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Reactions of S_4N_4 with Tertiary Phosphines—Synthesis of Phosphiniminocyclothiazenes and Their Reactions†

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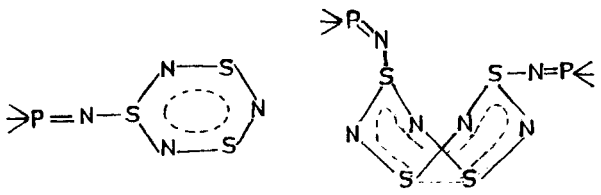
ABSTRACT

*The reactions of S_4N_4 with phosphines of the type $PhPR_2$ (**1–5**) and PhR′PR [**6–11** (R′ = dicyclohexylamino), R: **1,6** = pyrrolidino; **2,7** = piperidino; **3,8** = morpholino; **4,9** = N-methylpiperazino; **5,10** = hexamethylenimino; and **11** = anilino] afford the phosphiniminocyclotrithiazene derivatives, **12–22** at room temperature. Only in the case of the phosphine **10** was the disubstituted derivative **23** isolated (in 65% yield). The trithiazene derivatives of the chiral phosphines in refluxing CH_3CN produce the acyclic compounds $\rightarrow PN–S_3N$, **24–27** in ca. 60% yield. Norbornadiene reacts at room temperature with the cyclotrithiazene derivatives to give the addition products **28–35**. $\rightarrow P=N–S_3N_3$ derivatives are found to be stable in 2M NaOH. © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8**: 225–232, 1997.*

INTRODUCTION

In our earlier publications, we have reported the reactions of tetrasulfur tetranitride S_4N_4, with phosphines of the type R_3P [1] and Ph_2PR [2,3], where R is a cyclic secondary amino substituent. Whereas the compounds of type **A** are produced in all these reactions, compounds of type **B** are isolated only from the reactions with Ph_2PR. It was not clear to us whether this difference in the behavior is due to the increased number of amino substituents in the case of R_3P or the unsymmetrical nature of Ph_2PR.



A B

This has prompted us to undertake a study of such reactions with phosphines of type $PhPR_2$, where R is the same cyclic secondary amino group. Such a study also offered a basis for comparison of the reactions of S_4N_4 with sets of phosphines of type Ph_xPR_{3-x} (x = 0, 1, 2, and 3). In this regard, we have also considered it of interest to investigate the reactions of S_4N_4 with chiral phosphines, PhR′PR (R′ = dicyclohexylamino) that we have recently prepared [4]. In this article, we have discussed our results on (1) the study of the reactions of S_4N_4 with several new phosphines of type $PhPR_2$ (**1–5**) and Ph(DCA)PR (**6–11**) [4]; (2) the characterization of all the new compounds; and (3) some reactions of the cyclothiazene products isolated in this study.

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RESULTS AND DISCUSSION

Reactions with $PhPR_2$

All of the phosphines, **1–5**, produced the trithiazene derivatives as dark red crystalline solids in addition to the corresponding phosphine sulfides according to the following equation:

$$\underset{\textbf{1–5}}{2PhPR_2} \rightarrow PhR_2PN\text{-}S_3N_3 + PhR_2PS \quad (1)$$

12 R = pyrrolidino
13 R = piperidino
14 R = morpholino
15 R = N-methylpiperazino
16 R = hexamethylenimino

Excepting the case of **14**, the yields of the cyclotrithiazene derivatives vary in the range of 55–70%. For reasons unknown, considerable difficulty was experienced in the isolation of **14**. However, a reaction performed only in benzene–hexane (1:1) solution led to its easy isolation.

The molar ratios of the phosphines to S_4N_4 should be between 2 and 3 to isolate the cyclotrithiazene derivative in the maximum yield. Higher molar ratio reactions, performed at low temperature did not produce the 1,5-disubstituted tetrasulfur tetranitride derivative (analog of **B**). Also, the reactions carried out under refluxing CH_3CN conditions did not produce the acyclic -S_3N derivatives. In these aspects, these phosphines closely resemble R_3P [1].

Reactions with PhR′RP

All of these phosphines, **6–11**, produced the monosubstituted -S_3N_3 derivatives in near quantitative yield according to Equation (2) (see Table 2).

$$\underset{\textbf{6–11}}{2PhR'RP} \rightarrow PhR'RPN\text{-}S_3N_3 + PhR'RPS \quad (2)$$

R′ = dicyclohexylamino

17 R = pyrrolidino
18 R = piperidino
19 R = morpholino
20 R = N-methylpiperazino
21 R = hexamethylenimino
22 R = anilino

The reactions were found to be relatively fast and were completed within 8 hours. The yields of the products were found to be diminished when the molar ratio of the phosphine to S_4N_4 was greater than 2. Only in the case of the phosphine **11** was the corresponding 1,5-disubstituted derivative isolated as a pale pinkish yellow solid from a reaction involving a 1:3 molar ratio. Unlike the phosphines, $PhPR_2$, all of the chiral phosphines, **6–10**, produced the acyclic derivatives, -S_3N as dark pinkish red crystalline solids with a green metallic luster from a 1:2 reaction in refluxing CH_3CN. They were also obtained by the thermolysis of the corresponding trithiazene derivatives (see discussion below).

We have reported earlier that, when R is a 2-pyridylamino group, in the case of both Ph_2PR and PhR′PR, the $>PS_2N_3$ heterocycle was formed [9,10]. Later, we found that, even when R is an anilino substituent, the $>PS_2N_3$ ring system was formed in the case of the Ph_2PR reactions [11]. To our surprise, we found that the PhR′(C_6H_5NH)P compound afforded the corresponding cyclotrithiazene derivative (**11**) in 65% yield and did not undergo transformation to the $>PS_2N_3$ ring.

Characterization of the Cyclotrithiazene Derivatives

The monosubstituted phosphiniminocyclotrithiazene derivatives are dark red crystalline compounds with a characteristic UV-visible absorption at around 480 and 330 nm. These values are in good agreement with those given in earlier reports [12a,b]. An additional absorption around 280 nm was also observed in these cases. This transition, which is probably due to the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ of the $\rightarrow P=N$ moiety, is seen in the examples $R_3PN\text{–}S_3N_3$ [1,14], $PhR_2PNS_3N_3$, and PhR′RPN-S_3N_3 (this work), but masked and therefore not seen in the case of compounds containing more phenyl groups, such as $Ph_3PN\text{–}S_3N_3$ [12] or $Ph_2RPN\text{–}S_3N_3$ [2,3]. The infrared spectra show a fairly unaffected band at 1100 ± 20 cm^{-1} for $\nu_{P=N}$ and at around 940 cm^{-1} for $\nu_{S\text{-}N}$ like those reported earlier [2,3,12].

In accordance with the earlier observation [3], the ^1H NMR signal due to the phenyl protons that appear as a broad singlet in the case of $PhPR_2$ splits in the ratio 2:3 in pentavalent phosphorus species, viz., the sulfide as well as in the -S_3N_3 derivatives, due to the electronic anisotropy associated with the $\rightarrow P=N$ bond. In the case of the chiral phosphines, the signal due to the N–CH protons of the dicyclohexylamino group experience a gradual downfield shift on going from the phosphine to the -S_3N_3 compound to the sulfide.

The ^{31}P-NMR chemical shift values of the phosphines, the sulfides, and the thiazene derivatives fall in distinctly different regions, enabling their unambiguous characterization. The trend in the chemical shift implies that the smaller rings attached to the phosphorus exert greater shielding, and the larger ring exerts the least. This trend is observed in the

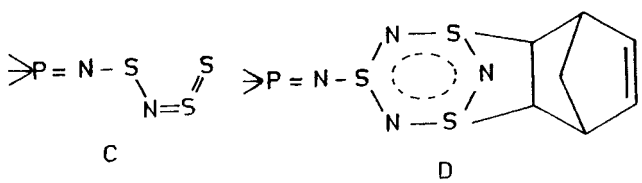
cases of Ph_2PR [2,3], $PhPR_2$, PhR′PR, and R_3P [1], where R is a cyclic secondary amino group.

The 1,5-disubstituted derivative (**23**) has been isolated only in the case of the phosphine PhR′($C_6H_{12}N$)P. Like the previously reported compounds [2,3,12–14], this is a pale pinkish yellow solid. The IR spectrum displays two characteristic bands at 1151 and 1102 for $\nu_{P=N}$, and at 952 and 925 cm^{-1} for $\nu_{S\text{-}N(ring)}$. In dilute solution, it undergoes facile ring contraction to the corresponding S_3N_3 derivative [2,3,14]. For the same reason, the ^{31}P-NMR spectrum had to be taken at -50°C, which displays two signals at $\delta = 36.3$ and 33.5, respectively, for the exo and the endo orientations of the phosphinimino groups. No noticeable change is observed up to 0°C, unlike the reported compounds [2,3,14]. Only at room temperature, a new peak at $\delta = 35.1$ characteristic of the S_3N_3 derivative, begins to appear, suggesting that this compound is quite stable below 0°C and in concentrated solutions. The mass spectrum of this compound under field desorption mode produces the molecular ion peak in low intensity.

The authenticity of the compound, **22**, is established by observing the molecular ion peak at $m/z = 532$ in its mass spectrum obtained under the field desorption mode. No solution phase transformation of this compound, even at higher temperature, was observed. The sharp $\nu_{N\text{-}H}$ band of the phosphine at 3360 cm^{-1} appears broad and is shifted to 3250 cm^{-1} in compound **22**. ^{1}H-NMR spectroscopy also reveals similar features, suggesting the existence of a fairly strong hydrogen bonding in the solid state.

Thermolysis of -S_3N_3 Derivatives

The acyclic derivative, →PN–S_3N (**C**), apart from Ph_3PN–S_3N [15], has been isolated only in the case of the unsymmetrical phosphine, $Ph_2(C_5H_{10}N)P$ [3]. In the present study, the thermolysis of the trithiazene derivatives of the chiral phosphines, in refluxing CH_3CN, produced the acyclic derivatives as dark pinkish red crystalline solids with a green metallic luster. However, a temperature corresponding to toluene reflux was necessary for the compound **19** to produce the -S_3N derivative, **26**. In the case of **20**, the corresponding acyclic derivative could not be isolated.



C D

Compounds **24**–**27** show a characteristic UV-visible spectrum, as reported earlier (see Table 3) [13], but the peak at 280 nm is not found, probably shifted to longer wavelengths due to the conjugation with the -S_3N moiety and the result of it merging with the peak at 310 nm. The infrared spectra are similar to those of corresponding -S_3N_3 derivatives, except for the absence of the $\nu_{S\text{-}N(ring)}$ vibration. No noticeable changes were observed in the case of ^{1}H- as well as the ^{31}P-NMR spectra (Table 3).

Reaction with Norbornadiene

All the trithiazene derivatives undergo a facile addition reaction with norbornadiene in CH_2Cl_2 at room temperature to produce the addition compound of type **D**, in accordance with the earlier observation [1,16,17]. These have been isolated in eight cases, and their characterization data are listed in Table 4. All are colorless crystalline solids. When heated, they turn red and melt with decomposition. Interestingly, irrespective of the melting points of the parent -S_3N_3 compounds, the adducts melt nearly in the same range. The $\nu_{S\text{-}N}$ shifts to a lower value in the infrared spectra of the norbornadiene adducts, and ^{1}H-NMR spectroscopy is very helpful in their characterization. The ^{31}P-NMR signals experience a slight upfield shift compared to the parent cyclotrithiazene derivatives.

Up to the present time, reactions with norbornadiene have not been reported with the 1,5-disubstituted derivatives. In this study, we have carried out this reaction with compound **23** and the 1,5-bis $[Ph_3PN]_2S_4N_4$ [12]. In both cases, the adducts of the corresponding -S_3N_3 derivatives were obtained. The presumed reaction pathway is given in the following scheme.

$$\underset{\mathbf{B}}{1,5\text{-}[{\rightarrow}PN\text{-}]_2S_4N_4} \xrightarrow{CH_2Cl_2} \underset{\mathbf{A}}{{\rightarrow}PN\text{-}S_3N_3} \xrightarrow{\text{norbornadiene}} {>}PN\text{-}S_3N_3{\cdot}C_7H_8$$

It has been shown that the 1,5-disubstituted derivatives, **B**, undergo the facile ring contraction to the trithiazene derivative in CH_2Cl_2 and $CHCl_3$, the only solvents in which they are soluble [2,3,14]. The trithiazene formed, **A**, reacted with norbornadiene to produce the corresponding addition product. Since the conversion of **B** to **A** is not quantitative, the yields of the isolated adducts from these reactions were low (ca. 20%).

The trithiazene derivatives synthesized in this study were found to decompose slowly in solution, as reported earlier with the analogous compounds

TABLE 1 Physical and Spectral Characteristics of Phosphines and Phosphine Sulfides[a]

Compound	Mp/Bp (°C)	^{31}P NMR δ	^{1}H NMR δ
$Ph(C_4H_8N)_2P$ (**1**)	112/0.1 mm Hg	87.2	7.56 (m, 5H), 3.41 (m, 8H), 2.03 (m, 8H)
$Ph(C_4H_8N)_2PS$	114/0.1 mm Hg	68.9	7.81 (m, 2H), 7.42 (m, 3H), 3.22 (m, 8H), 1.82 (m, 8H)
$Ph(C_5H_{10}N)_2P$ (**2**)	74	95.9	7.48 (m, 5H), 3.17 (m, 8H), 1.64 (m, 12H)
$Ph(C_5H_{10}N)_2PS$	94	76.4	7.91 (m, 2H), 7.41 (m, 3H), 2.97 (m, 8H), 1.40 (m, 12H)
$Ph(OC_4H_8N)_2P$ (**3**)	112	95.7	7.42 (m, 5H), 3.68 (t, 8H; $^{3}J_{H\text{-}H} = 8$ Hz), 3.12 (m, 8H)
$Ph(OC_4H_8N)_2PS$	114	76.5	7.91 (m, 2H), 7.46 (m, 3H), 3.61 (m, 8H), 3.05 (m, 8H)
$Ph(H_3CNC_4H_8N)_2P$ (**4**)	58	92.5	7.52 (m, 5H), 3.18 (m, 8H), 2.44 (m, 8H), 2.29 (s, 6H)
$Ph(H_3CNC_4H_8N)_2PS$	74	74.2	7.92 (m, 2H), 7.41 (m, 3H), 3.16 (m, 8H), 2.54 (m, 8H), 2.26 (s, 6H)
$Ph(C_6H_{12}N)_2P$ (**5**)	132/0.1 mm Hg	100.3	7.56 (m, 5H), 3.10 (m, 8H), 1.90 (m, 12H)
$Ph(C_6H_{12}N)_2PS$	138/0.1 mm Hg	76.5	7.91 (m, 2H), 7.41 (m, 3H), 3.16 (m, 8H), 1.72 (m, 16H)
$Ph(DCA)(C_6H_5NH)P$ (**11**)	140	57.2	7.75 (m, 4H), 7.34 (m, 4H), 6.69 (m, 2H) 4.56 (d, 1H; $^{2}J_{P\text{-}H} = 10$ Hz), 2.75 (m, 2H), 1.61 (m, 12H), 1.16 (m, 8H)
$Ph(DCA)(C_6H_5NH)PS$	154	59.5	7.92 (m, 2H), 7.42 (m, 3H), 7.07 (m, 5H), 3.11 (m, 2H), 1.64 (m, 12H), 1.02 (m, 8H)

[a]Phosphine sulfides are prepared by reacting the phosphine with elemental sulfur in benzene.

[17]. However, they are resistant to attack by 2M NaOH. Starting materials were recovered unaffected from these reactions.

EXPERIMENTAL

Tetrasulfur tetranitride was synthesized by the reported procedure and crystallized from toluene [5] (**Caution:** S_4N_4 may cause an explosion!!. Recommended safety procedures should be strictly observed [6].) $PhPCl_2$, pyrrolidine, piperidine, morpholine, N-methylpiperazine, and hexamethylenimine (Aldrich) were used as received. The phosphines, $PhPR_2$ (**1–5**) were prepared by the reaction of $PhPCl_2$ with the respective amines [7]. They have been characterized by various physical and spectral techniques. The physical and ^{31}P-NMR spectral characteristics are summarized in Table 1. The chiral phosphines PhR′RP (**6–10**) were prepared by the reported procedure [4]. The phosphine **11** has been prepared in a similar way by using an line. Its characteristic data are also summarized in Table 1.

All of the reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. The solvents employed were purified by standard methods [8]. The instruments used for recording various spectral data were described previously [3]. The melting points reported are uncorrected.

A number of reactions have been carried out with S_4N_4 and various phosphines. The results of only those reactions that produced the S–N derivatives in the maximum yield are listed in Table 2. The general procedures for obtaining various cyclothiazene derivatives in the maximum yield are given below with a typical example in each case. The results of the thermolysis, and addition reactions with norbornadiene, are summarized in Tables 3 and 4, respectively.

Reaction of S_4N_4 with $Ph(C_5H_{10}^N)_2P$, 1:2 Molar Ratio

To a stirred suspension of $Ph(C_5H_{10}^N)_2P$ (0.72 g, 2.8 mmol) in CH_3CN (20 mL) at room temperature, S_4N_4 (0.25 g, 1.4 mmol) was added as a solid all at once. The reaction mixture immediately developed a red orange color that slowly intensified with time. Within an hour, the entire amount of S_4N_4 had dissolved. After 24 hours, the deep red reaction mixture was cooled at -10°C for 12 hours. The dark red crystalline solid that separated was characterized as $Ph(C_5H_{10}^N)_2PN{-}S_3N_3$ (**13**) (See Table 2 for physical and spectral characteristics.)

After removal of (**13**), the residual reaction mixture was concentrated to 5 mL and cooled in the freezer to permit isolation of pale pinkish white crystals, identified as the phosphine sulfide, $Ph(C_5H_{10}^N)_2PS$ (Table 1).

Reaction with $Ph(DCA)(C_6H_{12}N)P$, 1:3 Molar Ratio

Solid tetrasulfur tetranitride (0.19 g, 1.1 mmol) was added to a stirred suspension of the title phosphine (1.23 g, 3.2 mmol) at room temperature. The reaction mixture developed a red color. After about 3 hours, a pale pinkish solid started to precipitate from the reaction mixture. At the end of 24 hours, the reaction mixture was filtered, the precipitate was washed with CH_3CN (2×4 mL), dried in vacuum,

TABLE 2 Physical and Spectral Characteristics of the Phosphiniminocyclotrithiazene Derivatives[a]

Compd. No.	*R-*	*Yield (%)*	*Mp (°C)*	*^{31}P NMR δ*	*UV-VIS λ_{max} (nm) (ε dm^3 mole^{-1} cm^{-1})*	*^{1}H NMR δ*	*Infrared[b] (cm^{-1})*
					$PhR_2PN\text{-}S_3N_3$		
12	C_4H_8N-	55	66	26.9	478 (4.2 × 10^3) 326 (3.4 × 10^3) 282 (3.3 × 10^3)	7.81 (m, 2H), 7.44 (m, 3H), 3.21 (q, 4H; $^3J_{H\text{-}H}$ = 5 Hz = $^3J_{P\text{-}H}$) 1.82 (m, 8H)	1457, 1195, 1153, 1135, 1110, 1065, 1018, 1010, 930(b), 737, 718, 688, 677
13	$C_5H_{10}N$-	68	124	32.5	478 (4.0 × 10^3) 327 (3.6 × 10^3) 284 (3.2 × 10^3)	7.87 (m, 2H), 7.42 (m, 3H), 3.12 (m, 8H), 1.58 (m, 12H)	1462, 1455, 1437, 1208, 1200, 1159, 1140, 1132, 905, 732, 715, 695, 607
14	OC_4H_8N-	25	118	30.8	480 (4.0 × 10^3) 329 (3.4 × 10^3) 285 (3.2 × 10^3)	7.82 (m, 2H), 7.42 (m, 3H), 3.62 (m, 8H), 3.05 (m, 8H)	1460, 1454, 1439, 1252, 1123, 1118, 1105, 1092, 1050, 1042, 1036, 1000, 942, 925, 922, 742, 713, 685, 648
15	$CH_3NC_4H_8N$-	64	126	31.1	4.83 (4.2 × 10^3) 330 (3.4 × 10^3) 284 (3.3 × 10^3)	7.80 (m, 2H), 7.41 (m, 3H), 3.14 (m, 8H), 2.52 (m, 8H), 2.24 (s, 6H)	1470, 1452, 1443, 1360, 1277, 1112, 1102, 1097, 962, 920, 730, 717, 608
16	$C_6H_{12}N$	62	124	35.4	482 (3.7 × 10^3) 330 (3.0 × 10^3) 284 (3.0 × 10^3)	7.81 (m, 2H), 7.42 (m, 3H), 3.16 (m, 8H), 1.76 (m, 12H)	1464, 1428, 1361, 1158, 1135, 1122, 1105, 1092, 1050, 1042, 1036, 1000, 942, 925, 922, 890, 742, 724, 713, 685, 648
					$Ph[(C_6H_{11})_2N]RPN\text{-}S_3N_3$		
17	C_4H_8N-	85	140	29.6	493 (7.0 × 10^3) 333 (3.5 × 10^3) 286 (3.5 × 10^3)	7.91 (m, 2H), 7.31 (m, 3H), 3.28 (m, 2H), 3.07 (m, 4H), 1.76 (m, 16H), 1.12 (m, 8H)	1434, 1197, 1166, 1155, 1132, 1112, 1098, 1072, 1048, 1028, 1016, 1000, 981, 945, 921, 893, 748, 698, 688, 642, 628, 605
18	$C_5H_{10}N$-	85	140	31.9	478 (4.2 × 10^3) 324 (2.9 × 10^3) 283 (3.0 × 10^3)	7.91 (m, 2H), 7.52 (m, 3H), 3.11 (m, 6H), 1.75 (m, 18H), 1.17 (m, 8H)	1458, 1438, 1340, 1205, 1190, 1170, 1152, 1118, 1100, 1068, 1055, 1030, 1000, 985, 965, 938, 898, 858, 773, 740, 730, 700, 690
19	OC_4H_8N-	90	158	31.5	477 (3.8 × 10^3) 326 (2.9 × 10^3) 280 (3.1 × 10^3)	7.95 (m, 2H), 7.52 (m, 3H), 3.71 (m, 4H), 3.08 (m, 6H), 1.81 (m, 12H), 1.16 (m, 8H)	1435, 1252, 1188, 1173, 1150, 1120, 1110, 1098, 1050, 970, 930, 740, 722, 690, 658, 640
20	$CH_3NC_4H_8N$-	70	136	31.8	478 (4.1 × 10^3) 326 (3.4 × 10^3) 283 (3.3 × 10^3)	7.92 (m, 2H), 7.47 (m, 3H), 3.06 (s, 3H), 1.69 (m, 12H), 1.16 (m, 8H)	1455, 1442, 1371, 1361, 1161, 1151, 1136, 1118, 1106, 1091, 1063, 1051, 1042, 1021, 995, 979, 967, 928, 886, 730, 688, 664
21	$C_6H_{12}N$-	75	126	35.1	480 (4.2 × 10^3) 332 (3.2 × 10^3) 283 (3.2 × 10^3)	7.85 (m, 2H), 7.36 (m, 5H), 3.71 (m, 4H), 2.94 (m, 2H), 1.70 (m, 20H), 1.13 (m, 8H)	1475, 1452, 1434, 1367, 1152, 1132, 1110, 1098, 1057, 992, 938(b), 890, 742, 727, 672, 642
22	C_6H_5NH	65	143	23.5	484 (4.2 × 10^3) 334 (3.2 × 10^3)	7.87 (m, 2H), 7.40 (m, 3H), 7.10 (m, 5H), 3.02 (m, 2H), 1.60 (m, 12H), 0.95 (m, 8H)	3276(b), 1597, 1497, 1453, 1438, 1388, 1278, 1222, 1168, 1118, 1089, 1053, 1028, 1003, 988, 957(b), 945, 893, 830, 798, 742, 704, 692, 643, 632, 618, 604

[a]The C, H, and N analyses were performed on all these compounds; the results are quite satisfactory.
[b]Only strong and very strong bands are reported.

TABLE 3 Physical and Spectral Characteristics of the PhR′RPN–S_3N Derivatives Synthesized[a]

Compd. No.	*R-*	*Yield (%)*	*Mp (°C)*	*^{31}P NMR δ*	*UV-VIS λ_{max} (nm) (ε, dm³ mole⁻¹ cm⁻¹)*	*^{1}H NMR δ*	*Infrared[b] (cm⁻¹)*
24	C_4H_8N-	50	162	27.2	507 (7.2×10^4); 322 (1.1×10^3)	7.88 (m, 2H), 7.48 (m, 3H), 3.35 (m, 4H), 3.06 (m, 2H), 1.75 (m, 16H), 1.15 (m, 8H)	1472, 1462, 1255, 1200(b), 1170, 1156, 1121, 1098, 1061, 1050, 1028, 1021, 1000, 985, 971, 908, 898, 745, 723, 700, 690, 653, 626
25	$C_5H_{10}N$-	45	162	31.3	498 (6.0×10^4); 317 (1.0×10^3)	7.87 (m, 2H), 7.51 (m, 3H), 3.11 (m, 6H), 1.62 (m, 18H), 1.19 (m, 8H)	1466, 1459, 1442, 1198, 1161, 1154, 1112, 1090, 1062, 1052, 1032, 995, 981, 954, 942, 718, 618
26	OC_4H_8N-	45	182	30.2	496 (1.2×10^4); 310 (1.3×10^3)	7.93 (m, 2H), 7.51 (m, 3H), 3.7 (m, 4H), 3.23 (m, 6H), 1.76 (m, 12H), 1.20 (m, 8H)	1473, 1461, 1433, 1363, 1253, 1188, 1163, 1153, 1137, 1123, 1110, 1097, 1075, 1073, 1050, 967, 914, 893, 743, 720, 694, 664, 623
27	$C_6H_{12}N$-	45	148	31.8	494 (1.3×10^4); 312 (3.2×10^3)	7.96 (m, 2H), 7.55 (m, 3H), 3.20 (m, 6H), 1.72 (m, 20H), 1.31 (m, 8H)	1472, 1468, 1441, 1370, 1168, 1148, 1120, 1097, 1048, 1000, 908, 896, 722, 698

[a]The results of the C, H, N analyses performed on most of these compounds are satisfactory.
[b]Only strong and very strong bands are reported.

and characterized as the 1,5-bis{$(C_6H_5)[(C_6H_{11})_2N](C_6H_{12}N)PN\}_2S_4N_4$ (**23**) (0.67 g, 65%). Mp 136°C (dec); IR (1600–600 cm^{-1}): 1455, 1442, 1178 (sh), 1167, 1154, 1138 (sh), 1123, 1110, 1102, 1062, 1050, 1030, 1012, 1002, 989, 953, 925, 908, 896, 748, 702, 620. ^{1}H NMR δ: 7.82 (m, 4H), 7.36 (m, 6H), 3.14 (m, 8H), 2.92 (m, 4H), 1.72 (m, 40H), 1.16 (m, 16H). ^{31}P NMR δ (at −50°C): 36.3 (s, 1P), 33.5 (s, 1P). MS (FD mode) (*m/z*): 984 [M^+; 2]. CHN anal. calcd for $C_{48}H_{78}N_{10}P_2S_4$ (%): C, 58.54; H, 7.26; N, 14.20. Found: C, 58.23; H, 7.02; N, 13.94.

From the filtrate, when worked up as in the previous reaction, only the corresponding phosphine sulfide [4] (0.4 g) was isolated.

Thermolysis of PhR′(C_4H_8N)PN–S_3N_3

The title compound (0.25 g, 0.5 mmol) was heated under reflux in CH_3CN (10 mL) for 4 hours. The solution gradually changed from the initial bright red color to a dark pinkish red. The reaction mixture was cooled at −10°C for 12 hours to permit isolation of a dark pinkish red crystalline solid with a green metallic luster, which was characterized as the acyclic derivative, PhR′(C_4H_8N)PN-S_3N (**24**). (See Table 3 for physical and spectral characteristics.) No other product could be isolated from the residual reaction mixture.

Reaction of PhR′(OC_4H_8N)PN-S_3N_3 with Norbornadiene

To a stirred solution of PhR′(OC_4H_8N)PN–S_3N_3 (0.25 g, 0.5 mmol) in CH_2Cl_2 (10 mL) at room temperature, norbornadiene (0.85 g, 9.2 mmol) was added all at once. The color of the solution slowly became pale reddish brown. After 24 hours, the reaction mixture was concentrated to about 3 mL, CH_3CN (10 mL) was added, and the mixture was cooled in the freezer for a day to isolate colorless crystals of the adduct (**34**) (See Table 4 for physical and spectral characteristics.)

Similar reactions were carried out with compound **23** and 1,5-bis$[Ph_3PN]_2S_4N_4$ (see discussion below).

Reaction with Alkali

The phosphiniminocyclotrithiazene (0.25 g) was added as a solid to a stirred solution of 2M NaOH (10 mL) at room temperature. After a 24 hour reaction period, the reaction mixture was filtered, and

TABLE 4 Physical and Spectral Characteristics of the Norbomadiene Addition Compounds[a] of $\rightarrow P=N-S_3N_3$ Derivatives

Compd. No.	*R-*	*Yield (%)*	*Mp (°C)*	*^{31}P NMR δ*	*^{1}H NMR δ*	*Infrared[b] (cm^{-1})*
				$R_2PhPN-S_3N_3$		
28	C_4H_8N-	50	124	27.5	7.56 (m, 5H), 6.42 (d, 2H), 5.32 (d, 2H), 3.08 (m, 10H), 1.93 (s, 1H), 1.46 (m, 8H), 1.26 (d, 1H)	1473, 1467, 1435, 1108, 1103, 1088, 1067, 1015, 916, 865, 730, 709, 639, 622
29	$C_5H_{10}N$-	55	126	32.5	7.52 (m, 5H), 6.41 (d, 2H), 5.37 (d, 2H), 3.04 (m, 10H), 1.91 (d, 1H), 1.49 (m, 12H), 1.28 (d, 1H)	1462, 1452, 1435, 1365, 1098, 1080, 1065, 950, 915, 898, 862, 752, 728, 712, 700, 663, 637
30	OC_4H_8N-	45	126	30.8	7.55 (m, 5H), 6.46 (d, 2H), 5.31 (d, 2H), 3.62 (m, 8H), 3.10 (m, 10H), 1.93 (d, 1H), 1.28 (d, 1H)	1472(sh), 1465, 1458, 1441, 1378, 1258, 1070, 967, 954, 911, 896, 869, 860, 852, 756, 738, 731, 720, 700, 640, 618, 605
31	$CH_3NC_4H_8N$-	52	126	31.5	7.53 (m, 5H), 6.47 (d, 2H), 5.16 (d, 2H), 3.10 (m, 10H), 2.25 (m, 14H), 1.92 (d, 1H) 1.26 (d, 1H)	1450, 1440, 1428, 1280, 1152, 1142, 1113, 1097, 1082, 1065, 957, 903, 856, 748, 609
				Ph R′ $RPN-S_3N_3$		
32	C_4H_8N-	60	126	28.4	7.32 (m, 5H), 6.41 (d, 2H), 5.16 (d, 2H), 3.28 (m, 6H), 1.88 (d, 1H), 1.66 (m, 16H), 1.17 (m, 9H)	1460, 1453(sh), 1425, 1147, 1112, 1087, 1067, 1040, 1012, 1000, 965, 917, 886(sh), 858, 845, 750, 728, 688, 630, 618(sh), 608
33	$C_5H_{10}N$-	60	124	31.3	7.44 (m, 5H), 6.39 (d, 2H), 5.11 (d, 2H), 3.17 (m, 6H), 1.92 (d, 1H), 1.60 (m, 20H), 1.15 (m, 9H)	1465(sh), 1400, 1421, 1163, 1157, 1113, 1100, 1091, 1051, 987, 946, 931, 915, 897, 891(sh), 865, 851, 762, 753, 736, 696, 635, 620
34	OC_4H_8N-	60	124	29.2	7.51 (m, 5H), 6.54 (d, 2H), 5.13 (d, 2H), 3.66 (m, 4H), 3.15 (m, 6H), 2.10 (d, 2H), 1.62 (m, 12H), 1.17 (m, 9H)	1455, 1450, 1252, 1242, 1158, 1150, 1124, 1114, 1104, 1074(sh), 1050, 1047, 990, 978, 952, 907(b), 864, 847, 738, 731, 693, 670, 640, 622, 612
35	$C_6H_{12}N$-	55	126	34.3	7.48 (m, 5H), 6.38 (d, 2H), 5.13 (d, 2H), 3.17 (m, 6H), 1.91 (d, 1H), 1.62 (m, 20H), 1.13 (m, 9H)	1430, 1102, 1076, 1050, 1036, 925, 912, 887, 861, 730, 615

[a]The results of the C, H, N analyses, performed on most of these compounds are quite satisfactory.
[b]Only strong and very strong bands are reported.

the precipitated red solid was identified as the unchanged starting material (0.24 g).

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