Cyclic S–N Compounds and Phosphorus Reagents Part 6*. Reactions of S_4N_4 with Symmetrical Tertiary Phosphines, R_3P (R = t-C_4H_9, c-C_6H_{11}, $C_6H_5CH_2$, *p*-$MeOC_6H_4$ and *p*-ClC_6H_4): Isolation and Characterization of Phosphinimino Substituted Cyclic Sulphur Nitrides

ANIL J. ELIAS and M. N. SUDHEENDRA RAO**

Department of Chemistry, Indian Institute of Technology, Madras 600 036 (India)

(Received January 18, 1989; revised May 8, 1989)

Abstract

Unlike Ph_3P, reactions of S_4N_4 with symmetrical tertiary phosphines, R_3P (R = t-butyl, cyclohexyl, benzyl, *p*-methoxyphenyl and *p*-chlorophenyl) afford only the corresponding phosphiniminocyclotrisulphurtrinitrides, $R_3PN{-}S_3N_3$ (**I–V**) in moderate to good yields. $(p\text{-}ClC_6H_4)_3P$ alone yields the disubstituted S_4N_4 derivative, 1,5-$[(p\text{-}ClC_6H_4)_3PN]_2S_4N_4$ (**VI**) in low yield which undergoes a ring contraction in solution. Among the red crystalline compounds **I–V**, those containing aliphatic substituents on phosphorus (**I–III**) are less stable both in solid and solution phases than those containing aromatic substituents (**IV** and **V**). Various spectroscopic data have been discussed.

Introduction

The merit of the reactions of phosphines and other phosphorus reagents with cyclothiazenes for realizing different types of phosphorus, sulphur and nitrogen containing inorganic heterocycles has been well demonstrated in recent years [2–6]. A better understanding as well as information on the general nature of these reactions within a class of compounds, are still far from being adequate. It may be safely assumed that this is in great part due to insufficient studies of this kind, known so far. For example, with regard to the reaction of S_4N_4 with phosphines of the type R_3P (sym-tertiary phosphines), only Ph_3P [2] reactions have been investigated in detail while those of $(c\text{-}C_6H_{11})_3P$ [7] and $(PhO)_3P$ [3] are only mentioned in brief in the literature. We have therefore undertaken detailed investigations of the reactions of S_4N_4 with five different sym-tertiary phosphines, R_3P [R = t-butyl, cyclohexyl, benzyl, *p*-methoxyphenyl and *p*-chlorophenyl] and report our results here.

*Part 5 is ref. 1.

**Author to whom correspondence should be addressed.

Experimental

Reagents

S_4N_4 synthesized using the reported procedure [8] was recrystallized from hot toluene before use. $(c\text{-}C_6H_{11})_3P$, $(C_6H_5CH_2)_3P$ (Ventron GmbH) and $(t\text{-}C_4H_9)_3P$ were procured and used as such. $(p\text{-}MeOC_6H_4)_3P$ and $(p\text{-}ClC_6H_4)_3P$ were prepared by the Grignard method described before [9, 10] and crystallized from hot ethanol. Solvent purification and instrument facilities made use of are the same as given elsewhere [11]. Reactions have been performed under different conditions with each phosphine and the results of only a few representative reactions that gave maximum yield of the heterocyclic products have been given in Table 1. Characterization data on the new compounds **I** to **VI** are given in Tables 2 and 3.

General Reaction Procedure

To a stirred solution of the phosphine in the specified solvent, a stoichiometric amount of S_4N_4 was added as solid over a period of 30 min and stirred for 24 h. The reaction mixture at this stage was filtered using a frit and the precipitate and filtrate portions were separately worked up to isolate different products. The details of the working up and characterization procedure are the same as described previously [11].

Results and Discussion

Reactions of S_4N_4 with R_3P [R = t-butyl, cyclohexyl, benzyl, *p*-methoxyphenyl and *p*-chlorophenyl] have been studied by changing the reaction temperature and solvent as well as the mole ratio of the reactants. Both acetonitrile and benzene reactions at room temperature afford the corresponding phosphiniminocyclotrisulphurtrinitrides, $R_3PN{-}S_3N_3$ (**I–V**) in 60–70% yield. This observation is similar to that found in the case of tertiary(amino)phosphines

0020-1693/89/$3.50

TABLE 1. Reactions of S_4N_4 with tertiary phosphines, R_3P

Reactants[a]		Reaction conditions[b]		Temperature (°C)	Products[a] isolated	Yield	
S_4N_4 (g) (mmol)	R_3P (g) (mmol)	Mole ratio S_4N_4/R_3P	Solvent (ml)			(g)	(%)[f]
0.20 (1.12)	0.46 (A) (2.27)	1:2	CH_3CN (20)	30	I VII S_4N_4	0.25 0.29 0.06	60
0.23 (1.25)	0.70 (B) (2.50)	1:2	C_6H_6 (25)[c]	30	II[d] VIII	0.35 0.38	65
0.24 (1.29)	0.72 (B) (2.58)	1:2	CH_3CN (20)	30	II VIII	0.38 0.39	68
0.16 (0.85)	0.52 (C) (1.90)	1:2	CH_3CN (20)	30	III IX	0.25 0.35	63
0.35 (1.89)	1.33 (D) (3.78)	1:2	CH_3CN (25)	30	IV	0.62	65
0.31 (1.66)	1.21 (E) (3.32)	1:2	CH_3CN (30)	30	V XI	0.61 0.75	71
0.17 (0.95)	1.17 (E) (3.24)	1:3.5[e]	C_6H_6 (20)	15	VI XI	0.10 0.60	17

[a] $(t\text{-}C_4H_9)_3P$: A; $(c\text{-}C_6H_{11})_3P$: B; $(C_6H_5CH_2)_3P$: C; $(p\text{-}CH_3OC_6H_4)_3P$: D and $(p\text{-}ClC_6H_4)_3P$: E. $(t\text{-}C_4H_9)_3PNS_3N_3$ (I); $(c\text{-}C_6H_{11})_3PN\text{-}S_3N_3$ (II); $(C_6H_5CH_2)_3PN\text{-}S_3N_3$ (III); $(p\text{-}CH_3OC_6H_4)_3PN\text{-}S_3N_3$ (IV); $(p\text{-}ClC_6H_4)_3PN\text{-}S_3N_3$ (V), 1,5-$[(p\text{-}ClC_6H_4)_3PN]_2S_4N_4$ (VI); $(t\text{-}C_4H_9)_3PS$ (VII); $(c\text{-}C_6H_{11})_3PS$ (VIII); $(C_6H_5CH_2)_3PS$ (IX); $(p\text{-}CH_3OC_6H_4)_3PS$ (X); $(p\text{-}ClC_6H_4)_3PS$ (XI). [b] In all the reactions, the reaction period was kept constant (24 h). [c] This reaction proceeds equally well in all other cases; however, the isolable yield of I was only *c.* 40%. [d] Isolation of this compound in only 10% yield has been reported in the previous study [7]. [e] In all other cases, this reaction gave only R_3PS and/or $R_3PN\text{-}S_3N_3$ (Yield: 20–40%). [f] Percentage yields are based on nitrogen.

TABLE 2. Physical and analytical data of compounds I–VI

Compound	Colour	Maximum yield (%)	Melting point (°C)	Analytical data[a]		
				C	H	N
$(t\text{-}C_4H_9)_3PN\text{-}S_3N_3$ (I)	red	53	94			
$(c\text{-}C_6H_{11})_3PN\text{-}S_3N_3$ (II)	red	68	130	49.9 (50.4)	7.7 (7.5)	13.0 (13.3)
$(C_6H_5CH_2)_3PN\text{-}S_3N_3$ (III)	red	68	127	55.2 (55.3)	4.6 (4.7)	12.3 (12.3)
$(p\text{-}MeOC_6H_4)_3PN\text{-}S_3N_3$ (IV)	red	65	102	50.0 (49.5)	4.2 (4.6)	11.1 (12.0)
$(p\text{-}ClC_6H_4)_3PN\text{-}S_3N_3$ (V)	red	66	170			
1,5-$[(p\text{-}ClC_6H_4)_3PN]_2S_4N_4$ (VI)	pinkish white	17	152 (dec.)	54.2 (53.9)	3.1 (3.0)	10.9 (10.5)

[a] Calculated values in parentheses.

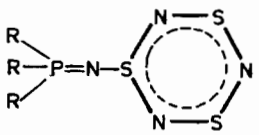
[12]. The heterocyclic products of the type 1,5-$[R_3PN]_2S_4N_4$ and $(R_3PN)_3S^+S_4N_5^-$ which are readily isolated in the case of Ph_3P [2] are not obtained in the present study except that tris(*p*-chlorophenyl)-phosphine affords the disubstituted tetrasulphurtetranitride, 1,5-$[(p\text{-}ClC_6H_4)_3PN]_2S_4N_4$ **(VI)** in low yield from a low temperature reaction. A notable difference in this study is that we isolated compound **VI** from the benzene reaction while 1,5-$(Ph_3PN)_2S_4N_4$ [2] and 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$ [11] were isolated from the acetonitrile medium only.

Among the phosphines tried, $(t\text{-}C_4H_9)_3P$ (pK_a 11.40) [9] reacts very fast with S_4N_4 in an exothermic manner while $(p\text{-}ClC_6H_4)_3P$ (pK_a 1.03) reacts very slowly. The sulphides of the above phosphines which are the byproducts of these reactions (eqn. (1))

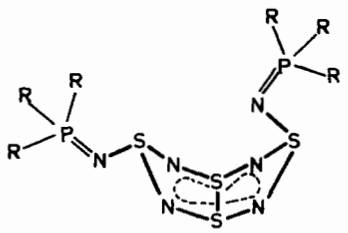
TABLE 3. Infrared, UV–Vis and NMR spectral data of compounds I–VI

Compound no.	IR $\nu(cm^{-1})$[a]	^1H NMR δ (ppm)	UV–Vis λ_{max} [ϵ in mol^{-1} dm^3 cm^{-1}]	$^{31}P\{^1H\}$ δ (ppm)
I	1490s, 1400m, 1370s, 1200s, b 1180vs, 1149vs, b, 1030s 1025s, 975s, 935vs, b, 810s 735vs, 690m, 670m, 630s.	1.47(d) ($^3J_{PH}$ 14.0 Hz)	484[3.1 × 10^3] 331[2.4 × 10^3] 285[2.1 × 10^3]	23.8
II	1175m, 1138vs, 1100s, 1088m, 1052m, 1008m, 965m, 940s, 922s, 905s, 890m, 850s, 791s, 730vs, 695m, 685m, 630vs.	1.33 (s, 5H) 1.88 (s, 5H) 2.15 (s, 1H)	485[3.6 × 10^3] 335[2.9 × 10^3] 286[3.0 × 10^3]	45.6
III	1490s, 1230m, 1200m, 1135s, 1100vs, 1070s, 1030m, 960m, 940vs, 920m, 870s, 840s, 782m, 750m, 730vs, 698vs, 620m, 610m.	3.18 (d, 6H) ($^3J_{PH}$ 13.8 Hz) 7.28 (s, 15H)	482[3.6 × 10^3] 328[3.3 × 10^3]	40.4
IV	1592s, 1569m, 1500s, 1465vs 1305m, 1290m, 1260vs, 1180m, 1117vs, 1080s, 1030m, 970m, 932m, 830m, 800m, 725m, 675m, 665m.	3.85 (s, 9H) 6.90–7.80(m, 12H)	478[3.5 × 10^3] 330[3.1 × 10^3]	24.7
V	1575s, 1480s, 1119s, 1090vs, 1012s, 970m, 929s, 780m, 760s, 725s, 620m.	7.32–7.80 (m)	480[3.0 × 10^3] 328[2.8 × 10^3]	23.1
VI	1565m, 1480s, 1181m, 1140s, 1120vs, 1094vs, 1065vs, 1015vs, 970vs, 916vs, 840m, 824s, 775m, 760vs, 725m, 640s	7.30–7.85 (m)	[b]	22.8 16.5[c]

[a] Weak and very weak bands have been omitted. [b] Could not be measured due to decomposition in solution. [c] From the spectrum recorded at −40 °C.



I : R = t-C_4H_9-
II : R = c-C_6H_{11}-
III : R = $C_6H_5CH_2$-
IV : R = *p*-$MeOC_6H_4$-
V : R = *p*-ClC_6H_4-



VI : R = *p*-ClC_6H_4-

have also been isolated in all the cases in good yield (*c.* 70%). $(C_6H_5CH_2)_3PS$, by virtue of its highly insoluble nature, precipitates out almost entirely in all its reactions thus posing least difficulty in the isolation of compound **III** in the pure form.

$$2R_3P + S_4N_4 \longrightarrow R_3PN{-}S_3N_3 + R_3PS \qquad (1)$$

Compounds **I–V** are red crystalline solids that dissolve readily in solvents like CH_2Cl_2, C_6H_6 and slowly in CH_3CN. All have sharp melting points. Strikingly $(p\text{-}ClC_6H_4)_3PN\text{-}S_3N_3$ has the highest melting point (170 °C) among the compounds of this type known so far. Accordingly, this compound is recovered unchanged from refluxing CH_3CN solution whereas the other compounds of this type are not. The solution stability of compounds **I–V** at room temperature is also different. It is found that the benzene solution of compounds **I–III** (containing only aliphatic substituents on P) on standing decolorizes much faster than those of compounds **IV** and **V** (with only aromatic substituents on P).

Table 3 shows the characteristic UV–Vis absorptions expected of a monosubstituted cyclotrisulphur-

trinitride [13] for compounds **I** to **V**. Also, in the case of $(c\text{-}C_6H_{11})_3PN{-}S_3N_3$ and $(t\text{-}C_4H_9)_3PN{-}S_3N_3$ an additional absorption at *c.* 285 nm attributable to the transition arising from the $\geqslant P{=}N{-}$ group is observed. (Cyclic amino)phosphiniminocyclotrisulphurtrinitrides prepared in our laboratory also exhibit this feature [12].

The characteristic ring vibration of the phosphinimino substituted S_3N_3 at 930–940 cm^{-1} is also observed in the infrared spectra of compounds **I**–**V** [12]. An interesting feature in the infrared spectra is with $\nu(P{=}N)$ whose value is comparatively higher for compounds **I**–**III** (1100, 1140 and 1150 cm^{-1} respectively) than those for compounds **IV** and **V** (1080 and 1090 cm^{-1} respectively). This observation implies strengthening of the P=N bond and a corresponding weakening of the exocyclic S–N bond in **I**–**III**. The increased thermal and solution phase instability observed for these compounds also support this contention. In addition, a common feature in the electron impact mass spectra of compounds **II**–**V** is that the fragment $'R_3PN'$ is observed in moderate to good intensity in all cases.

The proton and $^{31}P\{^1H\}$ NMR spectral data on compounds **I**–**VI** are given in Table 3. Except in the case of **II** and **III**, the phosphorus chemical shifts resemble those observed for $(C_6H_5)_x(p\text{-}CH_3C_6H_4)_{3-x}PN{-}S_3N_3$ ($x = 0$–3) [12]. However, Appel *et al.* have reported [14] a value of 44.0 ppm (δ_P) for a similar compound, $N_3S_3NP(CH_3)_2(CH_2)_3(CH_3)_2PNS_3N_3$.

The only disubstituted S_4N_4 derivative to be obtained in this study is $1,5\text{-}[(p\text{-}ClC_6H_4)_3PN]_2S_4N_4$. The stereochemical non-equivalence of its substituents was established by the observation of two phosphorus signals of equal intensity in its $^{31}P\{^1H\}$ NMR spectrum recorded at −40 °C. This is in accordance with the *exo*- and *endo*-orientation of the substituents which is also the case with $1,5\text{-}(Ph_3PN)_2S_4N_4$ [2] and $1,5\text{-}[(OC_4H_8N)Ph_2PN]_2S_4N_4$ [11]. The phosphorus chemical shifts are slightly more shielded compared to those in $1,5\text{-}[(p\text{-tolyl})_xPh_{3-x}PN]_2S_4N_4$ [$x = 0$, 1, 2 and 3] [12]. Similar to the recent observation [11], this compound also undergoes ring contraction readily in solution at room temperature and crystals of compound **V** are isolated from the solution of the decomposition.

Acknowledgements

Anil J. Elias thanks CSIR India for a Senior Research Fellowship. Our grateful thanks are due to Prof. Dr H. W. Roesky, Göttingen, F.R.G. for a gift sample of $(t\text{-butyl})_3P$. Thanks are also due to Dr N. Chandrakumar, CLRI, Madras for recording the low temperature $^{31}P\{^1H\}$ NMR spectra.

References

1 A. J. Elias and M. N. S. Rao, *Phosphorus, Sulfur Silicon, 41* (1989) 367.
2 J. Bojes, T. Chivers, A. W. Cordes, G. MacLean and R. T. Oakley, *Inorg. Chem., 20* (1981) 16.
3 N. Burford, T. Chivers, A. W. Cordes, W. G. Laidlaw, M. C. Noble, R. T. Oakley and P. N. Swepston, *J. Am. Chem. Soc., 104* (1982) 1282.
4 T. Chivers and M. N. S. Rao, *Inorg. Chem., 23* (1984) 3605.
5 H. W. Roesky, J. Lucas, M. Noltemyer and G. M. Sheldrick, *Chem. Ber., 117* (1984) 1583.
6 T. Chivers, K. S. Dhathatreyan, S. W. Liblong and T. Parks, *Inorg. Chem., 27* (1988) 1305, and refs. therein.
7 H. L. Krauss and H. Jung, *Z. Naturforsch., Teil B, 16* (1961) 624.
8 M. Villena-Blanco and W. L. Jolly, *Inorg. Synth., 9* (1967) 98.
9 T. Allman and R. G. Goel, *Can. J. Chem., 60* (1982) 716.
10 A. E. Senear, W. Valient and J. Wirth, *J. Org. Chem., 25* (1960) 2001.
11 C. J. Thomas and M. N. S. Rao, *J. Chem. Soc., Dalton Trans.,* (1988) 1445.
12 A. J. Elias and M. N. S. Rao, unpublished results.
13 T. Chivers, *Chem. Rev., 85* (1985) 3451.
14 I. Ruppert, V. Bastian and R. Appel, *Chem. Ber., 107* (1974) 3426.