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Cyclic S–N Compounds and Phosphorus Reagents: Part X. Synthesis and Characterization of Phosphinimino-Substituted S–N Heterocycles

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ABSTRACT

Room temperature reactions of S_4N_4 with (amino) diphenylphosphines, $(R)Ph_2P$, have basically yielded two different types of S—N heterocycles under two different stoichiometric conditions. Phosphiniminocyclotrithiatriazenes, $(R)Ph_2PN—S_3N_3$ ($R = C_4H_8N—$, $C_5H_{10}N—$, $C_6H_{12}N—$, $CH_3NC_4H_8N—$, $(C_6H_{11})_2N—$, and $(C_6H_5CH_2)_2N—$) have been obtained (yield 45–76%) from a 1:2 mole ratio (S_4N_4:$(R)Ph_2P$) reaction, while the disubstituted S_4N_4 derivatives, 1,5-$[Ph_2(R)PN]_2S_4N_4$ ($R = C_4N_8N—$, $C_5H_{10}N—$, and $C_6H_{12}N—$) have been obtained (yield 30–45%) only from a 1:3.5–4 mole ratio reaction. All the 1,5-$[Ph_2(R)PN]_2S_4N_4$ derivatives prepared in this study undergo a room temperature solution phase transformation to the corresponding $(R)Ph_2PN—S_3N_3$ heterocycles.

INTRODUCTION

All the reactions known for the synthesis of phosphiniminotrisulfurtrinitrides, $\rightarrow P{=}N—S_3N_3$ [1–9] and 1,5-bis(phosphinimino)tetrasulfurtetranitrides, 1,5-$[\rightarrow P{=}N]_2S_4N_4$ [2–4, 6, 10–13] involve S_4N_4 or its derivatives as one of the main starting materials. As a continuation of our reactivity studies of S—N reagents with various phosphorus compounds [1–4, 10–11], we herein describe the synthesis and characterization of ten new phosphinimino substituted S—N compounds by making use of S_4N_4 and aminophosphines, $(R)Ph_2P$, as the starting materials.

RESULTS AND DISCUSSION

Although reactions of S_4N_4 with several tertiary phosphines have been reported in the literature [1–4, 6, 9], only three examples of 1,5-disubstituted S_4N_4 derivatives of the type $[\rightarrow PN]_2S_4N_4$ [2, 3, 6, 10–12] are so far known. In this study, of the six (amino)diphenylphosphines, $(R)Ph_2P$, chosen for investigations, three of them ($R = C_4H_8N—$, $C_5H_{10}N—$, and $C_6H_{12}N—$) have readily given the 1,5-bis(phosphinimino)tetrasulfurtetranitride derivatives when the mole ratio of S_4N_4 to phosphine is 1:4 and the solvent is CH_3CN. This result is identical to our earlier report on the reaction of S_4N_4 with (morpholino)diphenylphosphine, except for the fact that reactions performed at low temperature (ca. 15°C) have favored the formation of 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$ [3]. From the other examples of phosphines, $(R)Ph_2P$ ($R = CH_3NC_4H_8N—$, $(C_6H_{11})_2N—$, and $(C_6H_5CH_2)_2N—$), no 1,5-$[(R)Ph_2PN]_2S_4N_4$ could be isolated even at low temperature. Like 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$, all the analogous derivatives synthesized in this study (compounds **7**, **8**,

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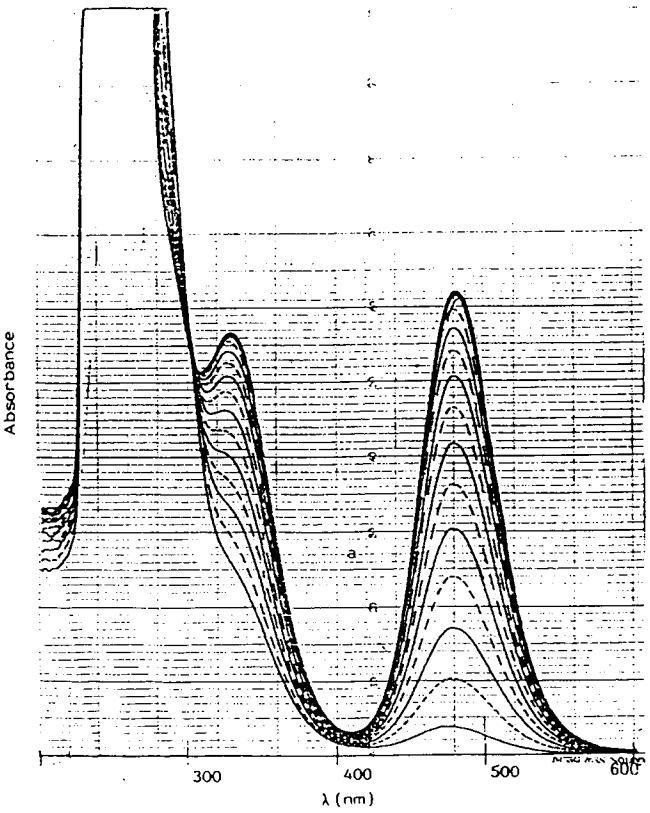

FIGURE 1A Uv-visible spectrum of 1.5-$[(C_4H_8N)Ph_2PN]_2S_4N_4$ in solution (3 mg in 10 mL $CHCl_3$) showing the conversion to $(C_4H_8N)Ph_2PN—S_3N_3$ with time at rt. Time between two scans is ca. 3 min. This conversion is over within 45 min. (15 scans).

and **9**) are also very stable in the solid phase (samples in sealed ampules were unchanged for about 4 years), but they undergo decomposition in the solution phase to the corresponding trisulfurtrinitrides (compounds **1**, **2**, and **3**) within 24 h even at room temperature [3]. The rate of transformation is higher at higher temperatures and also at increased dilutions. These effects have been verified by time dependent uv-visible studies (Fig.1A) as well as by variable temperature ^{31}P-NMR studies (Fig.1B) and the results are identical to our earlier study [3]. As a result of this solution phase decomposition, nmr spectra of these compounds have been reported at low temperature (−40°C). At low temperature, ^{31}P-NMR spectra (Table 4) of compounds **7**, **8**, and **9** gave two sharp signals of equal intensities because of the exo and endo orientations of the phosphinimino groups on the 1,5-positions of sulfur atoms in S_4N_4. This observation is very similar to the stereochemical nonequivalence of phosphinimino groups in $[(R)Ph_2PN]_2S_4N_4$ (R = Ph, OC_4H_8N) [3, 6] and also in the case of amino groups in bis(amino) S_4N_4 derivatives reported by Roesky et al. [14]. We believe that the endo substituents are more shielded compared to the exo substituents, which can be explained in terms of the anisotropic shielding and deshielding effect of the S—N ring current in $—S_4N_4—$. It is interesting to note that in all the reported $(phosphinimino)_2S_4N_4$ derivatives [2, 3, 6, 13] and also in compounds **7**, **8**, and **9** the chemical shift value of the downfield signal is very close to the chemical shift value of the corresponding phosphinimino-S_3N_3 derivatives. It should also be noted that, in the infrared spectra of compounds **7**, **8**, and **9**, two characteristic S—N absorptions: 960 (s) and 905 (vs); 965 (vs) and 915 (vs); 968 (s) and 918 (vs), have been observed, respectively, for $C_4H_8N—$, $C_5H_{10}N—$, and $C_6H_{12}N—$ derivatives, while the PN absorptions have been observed at ca. 1160 and 1130 cm^{-1}. Mass spectra of compounds **7**, **8**, and **9** do not give molecular ion peaks and are identical to the mass spectrum of $[(OC_4H_8N)Ph_2PN]_2S_4N_4$ [3].

The trisulfurtrinitrides, $(R)Ph_2PN—S_3N_3$ have been isolated from all the phosphines utilized in this study under several reaction conditions (Table

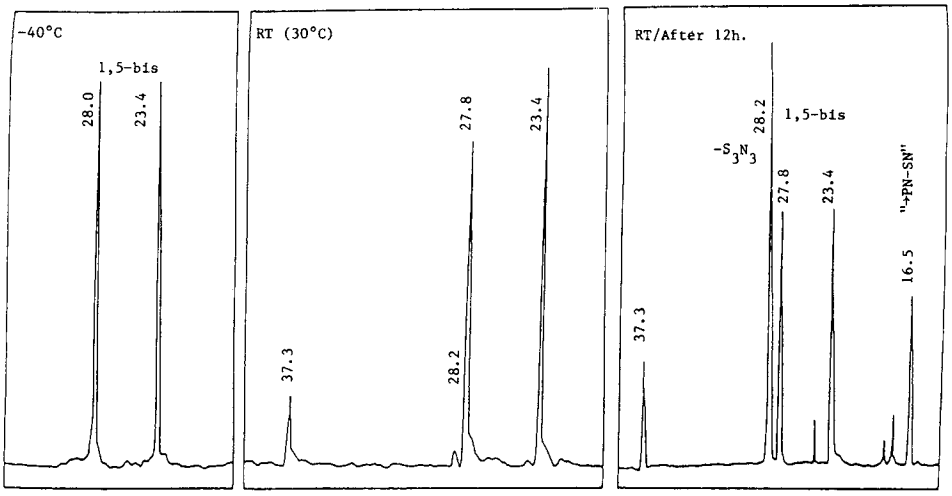

FIGURE 1b $^{31}P\{^1H\}$ NMR spectra of 1,5-$[(C_4H_8N)Ph_2PN]_2S_4N_4$ (50 mg in 1 mL $CDCl_3$) showing its conversion to $(C_4H_8N)Ph_2PN—S_3N_3$ with time and temperatures. This conversion is not fully over within 12 h.

TABLE 1 Various Reactions of S_4N_4 with Phosphines, $Ph_2(R)P$, Leading to the Isolation of Phosphinimino-Substituted S—N Heterocycles[d]

		Molar Ratio of S_4N_4: Phosphine								
Sl. No.	*Phosphine*	*CH_3CN RT 1:1[a]*	*CH_3CN RT 1:2*	*CH_3CN RT 1:3*	*CH_3CN RT 1:4*	*CH_3CN RT 1:5*	*CH_3CN 45°C 1:2.5*	*CH_3CN 80°C 1:2*	*C_6H_6 RT 1:2*	*$CHCl_3$ RT 1:2*
1	$(C_4H_8N)Ph_2P$	I(20)	I(32)	II(20)	II(30)	[b]	I(45)	[c]	I(40)	I(39)
2	$(C_5H_{10}N)Ph_2P$	I(30)	I(66)	I(67)	II(29)	[b]	I(69)	III(54)	I(47)	I(56)
3	$(C_6H_{12}N)Ph_2P$	I(36)	I(72)	I(43)	II(46)	[b]	I(74)	[c]	I(62)	I(65)
4	$(CH_3NC_4H_8N)Ph_2P$	I(36)	I(63)	I(59)	I(11)	[b]	I(76)	[c]	I(60)	I(61)
5	$(C_6H_{11})_2NPh_2P$	I(15)	I(38)	I(25)	I(10)	[b]	I(35)	[c]	I(35)	I(37)
6	$(C_6H_5CH_2)_2NPh_2P$	I(30)	I(53)	I(51)	I(21)	[b]	I(58)	[c]	I(48)	I(50)

Note: I = $Ph_2(R)PN—S_3N_3$; II = $1,5\text{-}[Ph_2(R)PN]_2S_4N_4$; III = $Ph_2(R)PN—S_3N$, an acyclic compound.
a. Incomplete reaction from which ca. 50% of the starting material, S_4N_4, was isolated.
b. Only phosphine sulphide, $Ph_2(R)P(S)$, could be isolated from this reaction.
c. Only spectral evidence for the formation of III, $Ph_2(R)PN—S_3N$.
d. Numbers in parentheses refer to the isolated yields. Yields were calculated on the basis of the S—N content of S_4N_4.

1). However, maximum yields have been obtained only when the mole ratio of S_4N_4 to phosphine is 1:2 or 1:2.5. From this study as well as from the earlier reports on the reactions of S_4N_4 with tertiary phosphines [1–4, 6, 9], it is evident that $\rightarrow P{=}N—S_3N_3$ is the most stable product in these types of reactions. All the $(R)Ph_2PN—S_3N_3$ derivatives (compounds **1–6**) are red crystalline materials and are relatively stable toward air and moisture. However, on prolonged exposure to the atmosphere, they change to white solids whose ^{31}P-NMR chemical shift values correspond to the chemical shift values of the respective aminophosphonium salts [15]. It is to be noted that the electronic arrangement in the $—S_3N_3$ ring is not significantly influenced by the presence of various R groups on the phosphorus atom, as evidenced by the unaltered λ_{max} values [1–3, 5–6, 16]. The IR, NMR, and MS data are quite similar to the previously reported (amino)diphenylphosphiniminotrisulfurtrinitride [3].

The acyclic derivative, $(R)Ph_2PN—S_3N$ [17] has been isolated and fully characterized only in the case of $(C_5H_{10}N)Ph_2PN—S_3N$, although we have some spectral evidence (uv-visible and ^{31}P-NMR) for the formation of these compounds in other cases also. The difficulty in isolating these compounds could be from separation problems associated with the complexity of the reaction mixture.

The ^{1}H-NMR spectra (90 MHz) of all the phosphines, $(R)Ph_2P$, chosen in this study have given a unique spectral pattern in which the two phenyl groups appear as a singlet in the aromatic region. Under identical conditions, the oxidized derivatives, $(R)Ph_2P{=}X$ (X = O, S, N—R′) have shown two complex sets of multiplets with intensity ratios of 2:3 (Tables 3 and 5). This observation could be explained in terms of the anisotropic effect of the $\rightarrow P{=}X$ multiple bond which makes the ortho protons in the deshielding cone of the $\rightarrow P{=}X$ bond. An analogous situation has been reported in the case of aromatic carbonyl compounds [18].

SUMMARY

From this study as well as from the previous reports [1–3, 6, 13], it is clear that $\rightarrow P{=}N—S_3N_3$ derivatives are formed as per the following equation:

$$S_4N_4 + 2R_3P \rightarrow R_3P(S) + R_3PN—S_3N_3 \quad (1)$$

Very little is known about the mechanistic aspects of the formation of $1,5\text{-}(R_3PN)_2S_4N_4$ [6]. This study suggests that the formation of $1,5\text{-}(R_3PN)_2S_4N_4$ is favored when the mole ratio of S_4N_4 to R_3P is 1:4.

$$S_4N_4 + 4R_3P \rightarrow \tfrac{1}{2}\,1,5\text{-}(R_3PN)_2S_4N_4 + 2R_3P(S) + \text{“}R_3PN\text{”} \quad (2)$$

When we reinvestigated the known reaction of S_4N_4 with Ph_3P by varying the mole ratio of the reactants from 1:2 to 1:4 the yield of $1,5\text{-}[Ph_3PN]_2S_4N_4$ was increased from ca. 40% [6, 13] to ca. 65%. Recently we reported that $R_3PN—S_3N_3$ heterocycles undergo a ring expansion reaction in the presence of two moles of phosphine [10]

$$R_3PN—S_3N_3 + 2R_3P \rightarrow \tfrac{1}{2}\,1,5\text{-}[R_3PN)_2S_4N_4 + R_3P(S) + \text{“}R_3PN\text{”} \quad (3)$$

From Equations 1, 2, and 3, as well as from our earlier report on the cooperative effect [4], it appears that $R_3PN—S_3N_3$ derivatives are the most stable intermediates for the formation of $1,5\text{-}(R_3PN)_2S_4N_4$. However, in the solution phase, 1,5-

TABLE 2 Analytical and Physical Data for New Compounds

Compound	MP (°C)	Color	Maximum Yield (%)	Analysis (%) Calculated C	H	N	Found C	H	N
$(C_4H_8N)Ph_2PN—S_3N_3$ (1)	114	Dark red	45	46.16	4.45	17.19	46.39	4.69	17.13
$(C_5H_{10}N)Ph_2PN—S_3N_3$ (2)	138	Dark red	69	48.44	4.78	16.61	48.96	4.71	16.75
$(C_6H_{12}N)Ph_2PN—S_3N_3$ (3)	133	Red	74	49.59	5.87	16.02	50.03	5.88	16.35
$(CH_3NC_4H_8N)Ph_2PN—S_3N_3$ (4)	150 dec.	Red	76	46.76	4.81	19.21	46.60	4.83	19.27
$(C_6H_5CH_2)_2NPh_2PN—S_3N_3$ (5)	109	Orange red	58	59.11	4.57	13.91	58.79	4.53	13.95
$(C_6H_{11})_2NPh_2PN—S_3N_3$ (6)	132	Orange red	38	55.86	6.58	13.58	56.11	6.81	13.21
$1,5\text{-}[Ph_2(C_4H_8N)PN]_2S_4N_4$ (7)	125 dec.	Cream yellow	30	53.16	5.03	15.50	53.32	5.14	15.61
$1,5\text{-}[Ph_2(C_5H_{10}N)PN]_2S_4N_4$ (8)	125 dec.	Cream yellow	29	54.38	5.37	14.92	54.34	5.26	14.81
$1,5\text{-}[Ph_2(C_6H_{12}N)PN]_2S_4N_4$ (9)	132 dec.	Cream yellow	46	55.50	5.69	14.39	55.89	5.76	14.16
$(C_5H_{10}N)Ph_2PN—S_3N$ (10)	118	Purple red	54	51.88	5.12	10.68	52.41	5.33	10.91
$(CH_3NC_4H_8N)Ph_2P$ (11)	68	Colorless	95	71.81	7.45	9.85	71.76	7.43	9.93
$(CH_3NC_4H_8N)Ph_2P(S)$ (12)	113	White	98	64.54	6.69	8.86	64.59	6.63	8.88

$(R_3PN)_2S_4N_4$ undergoes decomposition to $R_3PN—S_3N_3$ [3].

$$1,5\text{-}(R_3PN)_2S_4N_4 \xrightarrow{\text{in solution/rt}} R_3PN - S_3N_3 + \text{"}R_3PN - SN\text{"} \quad (4)$$

That no 1,5-bis derivatives could be obtained in the case of $(R)Ph_2P$ ($(R = (C_6H_{11})_2N—$, $CH_3NC_4H_8N—$, $(C_6H_5CH_2)_2N—$) may be because of the relatively high instabilities of such derivatives.

EXPERIMENTAL

All the reactions and subsequent workup were done under an inert atmosphere using dry N_2 gas. Solvents such as CH_3CN, Et_2O, $CHCl_3$, and hexane were purified by standard procedures [19–21] described previously [1–3]. S_4N_4 was synthesized by the literature method [22] and recrystallized from toluene before use. (**CAUTION!** S_4N_4 may cause severe explosion. Recommended safety precautions [23] have to be employed.) Aminodiphenylphosphines, $(R)Ph_2P$ ($R = C_4H_8N—$, $C_5H_{10}N—$, $C_6H_{12}N—$, $CH_3NC_4H_8N—$, $(C_6H_5CH_2)_2N—$, and $(C_6H_{11})_2N—$) were synthesized by the aminolysis reaction of Ph_2PCl with the respective amines [24–28]. Ph_2PCl and the amines were purchased from Aldrich Inc. and distilled before use.

Infrared spectra (spectra as nujol mulls, values in cm^{-1}) were recorded on a Perkin Elmer 1430 spectrophotometer. Shimadzu UV 240 and Hitachi 220A (CH_2Cl_2 solution) spectrophotometers were used for recording the UV-visible spectra. ^{1}H-NMR spectra were recorded as $CDCl_3$ solutions of the compound with TMS as the internal standard using Varian EM390 and Bruker WH250 instruments. ^{31}P-NMR spectra were recorded in $CDCl_3$ solvent using a Varian XL-100 spectrometer with 85% H_3PO_4 as the external reference. Mass spectra were recorded on a Finigan Mat 8280 GC-MS Spectrometer operated at 70 eV. Carbon, H, and N analyses were done at Central College Bangalore, India, and also at Messrs. Beller, Goettingen, Germany. Melting points were determined in sealed tubes and are uncorrected.

Reactions of S_4N_4 with $(R)Ph_2P$

Reactions of aminophosphines, $(R)Ph_2P$, with S_4N_4 were performed in C_6H_6, CH_3CN, $CHCl_3$, toluene, Et_2O, and THF under different conditions at various temperatures. Only selected reactions are listed (Table 1).

General Procedure for the Synthesis of $(R)Ph_2PN—S_3N_3$ ($R = C_4H_8N—$, $C_5H_{10}N—$, $C_6H_{12}N—$, $CH_3NC_4H_8N—$, $(C_6H_5CH_2)_2N—$, and $(C_6H_{11})_2N—$)

To a stirred suspension of $(R)Ph_2P$ (10 mmol) in CH_3CN (40 mL), S_4N_4 (0.92 g, 5 mmol) was added over a period of 10 minutes at room temperature. It was then slowly warmed to 45–50°C and stirred for about 24 h. The red precipitate thus obtained was separated by filtration using a frit. It was then recrystallized in a mixture of C_6H_6 and CH_3CN (10 : 5 mL) at 0°C to obtain red crystals of $(R)Ph_2PN—S_3N_3$. The yield, physical and spectral data are listed in Tables 1, 2, 3, and 4. The original filtrate was allowed to evaporate at room temperature to obtain a pinkish-white solid that was recrystallized in a $CH_2Cl_2—CH_3CN$ (1 : 1) mixture to

TABLE 3 Infrared, Uv-Visible, and ^{1}H-NMR Spectra of the S—N Compounds (**1**–**10**).

Compound	*Infrared** ν (cm^{-1})	*Uv-visible* λ max (nm)	ε ($dm^3\ mol^{-1}\ cm^{-1}$)	*^{1}H-NMR* δ(PPM)
1	1445(s), 1160(m), 1135(vs), 1120(vs), 1115(s, sh), 1095(s), 1075(m, sh), 940(vs), 740(s), 705(s), 695(m).	483 332	4.41×10^3 3.38×10^3	1.70 (m, 4H), 2.97 (m, 4H), 7.12–7.30 (m, 6H), 7.55–7.85 (m, 4H); $^3J_{PH}$ = 7.5 Hz and $^3J_{HH}$ = 6.0 Hz
2	1440(s), 1200(s), 1160(m), 1120(vs), 1100(s), 1070(s), 1060(s), 1030(m), 965(s, sh), 960(vs), 940(s), 800(m), 760(m), 730(s, sh), 725(s), 700(s), 690(m).	483 332	4.38×10^3 3.47×10^3	1.55 (br., 6H), 2.80 (br., 4H), 7.15–7.25 (m, 6H), 7.60–7.90 (m, 4H).
3	1440(s), 1115(s), 1145(vs), 1120(s), 1005(m), 970(m), 945(s), 900(m), 760(m), 740(s), 730(s, sh), 710(m), 700(s), 690(m, sh), 620(m).	483 332	4.89×10^3 4.16×10^3	1.40 (br., 4H), 4H), 7.0–7.15 (m, 6H), 7.45–7.63 (m, 4H); $^3J_{PH}$ = 8.6 Hz; $^3J_{HH}$ = 6.0 Hz.
4	1400(m, sh), 1440(s), 1370(m), 1290(m), 1190(m, sh), 1162(m), 1145(vs), 1130(vs), 1115(vs), 1105(s), 1075(m), 980(s), 930(s), 752(m), 730(s), 690(m).	483 328	3.27×10^3 2.71×10^3	2.20 (s, 3H), 2.30 (t, 4H), 2.85 (q, 4H), 7.12–7.30 (m, 6H), 7.60–7.85 (m, 4H); $^3J_{PH}$ = 4.5 Hz and $^3J_{HH}$ = 5.5 Hz.
5	1480(m, sh), 1460(vs), 1432(s), 1370(s), 1360(m), 1138(vs), 1120(vs), 1110(vs), 1062(s), 965(m), 938(vs), 818(s), 810(s), 785(s), 755(m), 745(vs, sh), 738(vs), 695(vs), 620(m), 605(s).	481 332	3.58×10^3 3.14×10^3	4.15 (s, 2H), 4.25 (s, 2H), 6.82–7.10 (m, 10H), 7.15–7.32 (m, 6H), 7.50–7.78 (m, 4H); $^3J_{PH}$ = 9 Hz.
6	1480(m, sh), 1440(s), 1400(m), 1165(s), 1155(vs), 1115(vs), 1110(vs), 1092(vs), 1075(m, sh), 1050(vs), 1030(m), 1000(s), 985(s), 975(s), 950(vs), 890(m), 850(m), 800(m), 780(s), 750(sh, s), 740(vs), 720(m), 700(vs), 670(m), 600(s).	478 330	4.26×10^3 3.43×10^3	1.05 (t, 6H), 1.75 (br., 14H), 3.05 (m, 2H), 7.0–7.9(m, 6H), 7.95–8.05 (m, 4H).
7	1480(m, sh), 1440(vs), 1200(s), 1160(s), 1125(vs, br), 1120(vs), 1095(vs, br), 1070(vs, sh), 1010(s), 1000(s), 960(vs), 905(vs), 870(m), 725(vs), 690(s), 630(s).	[a]		1.52–2.00 (m, 4H), 2.62–3.20 (m, 4H), 7.00–7.31 (m, 6H), 7.32–7.90 (m, 4H).
8	1480(m, sh), 1440(vs), 1205(m), 1160(m), 1130(vs), 1100(vs), 1070(s), 965(vs), 955(s, sh), 915(vs), 730(s), 720(s), 700(m), 640(s).	[a]		1.30 (br., 6H), 1.75 (br., 4H), 6.80–7.30 (m, 6H), 7.35–7.80(m, 4H).
9	1480(m, sh), 1445(vs), 1130(vs), 1100(s), 1045(m), 968(s), 918(vs), 730(s), 720(m), 700(m), 640(m), 610(m).	[a]		1.40 (m, 8H), 2.75 (br., 4H), 6.80–7.30 (m, 6H), 7.35–7.80 (m, 4H).
10	1445(s), 1210(m), 1168(m), 1125(vs), 1100(vs), 1080(vs), 1035(s), 1005(m), 971(s), 900(m), 760(m), 755(m), 732(s), 728(s), 705(s), 700(m, sh), 660(m), 635(s, sh).	504 315	3.19×10^3 4.66×10^2	1.50 (br., 6H), 2.91 (br., 4H), 6.85–7.35 (m, 6H), 7.42–7.80 (m, 4H).

**Note*: Weak and very weak peaks (1600-600 cm^{-1}) are not listed.

[a] Uv-visible spectrum could not be obtained because of the solution phase transformation of 1,5-$[Ph_2(R)PN]_2S_4N_4$ to $(R)Ph_2PN—S_3N_3$ in solution. However, these compounds may have a typical absorption at ca. 330 nm.

TABLE 4 $^{31}P\{^1H\}$-NMR Chemical Shifts (δ) of the Phosphines, Phosphine Sulfides, and Their S—N Derivatives in Chloroform-d

R	*(R)Ph_2P*	*(R)$Ph_2P(S)$*	*(R)$Ph_2PN—S_3N_3$*	*1,5-[Ph_2(R)PN]$_2S_4N_4$**	*(R)$Ph_2PN—S_3N$*
C_4H_8N—	47.5	65.1	28.2	28.0 and 23.4	24.2[a]
$C_5H_{10}N$—	62.9	67.7	32.0	33.1 and 27.2	28.9
$C_6H_{12}N$—	65.1	69.5	34.3	34.7 and 30.1	31.2[a]
$CH_3NC_4H_8N$—	61.1	67.3	31.8	— —	28.8[a]
$(C_6H_5CH_2)_2N$—	66.5	70.8	32.0	— —	28.8[a]
$(C_6H_{11})_2N$—	40.5	63.3	32.6	— —	29.6[a]

**Note*: Spectrum was recorded at −40°C because of the solution phase decomposition of 1,5-[Ph_2(R)PN]$_2S_4N_4$ to (R)$Ph_2PN—S_3N_3$ at room temperature.

[a]Only spectral evidence. Compounds could not be isolated and fully characterized.

obtain colorless crystals of (R)Ph_2P(S). The ^{31}P and ^{1}H-NMR data are listed in Tables 4 and 5.

General Procedure for the Synthesis of 1,5-[(R)Ph_2PN]$_2S_4N_4$ (R = C_4H_8N—, $C_5H_{10}N$—, $C_6H_{12}N$)

Tetrasulfurtetranitride (0.92 g, 5 mmol) was added to a stirred suspension of (R)Ph_2P (20 mmol) in CH_3CN (ca. 50 mL) at 5°C (ice water bath). It was then slowly warmed to room temperature (ca. 25°C). After 4–6 h of stirring at room temperature a cream-yellow precipitate was observed. This precipitate was separated by filtration after 24 h, washed with CH_3CN (10 mL × 2), followed by C_6H_6 (10 mL), and dried under vacuum to obtain an analytically pure sample of 1,5-[(R)Ph_2PN]$_2S_4N_4$. The yields, melting point and spectral data are listed in Tables 1, 2, 3, and 4. Phosphine sulphides were also isolated from the filtrate by a similar method to that employed in the previous reaction.

Synthesis of (R)$Ph_2PN—S_3N$ (R = $C_5H_{10}N$—)

The phosphine ($C_5H_{10}N$)Ph_2P (10 mmol) was reacted with S_4N_4 (5 mmol) in CH_3CN (30 mL) at reflux for 12 h. The red colored solution was concentrated to ca. 10 mL and cooled at ca. −20°C for a day to obtain purplish-red crystals of (R)$Ph_2PN—S_3N$. Phosphine sulphide was isolated from the remaining part of the reaction mixture.

Solution Phase Transformations of 1,5-[(R)Ph_2PN]$_2S_4N_4$ to (R)$Ph_2PN—S_3N_3$ (R = C_4H_8N—, $C_5H_{10}N$—, and $C_6H_{12}N$—)

The distributed S_4N_4 derivative, 1,5-[(R)Ph_2PN]$_2$ S_4N_4 (1 mmol), was dissolved in the minimum quantity of $CHCl_3$ (ca. 7 mL) and stirred at room temperature (ca. 25–35°C) for about 24–36 h. It was then concentrated to 2 mL, mixed with CH_3CN (2 mL), and cooled at 0°C for a day to obtain red crystals of (R)$Ph_2PN—S_3N_3$ (yield ca. 65%). From the residual filtrate no other products could be isolated.

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TABLE 5 ^{1}H-NMR Spectra (90 MHz) of the Phosphines, (R)Ph_2P, and Their Sulfides, (R)$Ph_2P(S)$: A Comparison

R	*(R)Ph_2P*	*(R)$Ph_2P(S)$*
C_4H_8N—	1.60 (m, 4H), 1.80 (m, 4H), 7.00 (s, 10H)	1.85 (m, 4H), 2.90 (m, 4H), 7.00–7.20 (m, 6H), 7.58–7.88 (m, 4H), $^3J_{HH}$ = 5.0 Hz and $^3J_{PH}$ = 8.0 Hz
$C_5H_{10}N$—	1.40 (s, br., 6H), 2.80 (d, 4H), 7.16 (s, 10H)	1.52 (s, 6H), 1.70(d, 4H), 7.05–7.15 (m, 6H), 7.50–7.80 (m, 4H).
$C_6H_{12}N$—	1.40 (s, 8H), 3.00 (m, 4H), 7.00 (s, 10H)	1.60 (s, 8H), 2.90 (m, 4H), 7.05–7.25 (m, 6H), 7.90–8.15 (m, 4H).
$CH_3NC_4H_8N$—	2.10 (s, 3H), 2.20 (t, 4H), 2.80 (m, 4H), 7.00 (m, 10H), $^3J_{HH}$ = 4.5 Hz and $^3J_{HH}$ = 4.5 Hz	2.10 (s, 3H), 2.25 (t, 4H), 2.60 (q, 4H), 7.00–7.18 (m, 6H), 7.50–7.80 (m, 4H) $^3J_{HH}$ = 4.7 Hz and $^3J_{PH}$ = 5.0 Hz.
$(C_6H_5CH_2)_2N$—	4.00 (s, 2H), 4.10 (s, 2H), 7.00–7.38 (m, br., 10H), $^3J_{PH}$ = 9 Hz	4.00 (s, 2H), 4.11 (s, 2H), 6.90 (m, 10H), 7.00–7.20 (m, 6H), 7.50–7.72 (m, 4H). $^3J_{PH}$ = 10 Hz.
$(C_6H_{11})_2N$—	1.00 (s, br., 8H), 1.50 (s, br., 12H) 3.75 (s, br., 2H), 7.00 (m, br., 10H)	0.90 (m, 6H), 1.61 (m, br., 14H), 2.95 (s, br., 2H), 7.05–7.15 (m, 6H, 7.60–7.90 (m, 4H).

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