph_2PN)_2(SN)]^+$ is prepared as a trihalide salt by addition of halogens ($Br_2$ or $I_2$) to $(Ph_2PN)_2(NSCl)$. Thermolysis at 155 °C or treatment with $Ph_3Sb$ converts $[(Ph_2PN)_2(SN)]^+Br_3^-$ to $(Ph_2PN)_2(NSBr)$. The halides $(Ph_2PN)_2(NSX)$ (X = Cl, Br, I) are readily hydrolyzed to $[Ph_2P(NH_2)N(NH_2)PPh_2]^+X^-$ in air.

## Introduction

As part of our investigations of the reactions of $S_4N_4$ with trivalent phosphorus reagents, e.g. $Ph_3P$,[1] $R_2PPR_2$ (R = Me, Ph),[2] and $Ph_2PH$,[3] we have now studied the reaction of $S_4N_4$ and $Ph_2PCl$ in detail. Although this reaction has not been reported previously, the reactions of $S_4N_4$ with $PCl_3$[4] and $PhPCl_2$[5] have been described. In both cases the only identified products were the salts $[RPCl_2NCl_2PR]^+Cl^-$ (R = Cl,[4] Ph[5]) and cyclophosphazenes, $(NPCl_2)_m$,[4] although the $^{31}P$ NMR spectrum of the $PhPCl_2$–$S_4N_4$ reaction mixture was very complex, suggesting the formation of additional products.

In this paper we report the full details of the preparation of the six-membered ring **1a** (X = Cl) from the reaction of $S_4N_4$ with $Ph_2PCl$.[6] We also describe the synthesis of derivatives of **1a** (X = I, Br, Ph, $NR_2$)[7] via simple substitution reactions and the formation of the cation $[(Ph_2PN)_2(SN)]^+$ by treatment of **1a** (X = Cl) with $Br_2$ or $I_2$. Finally, the reactions of $S_4N_4$ with $PCl_3$ and $PhPCl_2$ were briefly reinvestigated in the light of our results with the $Ph_2PCl$–$S_4N_4$ system.



**1a** (R = R′ = Ph)
**b** (R = Ph; R′ = Cl; X = Cl)
**c** (R = R′ = X = Cl)

## Experimental Section

**Reactions and General Procedures.** Tetrasulfur tetranitride was prepared by the standard procedure and recrystallized from toluene before use.[8] The following reagents were commercial samples: $Ph_2PCl$

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0020-1669/84/1323-3605$01.50/0 

Table I. Melting Points, Analytical Data, and $^{31}P$ NMR Chemical Shifts for $(Ph_2PN)_2(NSX)$ Derivatives and $[(Ph_2PN)_2(SN)]^+X_3^-$

| compd | mp, °C | analytical data,[a] % C | H | N | P | S | X | $\delta(^{31}P)$[b] |
|---|---|---|---|---|---|---|---|---|
| $(Ph_2PN)_2(NSCl)$ | 174–175 | 60.17 (60.06) | 4.29 (4.21) | 8.98 (8.76) | 12.59 (12.91) | | | +7.8 |
| $(Ph_2PN)_2(NSBr)\cdot MeCN$ | | 55.59 (55.00) | 4.16 (3.85) | 8.62 (8.02) | | | 16.25 (15.24) | +8.2 |
| $(Ph_2PN)_2(NSI)\cdot{}^1/_2MeCN$ | 117 dec | 50.24 (50.73) | 4.00 (3.67) | 8.39 (8.28) | 9.90 (10.46) | 5.34 (5.42) | 19.47 (21.44) | +9.9 |
| $[(Ph_2PN)_2(SN)]^+Br_3^-$ | ca. 150 dec | 42.10 (42.13) | 3.08 (2.95) | 6.24 (6.14) | | | | +9.3 |
| $[(Ph_2PN)_2(SN)]^+I_3^-$ | *c* | 37.18 (34.93) | 2.63 (2.45) | 5.45 (5.10) | | | | +9.5 |
| $(Ph_2PN)_2(NSPh)$ | 146–148 | 68.47 (69.08) | 4.75 (4.84) | 7.92 (8.06) | | | | +10.0 |
| $(Ph_2PN)_2(NSNMe_2)$ | 123–124 | 63.68 (63.91) | 5.38 (5.38) | 11.42 (11.47) | | | | +7.8 |
| $(Ph_2PN)_2(NSNEt_2)$ | 118–119 | 65.28 (65.28) | 5.89 (5.87) | 9.55 (10.85) | | | | +7.8 |
| $(Ph_2PN)_2(NSNC_5H_{10})$ | 136–138 | 65.91 (65.89) | 6.13 (5.73) | 10.59 (10.60) | | | | +7.5 |

[a] Calculated values in parentheses; X = halogen. [b] In $CDCl_3$; chemical shifts are in ppm relative to external 85% $H_3PO_4$. [c] Crystals became opaque at ca. 100 °C and decomposed at ca. 180 °C, and at 200 °C crystals of $I_2$ were observed on the cooler part of the capillary tube.

(Aldrich), $PhPCl_2$ (Aldrich), $PCl_3$ (Matheson Coleman and Bell), $Me_3SiNMe_2$ (PCR), $Ph_2Hg$ (Eastman), $Et_2NH$ (Fisher), and piperidine (Fisher). The liquid reagents and all solvents were dried and distilled before use: acetonitrile from $P_2O_5$ and $CaH_2$, methylene dichloride from $P_2O_5$, toluene from sodium, and $CDCl_3$ from $P_2O_5$. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox and silica gel. All glassware was carefully flame-dried for the reactions of $S_4N_4$ with phosphorus(III) halides.

Infrared spectra (4000–250 $cm^{-1}$) were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. Raman spectra were obtained on samples in glass capillaries by using a Jarrell-Ash Model 25-100 double monochromator calibrated with carbon tetrachloride. A Coherent Radiation CR3 argon ion laser was used to produce exciting lines at 488.0 and 514.5 nm. $^1H$ and $^{31}P$ NMR spectra were recorded with a Varian XL-200 spectrometer. $^{31}P$ NMR chemical shifts are reported relative to external 85% $H_3PO_4$. Mass spectra were obtained with a Varian CH-5 instrument operating at 70 eV. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary, and by MHW Laboratories, Phoenix, AZ. Analytical data, melting points, and $^{31}P$ NMR chemical shifts for new compounds are given in Table I.

**Reaction of Chlorodiphenylphosphine with $S_4N_4$ (3:1 Molar Ratio).** Chlorodiphenylphosphine (3.60 g, 16.3 mmol) was added dropwise (15 min) to a stirred suspension of $S_4N_4$ (1.00 g, 5.4 mmol) in acetonitrile (25 mL). The reaction mixture was heated at reflux for 3 h, and the solution changed from deep red to orange and, finally, to a yellow color. After cooling to room temperature, the solution was filtered to remove a yellow precipitate of $[S_4N_3]^+Cl^-$ (0.45 g, 2.2 mmol) identified by its IR spectrum.[9] The filtrate was stored at −20 °C for 1 day to give yellow crystals of $(Ph_2PN)_2(NSCl)$ (2.20 g, 4.6 mmol). Analytical data, the melting point and $^{31}P$ NMR data are given in Table I. IR (major bands): 1439 s, 1205 vs, 1183 s, 1160 m, 1127 vs, 1048 s, 1000 m, 728 s, 692 s, 548 vs, 513 s, 482 m, 430 m, 385 m $cm^{-1}$.

**Reaction of Chlorodiphenylphosphine with $S_4N_4$ (12:1 Molar Ratio).** Chlorodiphenylphosphine (3.60 g, 16.3 mmol) was added dropwise (5 min) to a stirred suspension of $S_4N_4$ (0.25 g, 1.4 mmol) in acetonitrile (25 mL). The reaction mixture was stirred at 23 °C for 18 h to give a pale yellow solution. Removal of solvent gave a pale yellow oil which was washed with toluene (25 mL), giving a white precipitate. After being washed with pentane (2 × 5 mL) and drying in vacuo, the product was recrystallized from acetonitrile to give $[Ph_2ClPNPClPh_2]^+Cl^-$. Anal. Calcd for $C_{24}H_{20}Cl_3NP_2$: C, 58.72; H, 4.08; N, 2.85. Found: C, 57.13; H, 3.98; N, 3.09. The $\{^1H\}^{31}P$ NMR spectrum (in $CH_2Cl_2/CDCl_3$) showed a singlet at +43.9 ppm (referenced to external 85% $H_3PO_4$; cf. lit.[10] +44.3 ppm).

**Reaction of Phenyldichlorophosphine with $S_4N_4$.** A solution of $PhPCl_2$ (2.95 g, 16.5 mmol) in acetonitrile (10 mL) was added dropwise to a stirred slurry of $S_4N_4$ (1.0 g, 5.4 mmol) in acetonitrile (20 mL) at 22 °C during 1 h. An exothermic reaction ensued, and all $S_4N_4$ had disappeared 10 min after completion of the addition. After 4 h, solvent was removed to give a thick yellow oil, which was washed with *n*-hexane (5 × 12 mL). The residue was dissolved in acetonitrile (20 mL). The hexane extract was cooled to −20 °C for 4 days to give a white solid, which was recrystallized from acetonitrile, giving almost colorless (pale yellow tinge) platelets of $[NP(Cl)Ph]_2(NSCl)$ (0.55 g). Anal. Calcd. for $C_{12}H_{10}Cl_3N_3P_2S$: C, 36.32; H, 2.52; Cl, 26.86; N, 10.59; P, 15.64; S, 8.07. Found: C, 36.66; H, 2.69; Cl, 26.59; N, 10.50; P, 15.67 (by difference); S, 7.89. A second crop (0.11 g) was obtained on further cooling of the hexane extract. On standing at 22 °C, the acetonitrile extract produced *c*-$S_8$ (0.10 g), identified by its mass spectrum.

**Reaction of Phosphorus Trichloride with $S_4N_4$.** A solution of $PCl_3$ (2.26 g, 16.5 mmol) in acetonitrile (10 mL) was added dropwise to a stirred slurry of $S_4N_4$ (1.0 g, 5.4 mmol) at 22 °C during 0.5 h. An exothermic reaction resulted in the formation of a red solution and a yellow precipitate, which subsequently redissolved with the formation of a red oil. After 20 h at 22 °C, solvent was removed from the orange solution to give a brownish yellow, moisture-sensitive oil. Treatment with *n*-pentane left a pale yellow oil whose IR spectrum contained the major bands reported for $(Cl_2PN)_2(ClSN)$.[12] The $^{31}P$ NMR spectrum of this oil (in $CH_2Cl_2$) showed major peaks at +29.7 ($SPCl_3$) and +25.0 ppm [cf. lit.[12] +24.5 ppm for $(Cl_2PN)_2(ClSN)$] in addition to smaller peaks at +31.5, +20.6, +4.1, −3.5, −20.3, and −20.7 ppm, which are likely due to salts of the type $[Cl_3P(NPCl_2)_nPCl_3]^+Cl^-$.[4,5] Attempted further purification of the oily product was unsuccessful.

**Hydrolysis of $(Ph_2PN)_2(NSCl)$.** A solution of $(Ph_2PN)_2(NSCl)$ (0.38 g, 0.8 mmol) in methylene dichloride (15 mL) containing a few drops of water was stirred at 22 °C for 4 h. Removal of solvent from the clear pale yellow solution gave a yellowish white solid identified as $[(H_2N)Ph_2PNPPh_2(NH_2)]^+Cl^-$ (0.36 g, 0.8 mmol) by comparison of its infrared and $^{31}P$ NMR spectra with those of an authentic sample.[11]

**Preparation of $(Ph_2PN)_2(NSI)$.** Finely powdered potassium iodide (0.35 g, 2.1 mmol) was added (20 min) to a stirred solution of $(Ph_2PN)_2(NSCl)$ (1.0 g, 2.1 mmol) in acetonitrile (25 mL). After 5 h at 23 °C, solvent was removed from the red solution. Addition of methylene dichloride to the residue produced potassium chloride (0.15 g, 2.0 mmol). Red crystals of $(Ph_2PN)_2(NSI)$ (0.98 g, 1.7 mmol) were obtained on cooling the filtrate to −20 °C (see Table I).

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Table II. Reactions of $S_4N_4$ with $Ph_2PCl$

| amt of $S_4N_4$, g | molar ratio $S_4N_4$:$Ph_2PCl$ | solvent (mL) | time, h/temp, °C | products isolated[a,b] precipitate | filtrate |
|---|---|---|---|---|---|
| 1.0 | 1:1 | $CH_2Cl_2$ (30) | 60/0 | $S_4N_4$ (250 mg)<br>$S_4N_3Cl$ (200 mg) | $S_4N_4$ (100 mg)<br>$(Ph_2PN)_2(NSCl)$ (400 mg) |
| 0.5 | 1:1 | $CH_3CN$ (20) | 60/22 | $S_4N_4$ (100 mg)<br>$S_4N_3Cl$ (100 mg) | $S_4N_4$ (50 mg)<br>$(Ph_2PN)_2(NSCl)$ (225 mg) |
| 0.5 | 1:1 | $C_6H_5CH_3$ (25) | 24/22 | $S_4N_3Cl$ (95 mg) | $S_4N_4$ (75 mg)<br>$(Ph_2PN)_3$ (100 mg)<br>$(Ph_2PN)_3 \cdot HCl$ (125 mg) |
| 0.5 | 1:2 | $CH_3CN$ (20) | 30/22 | $S_4N_4$ (125 mg)<br>$S_4N_3Cl$ (100 mg) | $(Ph_2PN)_2(NSCl)$ (475 mg)<br>$S_4N_4$ (25 mg)<br>$(Ph_2PN)_2(NSCl) \cdot CH_3CN$ (50 mg) |
| 2.0 | 1:3 | $CH_3CN$ (50) | 24/22 | $S_4N_3Cl$ (450 mg) | $(Ph_2PN)_2(NSCl)$ (3.2 g)<br>$(Ph_2PN)_2(NSCl) \cdot CH_3CN$ (400 mg) |
| 0.5 | 1:3 | $C_6H_5CH_3$ (25) | 24/22 | | $(Ph_2PN)_2(NSCl) \cdot CH_3CN$ (700 mg) |
| 1.0 | 1:3 | $CH_3CN$ (25) | 3/81 | $S_4N_3Cl$ (450 mg) | $(Ph_2PN)_2(NSCl)$ (2.2 g)[c] |
| 0.5 | 1:4 | $CH_3CN$ (50) | 30/22 | | $(Ph_2PN)_2(NSCl) \cdot CH_3CN$ (800 mg) |
| 0.25 | 1:4 | $CH_2Cl_2$ (15) | 96/22 | | $(Ph_2PN)_2(NSCl)$ (350 mg) |
| 0.25 | 1:12 | $CH_3CN$ (20) | 18/22 | | $[(Cl)Ph_2PNPPh_2(Cl)]^+Cl^-$ (1.4 g)[c] |

[a] The products $S_4N_4$,[8] $[S_4N_3]^+Cl^-$,[9] $(Ph_2PN)_3$,[15] $(Ph_2PN)_3 \cdot HCl$,[16] and $[(Cl)Ph_2PNPPh_2(Cl)]^+Cl^-$[10] were identified by their IR spectra. $Ph_2P(S)Cl$ was a major product in all cases ($^{31}P$ NMR spectrum). [b] The compound $(Ph_2PN)_2(NSCl)$ often contains solvent of crystallization when recrystallized from acetonitrile. The solvent can be removed by heating in vacuo at 80 °C. [c] See Experimental Section for details.

**Preparation of $(Ph_2PN)_2(NSPh)$.** Diphenylmercury (0.73 g, 2.4 mmol) was added (10 min) to a solution of $(Ph_2PN)_2(NSCl)$ (1.0 g, 2.1 mmol) in methylene dichloride (15 mL). After 24 h at 22 °C, a white precipitate of phenylmercuric chloride (0.34 g, 1.1 mmol) was removed by filtration. Cooling the filtrate to −20 °C produced more PhHgCl (0.09 g, 0.3 mmol). Solvent was removed, and the colorless residue was dissolved in acetonitrile (15 mL). White crystals of $(Ph_2PN)_2(NSPh)$ (0.65 g, 1.2 mmol) were obtained after 0.5 h at 22 °C, and a further crop (0.25 g, 0.5 mmol) crystallized out at −20 °C (see Table I).

**Preparation of $(Ph_2PN)_2(NSNMe_2)$.** An excess of $Me_3SiNMe_2$ (ca. 1 mL) was added dropwise (15 min) to a solution of $(Ph_2PN_2$-$(NSCl)$ (1.0 g, 2.1 mmol) in acetonitrile (25 mL). After 18 h at 22 °C, a small amount (0.02 g) of white crystals, subsequently identified as the dimer $(Ph_2PN)_4(NSNMe_2)_2$,[13] was removed by filtration. The filtrate was cooled to −20 °C to give white crystals of $(Ph_2PN)_2$-$(NSNMe_2)$ (0.81 g, 1.7 mmol; see Table I).

**Preparation of $(Ph_2PN)_2(NSNEt_2)$.** Diethylamine (ca. 0.5 mL) was added dropwise (10 min) to a solution of $(Ph_2PN)_2(NSCl)$ (1.1 g, 2.3 mmol) in methylene dichloride (25 mL). After 18 h at 22 °C, removal of solvent gave a reddish semisolid residue. Addition of toluene (25 mL) produced a white precipitate of $Et_2NH_2^+Cl^-$ (0.25 g, 2.3 mmol). The volume of the filtrate was reduced to 5 mL, and *n*-pentane (30 mL) was added. After 2 days at −20 °C, white crystals of $(Ph_2PN_2)_2(NSNEt_2)$ (0.58 g, 1.1 mmol) were obtained (see Table I).

**Preparation of $(Ph_2PN)_2(NSNC_5H_{10})$.** Piperidine (ca. 0.5 mL) was added dropwise (20 mm) to a solution of $(Ph_2PN)_2(NSCl)$ (1.1 g, 2.3 mmol) in methylene dichloride (5 mL). After 2.5 h at 22 °C, a white precipitate of $[C_5H_{10}NH_2]^+Cl^-$ (0.10 g) was removed by filtration. Solvent was removed from the filtrate in vacuo to give a reddish semisolid residue which was stirred with acetonitrile (25 mL) for 2 h. A mixture of $[C_5H_{10}NH_2]^+Cl^-$ (0.18 g) and $(Ph_2PN)_2$-$(NSNC_5H_{10})$ was filtered off and separated by washing with carbon tetrachloride (30 mL). The filtrate deposited colorless crystals of $(Ph_2PN)_2(NSNC_5H_{10})$ (0.60 g, 1.1 mmol) on standing at 22 °C (see Table I).

**Preparation of $[(Ph_2PN)_2(SN)]^+Br_3^-$.** A mixture of bromine (0.31 g, 1.9 mmol) and $(Ph_2PN)_2(NSCl)$ (0.46 g, 0.95 mmol) in $CH_2Cl_2$ (15 mL) was stirred at 22 °C for 3 h. Solvent was removed in vacuo, and the residue was treated with toluene (15 mL) to give an orange-red precipitate, which was recrystallized from $CH_2Cl_2$–MeCN (2:1) to give orange-red crystals of $[(Ph_2PN)_2(SN)]^+Br_3^-$ (0.56 g, 0.82 mmol) (see Table I). IR (major bands): 1437 s, 1223 sh vs, 1215 vs, 1181 s, 1129 s, 1110 vs, 1100 vs, 1085 m, 1040 s, 1032 s, 740 s, 731 s, 696 s, 545 vs, 523 m, 509 s, 378 m $cm^{-1}$.

**Preparation of $(Ph_2PN)_2(NSBr)$. (a) By Thermolysis of $[(Ph_2PN)_2(SN)]^+Br_3^-$.** A one-necked flask equipped with a side arm and containing solid $[(Ph_2PN)_2(SN)]^+Br_3^-$ (0.27 g, 0.39 mmol) was evacuated and placed in an oil bath at 135 °C. The temperature of the oil bath was increased slowly and held at 155 °C for 1 h, whereupon the crystals were observed to decompose. The solid residue was cooled to 22 °C and recrystallized from acetonitrile (15 mL). At −20 °C yellow crystals of $(Ph_2PN)_2(NSBr) \cdot MeCN$ (0.20 g, 0.35 mmol) were formed (see Table I). IR (major bands): 1437 s, 1215 vs, 1181 s, 1129 s, 1110 vs, 1085 m, 1040 s, 1032 s, 1000 m, 755 m, 740 s, 731 vs, 696 s, 545 vs, 523 m, 509 s, 378 m $cm^{-1}$.

**(b) By Reaction of $[(Ph_2PN)_2(SN)]^+Br_3^-$ with $Ph_3Sb$.** Solid $Ph_3Sb$ (0.075 g, 0.21 mmol) was added in small amounts to a stirred solution of $[(Ph_2PN)_2(SN)]^+Br_3^-$ (0.10 g, 0.15 mmol) in $CH_2Cl_2$ (15 mL) at 22 °C. The orange-red solution became yellow within 5 min. After 2 h, solvent was removed in vacuo, and the residue was treated with acetonitrile (10 mL). A yellow precipitate of $(Ph_2PN)_2(NSBr)$ (0.05 g) was removed by filtration. On cooling to −20 °C, the acetonitrile extract yielded $(Ph_2PN)_2(NSBr) \cdot MeCN$ (0.01 g) (IR spectrum identical with that obtained in part a above).

**Preparation of $[(Ph_2PN)_2(SN)]^+I_3^-$.** Crystals of iodine (2.0 g, 7.9 mmol) were added to a stirred solution of $(Ph_2PN)_2(NSCl)$ (1.9 g, 3.9 mmol) in $CH_2Cl_2$ (40 mL) at 22 °C during 15 min. After 5 h, solvent was removed from the dark red-brown solution. The solid residue was stirred with toluene (50 mL) for 2 h. The red-brown precipitate was removed by filtration and recrystallized from $CH_2Cl_2$–MeCN (3:2) at −20 °C to give red-brown, air-stable crystals of $[(Ph_2PN)_2(NS)]^+I_3^-$ (3.0 g, 3.6 mmol) (see Table I). When the molar ratio of $I_2$:$(Ph_2PN)_2(NSCl)$ was decreased to 1.5:1 or 1:1, the yield of $[(Ph_2PN)_2(NS)]^+I_3^-$ diminished to ca. 70% and 55%, respectively. IR spectrum (major bands): 1434 vs, 1240 vs, 1178 m, 1156 m, 1121 s, 1109 vs, 1100 sh s, 1090 sh s, 1064 m, 734 s, 725 s, 689 s, 540 vs, 508 s $cm^{-1}$.

## Results and Discussion

Prior to this work the only method available for the synthesis of heterocycles of type **1** was the reaction of $Me_3SiNSNSiMe_3$ with $PCl_5$.[12] This preparative route is of limited applicability, however, since other phosphorus(V) halides, e.g. $PF_5$,[17] $PhPF_4$,[17b] or $R_2PCl_3$ (R = Me, Ph),[18] produce the bicyclic compounds $R_2PS_3N_5$ on treatment with $Me_3SiNSNSiMe_3$.

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Thus it is important to point out that the reactions of $S_4N_4$ with phosphorus(III) halides, described below, represent a potentially versatile synthesis of ring systems of type **1** (cf. the wide range of derivatives known for cyclophosphazenes[15]).

**Reaction of $Ph_2PCl$ with $S_4N_4$.** The reaction of $Ph_2PCl$ with $S_4N_4$ was conducted under a variety of conditions using different solvents, a range of molar ratios (MR) of the reactants, and various temperatures (see Table II). The formation of $(Ph_2PN)_2(NSCl)$ (**1a**, X = Cl) was favored by polar solvents, and the optimum yield was obtained when a mixture of $Ph_2PCl$ and $S_4N_4$ (MR = 3:1) was heated in boiling acetonitrile for 3 h.

A proposed scheme for the $Ph_2PCl$–$S_4N_4$ reaction must also take account of the following facts: (i) $Ph_2P(S)Cl$ was a major product, (ii) $[S_4N_3]^+Cl^-$ was obtained in significant amounts in all reactions in which MR was ≤3:1, (iii) some $S_4N_4$ was recovered in those experiments in which MR was ≤2:1, and (iv) $S_2Cl_2$ was detected among the reaction products. These observations suggest the following overall stoichiometry for the reaction:

$$3S_4N_4 + 9Ph_2PCl \rightarrow 2(Ph_2PN)_2(NSCl) + 3Ph_2P(S)Cl + [S_4N_3]^+Cl^- + S_2Cl_2 \quad (1)$$

When a large excess of $Ph_2PCl$ was present (e.g. MR = 12:1), the only product isolated was $[(Ph_2(Cl)PNP(Cl)Ph_2]^+Cl^-$. In a separate experiment it was demonstrated that $(Ph_2PN_2)(NSCl)$ was completely consumed by reaction with 3 mol of $Ph_2PCl$ to give $Ph_2P(S)Cl$, $[Ph_2(Cl)PNP(Cl)Ph_2]^+Cl^-$, and two other minor phosphorus-containing products ($^{31}P$ NMR: +29.6, +21.6 ppm).

The steps involved in the formation of the heterocycle **1a** (X = Cl) are a matter of speculation. By analogy with our previous investigations of the reactions of trivalent phosphorus, e.g. $Ph_3P$[1] or $Ph_2PH$[3] with $S_4N_4$, we suggest initial nucleophilic attack by $Ph_2PCl$ at sulfur followed by migration of the substituent to nitrogen and ring opening to give $Ph_2P(Cl)NSNSNSNS$. Migration of chlorine from phosphorus to sulfur and fragmentation of this open-chain intermediate will give $(Ph_2PN)(ClSN)$, $S_4N_4$, and $c$-$S_8$ (the last two molecules will react further with $Ph_2PCl$). The first could dimerize to give molecules of the type $(Ph_2PN)_2(NSCl)_2$.[19] We have recently prepared the 1,3- and 1,5-isomers of this eight-membered ring and found the former to be unstable at room temperature with respect to loss of NSCl to give **1a** (X = Cl), while the latter is thermally stable.[20] Alternatively, the open-chain intermediate may react with $Ph_2PCl$ to give **1a** directly.

**Reactions of $S_4N_4$ with $PhPCl_2$ and $PCl_3$.** In the light of our results with the $Ph_2PCl$–$S_4N_4$ system we have reinvestigated the reactions of $S_4N_4$ with $PhPCl_2$ and $PCl_3$ in order to determine whether cyclic compounds are formed. In the earlier report of the $PhPCl_2$–$S_4N_4$ reaction a *large excess* of $PhPCl_2$ was used without solvent, and $[Ph(Cl_2)PNP(Cl_2)Ph]^+Cl^-$ was the only isolated product.[5] When we performed this reaction using a $PhPCl_2$: $S_4N_4$ molar ratio of 3:1 with MeCN as solvent at 23 °C, a very moisture-sensitive white crystalline solid that analyzed well for $[NP(Cl)Ph]_2(NSCl)$ (**1b**) was obtained. The base peak in the mass spectrum at $m/e$ 360 can be attributed to the ion $[[NP(^{35}Cl)Ph]_2(NS)]^+$ (cf. the base peak at $m/e$ 44 due to $[(Ph_2PN)_2(SN)]^+$ in the mass spectra of **1a** (X = Cl, Br, I)).

The $^{31}P$ NMR spectrum of the product of the $PhPCl_2$–$S_4N_4$ reaction at −50 °C (in *sym*-$C_2H_2Cl_4$) showed four sharp singlets at +30.4, +29.4, +26.3, and +23.0 ppm with approximate relative intensities of 1:3:2:6. As the temperature of the NMR sample is increased, these signals broaden until at +80 °C two singlets at +28.5 and +24.5 ppm, approximately equal in intensity, are observed. This change is reversible. An interpretation of the NMR data in terms of the expected isomers for **1b** is not apparent,[21] and it is possible that the spectral observations are complicated by the tendency of heterocycles of type **1** to undergo ionization of the sulfur–halogen bond.[22] The use of a substituted aryldichlorophosphine, e.g. $p$-$CH_3C_6H_4PCl_2$ or $p$-$FC_6H_4PCl_2$, for the reaction with $S_4N_4$ would provide an additional NMR probe that may help to identify the isomers.

The reaction of $PCl_3$ with $S_4N_4$ (3:1 moarl ratio) in acetonitrile produced **1c** as an oil that could not be purified satisfactorily.

**Substitution Reactions of $(Ph_2PN)_2(NSCl)$.** In preliminary reports we have described some facile ring-opening reactions of $(Ph_2PN)_2(NSCl)$ that occur via S–N bond cleavage under the influence of mild reducing agents, e.g. $Ph_3Sb$,[23] or nucleophiles, e.g. $Me_3SiNSNSiMe_3$.[6] With weak nucleophiles, e.g. $Ph_2Hg$ or $I^-$, however, simple substitution of the exocyclic substituent on sulfur can be effected in high yield. The bromide (**1a**; X = Br) cannot be prepared in this way, but it is obtained in excellent yields from $[(Ph_2PN)_2(SN)]^+Br_3^-$ on being heated to ca. 155 °C or by treatment with $Ph_3Sb$ in acetonitrile (vide infra). The halides (**1a**; X = Cl, Br, I) are all moisture-sensitive crystalline solids, that produce $[H_2NPh_2PNPPh_2NH_2]^+X^-$ on hydrolysis. Preliminary results indicate that the iodide is considerably less reactive than the chloride. For example, no reaction was observed when $(Ph_2PN)_2(NSI)$ was treated with $Me_3SiNSNSiMe_3$ or $Ph_3Sb$ in acetonitrile at room temperature. The phenyl derivative $(Ph_2PN)_2(NSPh)$ is stable toward moisture and exhibits high thermal stability (no decomposition after 1 h at 220 °C).

Secondary amines and (dialkylamino)trimethylsilane react readily with $(Ph_2PN)_2(NSCl)$ to give $(Ph_2PN)_2(NSNR_2)$ (R = Me, Et, $-(CH_2)_5-$) as white crystalline solids that have a strong tendency to undergo a ring-opening dimerization at room temperature in acetonitrile to give the 12-membered rings $(Ph_2PN)_4(NSNR_2)_2$.[13]

**Preparation of the Cation $[(Ph_2PN)_2(SN)]^+$.** The reaction of **1a** (X = Cl) with halogens produces the cation $[(Ph_2PN)_2(SN)]^+$ as trihalide salts (**2**) that undergo thermal

$$\underset{\textbf{1a}}{2(Ph_2PN)_2(NSCl)} + 3X_2 \xrightarrow{-Cl_2} \underset{\textbf{2}}{2[(Ph_2PN)_2(SN)]^+X_3^-} \xrightarrow[\text{or } Ph_3Sb]{\Delta} 2(Ph_2PN)_2(NSX) + X_2 \text{ (or } (Ph_3SbX_2))$$

X = Br, I

decomposition at ca. 150 °C (X = Br) with loss of a halogen molecule to give the corresponding halide (**1a**; X = Br, I).[24] The presence of $X_3^-$ ions was confirmed by observation of the characteristic $\nu_1$ vibration at 163 $cm^{-1}$ (X = Br) or 110 $cm^{-1}$ (X = I) in their Raman spectra.[25] Unlike the corresponding

(19) Roesky et al.[12] have proposed that a related eight-membered ring $(Cl_2PN)_2(ClSN)_2$ is an intermediate in the formation of **1c** from $PCl_5$ and $Me_3SiNSNSiMe_3$.

(20) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.

(21) Since the Cl bound to sulfur in **1a** projects above the ring, four isomers are possible for **1b**: a pair of structural isomers in which either both Ph substituents or both Cl substituents (on phosphorus) are on the same side of the ring as the S–Cl bond and a pair of optical isomers in which on Ph and one Cl substituent on each phosphorus are on the same side of the ring.

(22) The long S–Cl bond observed for **1a** (2.357 (2) Å)[6] and recent electrochemical data provide evidence in support of this contention: Chivers, T.; Hojo, M., unpublished results.

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(24) Similar thermal decompositions have been reported for $[S_4N_3]^+X_3^-$ (X = Br or I): Vincent, H.; Monteil, Y.; Berthet, M. P. *J. Inorg. Nucl. Chem.* **1980**, *42*.

halo derivatives, $(Ph_2PN)_2(NSX)$, which are very readily hydrolyzed by moisture (vide supra), the trihalide salts can be handled in air for long periods of time without hydrolysis occurring (infrared spectra). The salts **2** have also been prepared by the reaction of the 12-membered ring $(Ph_2PN)_4(SN)_2$ with halogens and by thermolysis of the 12-membered dication $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2$, whose structure has been established by X-ray crystallography.[20]

## Conclusion

The reaction of $S_4N_4$ with phosphorus(III) chlorides in acetonitrile provides a versatile synthesis of heterocycles containing the $P_2SN_3$ ring. The monofunctional heterocycle **1a** (X = Cl), obtained in excellent yield by this route, undergoes a number of simple substitution reactions with nucleophiles. The preparation of other halo derivatives of this ring system (**1a**; X = Br, I) provides an unusual opportunity to compare the reactivity of sulfur-halogen bonds in similar chemical environments. The structures of **1a** (X = Cl, I, Ph, $NMe_2$) and the tendency for ring-opening reactions to occur via S-N bond cleavage will be discussed in the context of the $\pi$-electronic structure of the $P_2SN_3$ ring in a subsequent paper.

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**Registry No.** **1a** (X = Cl), 84247-67-6; **1a** (X = Br), 90133-26-9; **1a** (X = I), 88008-07-5; **1a** (X = Ph), 91948-83-3; **1a** (X = $NMe_2$), 88008-11-1; **1a** (X = $NEt_2$), 89746-70-3; **1a** (X = $NC_5H_{10}$), 91948-84-4; **1b**, 91948-86-6; **1c**, 38595-77-6; $[(Ph_2PN)_2(SN)]^+Br_3^-$, 90133-25-8; $[(Ph_2PN)_2(SN)]^+I_3^-$, 91948-82-2; $[Ph_2ClPNPClPh_2]^+Cl^-$, 31239-04-0; $[Ph(Cl_2)PNP(Cl_2)Ph]^+Cl^-$, 91948-85-5; $[(H_2N)Ph_2PNPPh_2(NH_2)]^+Cl^-$, 2960-45-4; $S_4N_4$, 28950-34-7; $Ph_2PCl$, 1079-66-9; $PhPCl_2$, 644-97-3; $PCl_3$, 7719-12-2.

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# Photochemical Reduction of the Uranyl Ion with Dialkyl Sulfides

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The photochemical reduction of the uranyl ion by diethyl, di-*n*-propyl, and di-*n*-butyl sulfides has been investigated in acidified water-acetone medium by using radiations in the visible region (≥365 nm) from a medium-pressure mercury lamp. The photoreduction is independent of temperature. The quantum yield increases with an increase in dialkyl sulfide or hydrogen ion concentration. The plots of the reciprocal of the quantum yield vs. the reciprocal of initial dialkyl sulfide concentration are linear with intercepts on the ordinate axis. Stern-Volmer quenching constants have been calculated from luminescence measurements. It has been found that physical and chemical quenchings compete with each other. Electronic absorption spectra reveal that there is no ground-state interaction between the uranyl ion and the dialkyl sulfide. On the basis of product analysis, quantum yield of uranium(IV) formation, and Stern-Volmer quenching constants, a dynamic mechanism of oxygen atom transfer from the excited uranyl ion to dialkyl sulfide has been proposed.

## Introduction

The photochemistry of the uranyl ion has received considerable attention owing to its characteristic luminescence and power to photooxidize a variety of organic substrates and inorganic ions.[1-3] Both intra- and intermolecular mechanisms have been proposed.[1,3] The most important reactions of the photoexcited uranyl ion appear to be oxidations of substrates either by hydrogen abstraction[4-7] or by electron transfer.[8-11] The uranyl ion can also photosensitize certain processes by energy transfer[12] or by electron transfer.[13] Matsushima[14,15] has proposed an excited-state electron transfer process in the quenching of uranyl luminescence by aromatic hydrocarbons, without formation of any final redox product.

In earlier communications it has been reported that the photochemical reduction of the uranyl ion with triphenylarsine,[16a] triphenylantimony,[16b] triphenylphosphine,[16c] and triphenylbismuth[16d] proceeds via oxygen atom transfer, whereas a mechanism based on $\alpha$-hydrogen abstraction has been proposed for the photoreduction of uranyl ion with alkanenitriles.[17] In the present investigation, the photochemical reduction of uranyl ion with diethyl, di-*n*-propyl, and di-*n*-butyl sulfides has been studied.

## Experimental Section

Uranyl acetate (BDH AnalaR) was used as received. Diethyl sulfide, di-*n*-propyl sulfide, and di-*n*-butyl sulfide were prepared and purified as reported in the literature.[18] Sulfuric acid and acetone (both BDH AnalaR) were used without further purification. Deionized and doubly distilled water was used.

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