Cyclic Sulphur–Nitrogen Compounds and Phosphorus Reagents. Part 2.[1] Reactions of Tetrasulphur Tetranitride with (Morpholino)diphenylphosphine. First Observation of the Ring Contraction of 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$ to $(OC_4H_8N)Ph_2PNS_3N_3$ in Solution

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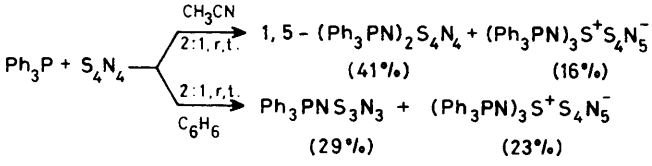
(Morpholino)diphenylphosphine, unlike PPh_3, gives only two new compounds, $(OC_4H_8N)Ph_2PNS_3N_3$, (**1**), and 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$, (**2**), on reacting with S_4N_4. The reaction temperature, solvent, and mole ratio of the reactants are critically important in their synthesis. For the first time a ring contraction of compound (**2**) to compound (**1**) in solution at room temperature has been observed and evidence for the elimination of the 'NSR' group (R = phosphinimino group) obtained.

Triphenylphosphine and tricyclohexylphosphine were the first examples of tertiary phosphines of the type PR_3 to react with S_4N_4 to give the heterocycles, $R_3PNS_3N_3$ (R = Ph or cyclo-C_6H_{11})[2] in 11 and 10% yields respectively. A recent re-investigation of the reaction of S_4N_4 and PPh_3 by Bojes *et al.*[3] led to the isolation of two other new cyclic compounds (Scheme 1) in addition to obtaining $Ph_3PNS_3N_3$ in better yield.



Scheme 1. Cyclic derivatives from the reactions of S_4N_4 and PPh_3

Contrary to this result, reactions of S_4N_4 with unsymmetrical phosphines, *e.g.* $PHMe_2$,[4] $PHPh_2$,[4] PPh_2Cl,[5] or $PPhCl_2$,[5] yielded ternary ring systems composed of phosphorus, sulphur, and nitrogen. This significant change in behaviour, though not fully understood, has been attributed to the presence of labile substituents on phosphorus. These are the only examples of such phosphines to be studied so far. We have therefore considered it necessary to carry out further investigations in this area and hope to throw light on the understanding of the diverse behaviour of phosphines with S_4N_4 in general.

(Morpholino)diphenylphosphine, chosen for this study, is different in its behaviour from the unsymmetrical phosphines cited above. We report here the synthesis of two new products, $(OC_4H_8N)Ph_2PNS_3N_3$ (**1**) and 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$ (**2**) and the first observation of the conversion of (**2**) to (**1**) in solution at room temperature.

† A mixture of S_2Cl_2 and SCl_2 (1:1) in CH_2Cl_2 solvent was used for ammoniolysis after chlorinating for 0.5 h. Sulphur, from the crude S_4N_4, was removed by a CS_2 wash. **CAUTION**: S_4N_4 may explode when struck, ground, or suddenly heated.

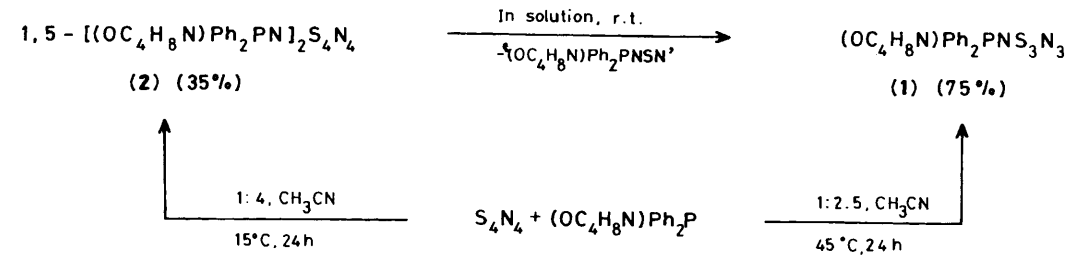
‡ Details of the procedure and its ^1H and ^{31}P n.m.r. data will be published elsewhere (C. J. Thomas and M. N. S. Rao, unpublished work).

§ **CAUTION**: Benzene is a potential carcinogen.

Experimental

Tetrasulphur tetranitride† and (morpholino)diphenylphosphine‡ were synthesized by slight modifications of the reported procedures[6,7] and recrystallised before use. Solvents (CH_3CN, C_6H_6,§ and $CHCl_3$) were distilled and stored over CaH_2, Na, and P_2O_5 respectively. All manipulations involving the phosphine were performed in an atmosphere of dry, oxygen-free nitrogen. I.r. spectra (4 000—600 cm^{-1}) were recorded as Nujol mulls on a Perkin-Elmer 781 spectrophotometer. A Shimatzu 240 spectrophotometer was used to obtain u.v.–visible spectra (200—800 nm, $CHCl_3$ solution). Proton and ^{31}P-{^1H} n.m.r. spectra were recorded as $CDCl_3$ solutions using EM-390 (90 MHz) and Varian XL-100 (40.5 MHz) spectrometers respectively. Tetramethylsilane, $SiMe_4$, and 85% H_3PO_4 were the corresponding reference compounds. Mass spectra were recorded with a Finnigan MAT8230 spectrometer operating at 70 eV. Carbon, H, and N analyses were performed at the Department of Chemistry, University of Capetown, Rondebosch, South Africa.

Preparation of $(OC_4H_8N)Ph_2PNS_3N_3$ (**1**).—To a stirred solution of (morpholino)diphenylphosphine (1.16 g, 4.25 mmol) in CH_3CN (20 cm^3), solid S_4N_4 (0.32 g, 1.74 mmol) was added in small quantities at 45 °C. After complete addition, the initial orange-yellow colour of the solution darkened to red. After 20 min all the S_4N_4 had disappeared and slow formation of a red precipitate began. After stirring for 24 h, the solid was filtered off and recrystallised (CH_3CN–C_6H_6, 1:1) to obtain dark red crystals of $(OC_4H_8N)Ph_2PNS_3N_3$ (**1**) (m.p. 138 °C; yield 0.51 g, 69%) (Found: C, 44.95; H, 4.15; N, 16.85. Calc. for $C_{16}H_{18}N_5OPS_3$: C, 45.35; H, 4.30; N, 16.55%). I.r.: 3 055vw, 1 592vw, 1 480w (sh), 1 443s, 1 370w, 1 329vw, 1 315vw, 1 300w, 1 282vw, 1 261m, 1 213vw, 1 180w (sh), 1 166m, 1 137vs, 1 120vs, 1 112s (sh), 1 091m, 1 075w, 1 030w, 1 021w, 1 000w, 975s, 939s, 905m, 861w, 849vw, 780w, 760m, 750w, 736s, 731s, 726m (sh), 720m, 700m, 668w, 621m, and 620m cm^{-1}. Mass spectrum (*m/z*): 423 (M^+, 1%); 395 ($M - N_2^+$, 2); 285 [$(OC_4H_8N)Ph_2PN^+$, 2]; 271 [$(OC_4H_8N)Ph_2P^+$, 3]; 200 (Ph_2PNH^+, 100); 184 ($S_4N_4^+$, 4); 138 ($S_3N_3^+$, 3); 92 ($S_2N_2^+$, 14); 78 (S_2N^+, 8); 64 (S_2^+, 11). N.m.r.: ^1H: 2.77 (m, 4 H), 3.47 (m, 4 H), 7.20 (complex m, 6 H), 7.62 (complex m, 4 H); $^3J_{HH}$ = 5, $^3J_{PH}$ = 4.5 Hz; ^{31}P: 31.2 (s, 1 P). U.v.–visible: $\lambda_{max.}$ 480 (ε 8.3 × 10^3) and 331 nm (7.2 × 10^3 dm^3 mol^{-1} cm^{-1}). From the filtrate a further quantity of (**1**) (50 mg, 7%) and the phosphine sulphide, $(OC_4H_8N)Ph_2P(S)$ (**3**),[8] were isolated.



Scheme 2. Optimum conditions for the synthesis of (**1**) and (**2**) and the ring contraction of (**2**)→(**1**) in solution. Percentage yield (in parentheses) based on nitrogen content of S_4N_4

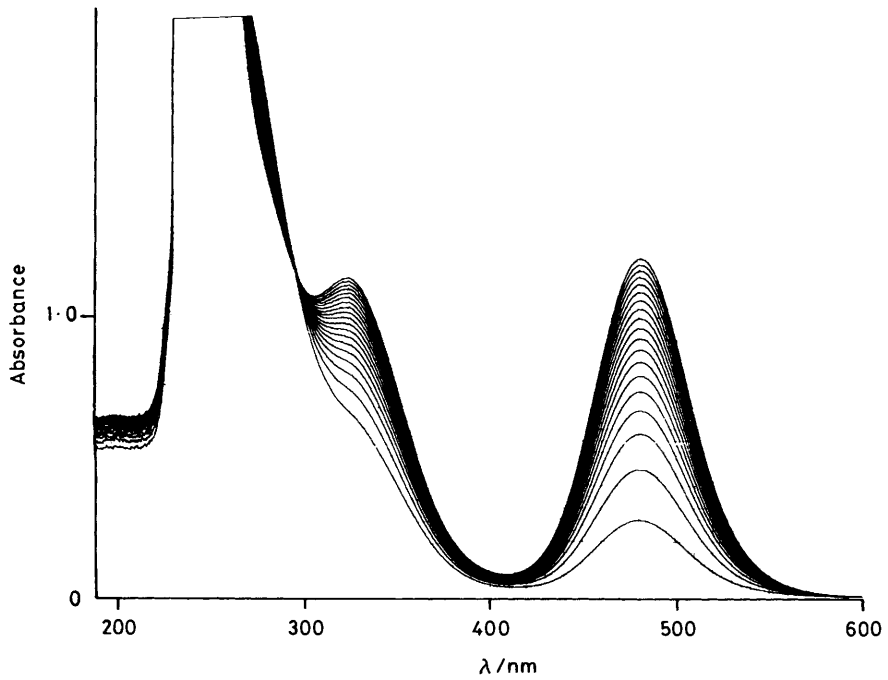


Figure. U.v.–visible spectrum showing the conversion of compound (**2**) to (**1**) in solution (time-gap between any two scans is *ca.* 3 min)

Preparation of 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$ (**2**).—The phosphine $PPh_2(NC_4H_8O)$ (1.26 g, 4.65 mmol) and S_4N_4 (0.21 g, 1.14 mmol) were reacted at 15 °C as described above. Filtering the reaction mixture after 24 h gave a cream yellow precipitate which was washed with CH_3CN (2 × 5 cm^3), diethyl ether (2 × 5 cm^3), dried under vacuum, and characterised as compound (**2**) [m.p. 124 °C (decomp.); yield 0.2 g, 35%) (Found: C, 49.95; H, 4.55; N, 14.95. Calc. for $C_{32}H_{36}N_8O_2P_2S_4$: C, 50.90, H, 4.80; N, 14.85%). I.r.: 3 061w, 1 596w, 1 485m, 1 435vs, 1 350vw, 1 320vw, 1 302w, 1 265s, 1 221vw, 1 182w (sh), 1 171m (sh), 1 160s, 1 140s, 1 120vs, 1 093vs, 1 081vs, 1 030w, 1 022w, 1 000w, 974vs, 920s, 895vs, 872m (sh), 850w, 790w (sh), 778m, 765m, 755m, 730s, 720s, 699s, 680vw, 643s, 625s (sh), 618s, and 605s cm^{-1}. Mass spectrum (*m/z*): 395 $[(OC_4H_8N)Ph_2PN{-}S_3N^+$, 2%]; 331 $[(OC_4H_8N)Ph_2PN{-}SN^+$, 10]; 285 $[(OC_4H_8N)Ph_2PN^+$, 6]; 200 (Ph_2PNH^+, 70); 184 (S_4N_4, 24); 152 ($S_3N_4^+$, 14); 139 ($S_3N_3H^+$, 26); 124 ($S_3N_2^+$, 38); 64 (S_2^+, 100). N.m.r.: ^1H: 2.55 (m, 4 H), 3.60 (br, s, 4 H); 7.20 (br, s, 6 H); 7.60 (m, 4 H); ^{31}P*: 31.60 (s, 1 P) and 27.00 (s, 1 P).

The filtrate, on standing in the refrigerator for *ca.* 7 d, yielded compounds (**1**) (0.11 g, 23%) and (**3**) (0.5 g).

* Chemical shifts were obtained from −30 °C spectrum. Downfield shifts are positive.

Conversion of (**2**) to (**1**).—Compound (**2**) (50 mg) was stirred in $CHCl_3$ (10 cm^3) at room temperature (r.t.) for 10 h, during which the resulting solution turned deep red in colour. The solvent $CHCl_3$ was removed and the residue redissolved in C_6H_6–CH_3CN (1:2 cm^3) and kept at room temperature. After 2 d, red crystals of (**1**) (12 mg) were isolated from the solution. Examination by thin layer chromatography of the reaction mixture was complicated by the decomposition of products on the silica gel plate. However, three distinct spots, of which the middle one corresponded to (**1**), could be observed.

Discussion

Only two new cyclic derivatives, (**1**) and (**2**), were obtained from the reactions of S_4N_4 with (morpholino)diphenylphosphine. The phosphine PPh_3 affords yet another compound which is ionic in nature (Scheme 1). Failure to isolate its analogue in the present study is probably due to the steric factors influencing the stability of the corresponding sulphonium cation. The six-membered heterocycle, $Ph_3PNS_3N_3$ was obtained in 29% yield only from reaction in benzene. It may be noted that the analogous compound, (**1**), described in this paper was readily obtained from reaction in CH_3CN in much higher yield (*ca.* 75%). Reactions at much higher temperatures were not attempted since $-S_3N_3$ derivatives are thermally sensitive.[9]

The cream yellow compound, $(Ph_3PN)_2S_4N_4$, is a stable solid

and is readily obtained from the room temperature reaction of S_4N_4 and PPh_3. The (morpholino)diphenylphosphine analogue of this, compound (**2**), is less stable thermally and is formed only from a low temperature reaction (Scheme 2). This observation led to the discovery of the ring contraction (**2**)→(**1**) which occurs readily at room temperature in solution.

Ring Contraction of 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$ (**2**) *to* $(OC_4H_8N)Ph_2PNS_3N_3$ (**1**) *in* $CHCl_3$.—The observation that compound (**2**), during its melting point determination, turned red before melting and that its solution developed a red colour within minutes gave clues to the transformation of (**2**) to (**1**). Also, the reaction yielding (**2**), when performed at room temperature (*ca.* 30 °C) yielded only compound (**1**), suggesting the ready occurrence of the conversion of (**2**) to (**1**) (Scheme 2). This was further confirmed by (*i*) following the change in the u.v.–visible spectrum of (**2**) as a function of time, (*ii*) a variable-temperature ^{31}P n.m.r. study, and finally (*iii*) isolating red crystals of (**1**) from solutions of (**2**) in *ca.* 45% yield (based on the equation given in Scheme 2).

A u.v.–visible spectrum characteristic of (**2**) could not be obtained. Attempts to record its spectrum gave absorptions characteristic of the $-S_3N_3$ ring itself in the first scan (Figure). However, the fact that the absorption coefficient of the absorption at 330 nm is much higher initially than expected for $-S_3N_3$ derivatives[10] suggests that (**2**) probably has an absorption around 330 nm. Repeat scans of the spectrum showed increasing intensity for both the peaks suggesting the formation of more and more compound (**1**) with time. The rate of conversion was found to be higher with increasing dilution.

The two phosphinimino substituents in $(Ph_3PN)_2S_4N_4$ are on the opposite sulphur atoms in S_4N_4 (1,5-positions) and are non-equivalent both in solid[11] and solution[3,12] phases. The ^{31}P n.m.r. spectrum of compound (**2**) at −30 °C shows two signals (31.6 and 27.0 p.p.m.) of equal intensity in support of the *exo–endo* orientation of the substituents. As the solution in the n.m.r. tube warms up, changes occur and new peaks start appearing. At the end of 1 h at room temperature, a fairly intense peak at 31.3 p.p.m. due to (**1**) is observed with a simultaneous decrease in the peak intensity of (**2**). After 24 h, two major peaks at 26.0 and 30.8 p.p.m. and other peaks of low intensity at 41.3, 31.1, 30.2, 27.5, and 20.1 p.p.m. are observed. Although the origin of all these peaks is not clear at the moment, we tentatively assign the peak at 30.8 p.p.m. to (**1**) and the other intense peak is to the fragment NSR or to any of its more stable forms. It may be noted that none of the peaks corresponded to that of the phosphine sulphide (**3**) (δ_P = 67.6 p.p.m.).

The isolation of (**1**) and the absence of phosphine sulphide in the solutions of (**2**) indicates that the fragment expelled in this conversion is 'NSR', where R is the $(OC_4H_8N)Ph_2PN$ group. A peak corresponding to this fragment found in the mass spectrum of (**2**) and not in that of (**1**) also supports this finding. This is probably the first time such an elimination involving a bulky phosphinimino group has been observed in the chemistry of cyclothiazenes.

Elimination of 'NSCl' was first reported in the chlorination of S_4N_4[13] with chlorine gas. Though 1,5-$S_4N_4Cl_2$[14] was suggested as one of the intermediates, it was not possible for previous workers to identify whether the elimination occurred before or after the addition of a second molecule of chlorine. Our work suggests that it may well be possible to isolate or detect from the solutions of 1,5-$S_4N_4Cl_2$, the compound S_3N_3Cl whose synthesis has not been achieved so far.[15] Very recently, elimination of 'NSCl' from a PSN ring[16] and of 'Me_2NCN' from a CNS ring[17] have been reported.

Conclusions

Replacement of one phenyl group in PPh_3 by a morpholino group exerts a noticeable influence on the products formed from its reactions with S_4N_4 and their yields. The ring contraction observed in this study suggests an alternative pathway for the formation of RS_3N_3 derivatives from the reactions of S_4N_4 and phosphines and also finds application in explaining some of the unaccounted peaks in the ^1H n.m.r. spectra of the reported 1,5-bis(amino) S_4N_4 derivatives.[18]

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References

1 Part 1, A. J. Elias, C. J. Thomas, and M. N. S. Rao, *Phosphorus Sulfur.*, 1987, **30**, 253.
2 H. L. Krauss and H. Jung, *Z. Naturforsch., Teil B*, 1961, **16**, 624.
3 J. Bojes, T. Chivers, A. W. Cordes, G. Maclean, and R. T. Oakley, *Inorg. Chem.*, 1981, **20**, 16.
4 N. Burford, T. Chivers, and J. F. Richardson, *Inorg. Chem.*, 1983, **22**, 1482.
5 T. Chivers and M. N. S. Rao, *Inorg. Chem.*, 1984, **23**, 3605.
6 M. Villena-Blanco and W. L. Jolly, *Inorg. Synth.*, 1967, **9**, 98.
7 N. L. Smith and H. Sisler, *J. Org. Chem.*, 1961, **26**, 5145.
8 G. Kamai, F. M. Kharrasova and E. A. Erre, *Zh. Obshch. Khim.*, 1972, **42**, 1295.
9 T. Chivers, A. W. Cordes, and P. N. Swepston, *Inorg. Chem.*, 1981, **20**, 2376.
10 T. Chivers, *Chem. Rev.*, 1985, **85(5)**, 341.
11 J. Bojes, T. Chivers, G. MacLean, R. T. Oakley, and A. W. Cordes, *Can. J. Chem.*, 1979, **57**, 3171.
12 T. Chivers, R. T. Oakley, O. J. Scherar, and G. Wohmershauser, *Inorg. Chem.*, 1981, **20**, 914.
13 J. Nelson and H. G. Heal, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 429.
14 L. Zborilova and P. Gebauer, *Z. Chem.*, 1979, **19**, 32.
15 T. Chivers and M. N. S. Rao, *Can. J. Chem.*, 1983, **61**, 1957.
16 N. Burford, T. Chivers, M. N. S. Rao, and J. F. Richardson, *Inorg. Chem.*, 1984, **23**, 1946.
17 T. Chivers, J. F. Richardson, and N. R. M. Smith, *Inorg. Chem.*, 1986, **25**, 47.
18 H. W. Roesky, C. Pelz, B. Krebs, and G. Henkel, *Chem. Ber.*, 1982, **115**, 1448.

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