

## Cyclic sulphur-nitrogen compounds and phosphorus reagents: Part IV<sup>1</sup>—Reactions of phosphiniminocyclotrisulphurtrinitride, (R) Ph<sub>2</sub>PN-S<sub>3</sub>N<sub>3</sub> (R = phenyl- and morpholino-) with Ph<sub>3</sub>P and (OC<sub>4</sub>H<sub>8</sub>N) Ph<sub>2</sub>P: six-membered to eight-membered ring (6→8) conversions

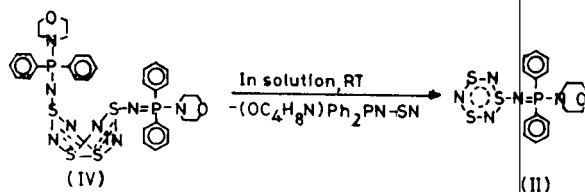
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Triphenylphosphine (A) reacts slowly with Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub>(I) both in CH<sub>3</sub>CN and C<sub>6</sub>H<sub>6</sub> to produce the known disubstituted eight-membered heterocycle, 1,5-(Ph<sub>3</sub>PN)<sub>2</sub>S<sub>4</sub>N<sub>4</sub>(III). The recently reported 1,5-[(OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>PN]<sub>2</sub>S<sub>4</sub>N<sub>4</sub> (IV) is obtained in better yield (ca. 70%) from the reaction between (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>PN-S<sub>3</sub>N<sub>3</sub>(II) and (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>P(B) in acetonitrile. However, reactions in benzene of (I) with (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>P and of (II) with Ph<sub>3</sub>P afford an inseparable mixture of (III) and (IV). Reaction temperature appears to be critical in these ring transformation reactions.

We have reported<sup>2</sup> that (morpholino)diphenylphosphine exerts a cooperative effect on the reactions of S<sub>4</sub>N<sub>4</sub> and Ph<sub>3</sub>P and produces the heterocycle, 1,5-(Ph<sub>3</sub>PN)<sub>2</sub>S<sub>4</sub>N<sub>4</sub>(III) (ref. 3) in better yield. No explanation was advanced at that time for this observation. Also, we find that Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub> undergoes a nucleophilic attack by amines of suitable strength to give compound (III) in good yield<sup>1</sup>. These findings as well as our recent observation of the ring contraction<sup>4, 5</sup> at room temperature of 1,5-[(R)Ph<sub>2</sub>PN]<sub>2</sub>S<sub>4</sub>N<sub>4</sub> to (R)Ph<sub>2</sub>PN-S<sub>3</sub>N<sub>3</sub> in solution (Scheme-1) prompted us to verify experimentally the possibility of observing ring expansion reaction of phosphiniminocyclotrihiazenes in presence of phosphines as nucleophiles to get 1,5-bis(phosphinimino)tetrathiazenes. We report in this paper a detailed study of the reactions of Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub> (I) and (OC<sub>4</sub>H<sub>8</sub>N) Ph<sub>2</sub>PN-S<sub>3</sub>N<sub>3</sub> (II) with Ph<sub>3</sub>P and (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>P, which offer the first examples of the reactions we sought for.



Scheme 1—Ring contraction of (IV) to (II) in solution at room temperature.

### Materials and Methods

Samples of (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>P (ref. 6), Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub> (ref. 3) and (OC<sub>4</sub>H<sub>8</sub>N) Ph<sub>2</sub>PN-S<sub>3</sub>N<sub>3</sub> (ref. 4) were prepared and recrystallized according to the literature methods. Triphenylphosphine (Fluka) was used as such. Solvents employed in this study (CH<sub>3</sub>CN, C<sub>6</sub>H<sub>6</sub>, CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O) were purified by standard procedures<sup>7</sup> before use. All the reactions were performed in an atmosphere of dry, oxygen free nitrogen gas. All the products isolated in this study: 1,5-(Ph<sub>3</sub>PN)<sub>2</sub>S<sub>4</sub>N<sub>4</sub> (refs 3, 8, 9), 1,5-[(OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>PN]<sub>2</sub>S<sub>4</sub>N<sub>4</sub> (ref. 4), Ph<sub>3</sub>P(S) (refs 3, 10) and (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>P(S) (refs 4, 11) are known compounds, whose characterisation data have been reported in literature. In the present study, they were characterized by comparing their physical (m.p.\*, colour, solubility), infrared and NMR (<sup>1</sup>H- and <sup>31</sup>P-†) spectral data with those of authentic samples prepared by reported procedures.

Only four representative reactions have been described in detail and the results of all other reactions have been summarised in Table 1.

\* The 1,5-bis(phosphinimino)tetrathiazenes decompose prior to melting.

† Spectrum was recorded at -30°C for 1,5-[(OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>PN]<sub>2</sub>S<sub>4</sub>N<sub>4</sub> due to its decomposition in solution at room temperature.

Table 1—Reactions of  $\text{Ph}_3\text{PN-S}_3\text{N}_3$ (I) and  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{PN-S}_3\text{N}_3$ (II) with  $\text{Ph}_3\text{P(A)}$  and  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{P(B)}$ 

| Reactants                                                         |                                    | Reaction solvent, temperature and period |       |        | Products isolated with yield*                                                     |
|-------------------------------------------------------------------|------------------------------------|------------------------------------------|-------|--------|-----------------------------------------------------------------------------------|
| (R)Ph <sub>2</sub> PN-S <sub>3</sub> N <sub>3</sub><br>(g);(mmol) | (R)Ph <sub>2</sub> P<br>(g);(mmol) | (ml)                                     | (°C)  | (d/h)  |                                                                                   |
| R = Phenyl-<br>(0.09); (0.22)                                     | R = Phenyl-<br>(0.11); (0.42)      | CH <sub>3</sub> CN (10);                 | (45); | (9h.)  | III (0.04g, 52%)<br>Ph <sub>3</sub> PS (0.05g)                                    |
| R = Phenyl-<br>(0.20); (0.48)                                     | R = Phenyl-<br>(0.25); (0.95)      | C <sub>6</sub> H <sub>6</sub> (10);      | (30); | (4d.)  | III (0.07g, 40%)<br>Ph <sub>3</sub> PS (0.10g)                                    |
| R = Phenyl-<br>(0.26); (0.63)                                     | R = Morpholino-<br>(0.34); (1.26)  | CH <sub>3</sub> CN (10);                 | (30); | (2d.)  | III (0.15g, 65%)<br>(OC <sub>4</sub> H <sub>8</sub> N)Ph <sub>2</sub> PS (0.10g)  |
| R = Phenyl-<br>(0.40); (0.97)                                     | R = Morpholino-<br>(0.52); (1.92)  | CH <sub>3</sub> CN (10);                 | (45); | (15h.) | III (0.21g, 59%)<br>(OC <sub>4</sub> H <sub>8</sub> N)Ph <sub>2</sub> PS (0.20g)  |
| R = Phenyl-<br>(0.40); (0.97)                                     | R = Morpholino-<br>(0.52); (1.92)  | C <sub>6</sub> H <sub>6</sub> (10);      | (45); | (15h.) | III (0.19g, 53%)<br>(OC <sub>4</sub> H <sub>8</sub> N)Ph <sub>2</sub> PS (0.21g)  |
| R = Phenyl-<br>(0.32); (0.77)                                     | R = Morpholino-<br>(0.21); (0.77)  | C <sub>6</sub> H <sub>6</sub> (10);      | (45); | (15h.) | III (0.07g, 20%)†<br>(OC <sub>4</sub> H <sub>8</sub> N)Ph <sub>2</sub> PS (0.07g) |
| R = Morpholino-<br>(0.14); (0.33)                                 | R = Morpholino-<br>(0.18); (0.66)  | CH <sub>3</sub> CN (10);                 | (45); | (2d.)  | (OC <sub>4</sub> H <sub>8</sub> N)Ph <sub>2</sub> PS (0.08g)                      |
| R = Morpholino-<br>(0.27); (0.64)                                 | R = Morpholino-<br>(0.35); (1.30)  | C <sub>6</sub> H <sub>6</sub> (10);      | (30); | (2d.)  | II (0.06g)<br>(OC <sub>4</sub> H <sub>8</sub> N)Ph <sub>2</sub> PS (0.07g)        |
| R = Morpholino-<br>(0.15); (0.36)                                 | R = Phenyl-<br>(0.19); (0.72)      | CH <sub>3</sub> CN (10);                 | (30); | (3d.)  | III (0.06, 46%)<br>Ph <sub>3</sub> PS (0.07g)                                     |
| R = Morpholino-<br>(0.24g); (0.57)                                | R = Phenyl-<br>(0.30); (1.15)      | CH <sub>3</sub> CN (10);                 | (45); | (10h.) | III (0.07g, 35%)<br>Ph <sub>3</sub> PS (0.05g)                                    |
| R = Morpholino-<br>(0.23g); (0.55)                                | R = Phenyl-<br>(1.29); (1.10)      | C <sub>6</sub> H <sub>6</sub> (10);      | (30); | (3d.)  | III + IV (0.12g)<br>Ph <sub>3</sub> PS (0.08g)                                    |

III = 1,5-(Ph<sub>3</sub>PN)<sub>2</sub>S<sub>4</sub>N<sub>4</sub>; IV = 1,5-[(OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>PN]<sub>2</sub>S<sub>4</sub>N<sub>4</sub>.

\* Yields of III and IV were calculated on the basis of the sulphur content of (R)Ph<sub>2</sub>PN-S<sub>3</sub>N<sub>3</sub>.

† The starting material, Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub> (0.08g), was also isolated.

### 1. Reactions of $\text{Ph}_3\text{PN-S}_3\text{N}_3$ (I) with $\text{Ph}_3\text{P(A)}$ in $\text{CH}_3\text{CN}$ at room temperature

To a stirred solution of Ph<sub>3</sub>P (0.25 g, 0.95 mmol) in CH<sub>3</sub>CN (10 ml) at room temperature (ca. 30°C), Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub> (0.20 g, 0.48 mmol) was added all at once. Only after the entire red solid went into solution (ca. 30 h) the formation of a cream yellow precipitate started. The reaction mixture was stirred for 12 h and filtered to separate the precipitate, which was washed with CH<sub>3</sub>CN (2 × 3ml) and Et<sub>2</sub>O (5 ml), dried *in vacuo* and characterized as 1,5-(Ph<sub>3</sub>PN)<sub>2</sub>S<sub>4</sub>N<sub>4</sub> (0.12 g, 62%) (m.p. 150°C, lit.<sup>9</sup> 151°C; <sup>31</sup>P-NMR: δ 23.8 and 18.2, lit.<sup>9</sup> 23.6 and 18.1 ppm). The filtrate on concentration and cooling at 0°C for 24 h gave Ph<sub>3</sub>P(S) (0.11 g) (m.p. 161°C; <sup>31</sup>P-NMR: δ 42.8 lit.<sup>9</sup> 42.6 ppm). No other product was isolated from the residual reaction mixture.

### 2. Reaction of $\text{Ph}_3\text{PN-S}_3\text{N}_3$ (I) with $\text{Ph}_3\text{P(A)}$ in $\text{C}_6\text{H}_6$ at 45°C

Triphenylphosphine (0.50 g, 1.91 mmol) was added, all at a time, to a stirred solution of Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub> (0.40 g, 0.97 mmol) in C<sub>6</sub>H<sub>6</sub> (15 ml) at 45°C (hot water bath). After three hours, the

formation of a pale pinkish solid was observed. The reaction mixture was filtered after 12 h and the solid obtained was washed with CH<sub>3</sub>CN (2 × 4 ml), dried *in vacuo* and characterized as 1,5-(Ph<sub>3</sub>PN)<sub>2</sub>S<sub>4</sub>N<sub>4</sub> (0.20 g; 57%). From the filtrate Ph<sub>3</sub>P(S) (0.21 g) was isolated.

### 3. Reaction of $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{PN-S}_3\text{N}_3$ (II) with $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{P(B)}$ in $\text{CH}_3\text{CN}$

(Morpholino)diphenylphosphine (0.42 g, 1.54 mmol) and (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>PN-S<sub>3</sub>N<sub>3</sub>(II) (0.33 g, 0.78 mmol) were stirred in CH<sub>3</sub>CN (10 ml) at room temperature (ca. 30°C). The initial red colour of the reaction mixture started fading only after 18 h. At this stage, the reaction flask was placed in a cold water bath (ca. 5°C), stirred for another 8 h and filtered to get a cream yellow solid, which was characterized as 1,5-[(OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>PN]<sub>2</sub>S<sub>4</sub>N<sub>4</sub>(IV) (0.21 g, 70%) (m.p. 125°C, lit.<sup>4</sup> 124°C; <sup>31</sup>P-NMR: δ 31.6 and 27.1, lit.<sup>4</sup> 31.6 and 27.0 ppm). The concentrated filtrate was passed through a silica gel column using CH<sub>2</sub>Cl<sub>2</sub> as eluant and from the eluate (OC<sub>4</sub>H<sub>8</sub>N)Ph<sub>2</sub>P(S) (0.12 g) (m.p. 108°C; <sup>31</sup>P-NMR: δ 67.6, lit.<sup>4</sup> 67.6 ppm) was isolated.

#### 4. Reaction of $\text{Ph}_3\text{PN-S}_3\text{N}_3(\text{I})$ with $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{P}(\text{B})$ in $\text{C}_6\text{H}_6$ at room temperature

Compound (I) (0.35 g, 0.85 mmol) and  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{P}$  (0.46 g, 1.70 mmol) were stirred in  $\text{C}_6\text{H}_6$  (10 ml) at room temperature for about 40 h and filtered to isolate a flocculent pale pink precipitate which on washing with  $\text{C}_6\text{H}_6$  ( $2 \times 5$  ml),  $\text{CH}_3\text{CN}$  ( $2 \times 5$  ml), and  $\text{Et}_2\text{O}$  ( $2 \times 5$  ml) left behind a pale yellow powdery solid (0.25 g), (m.p.  $135 \pm 3^\circ\text{C}$ ;  $^{31}\text{P-NMR}$ :  $\delta$  31.5, 27.1, 23.6 and 18.1 ppm) identified as a mixture (2:3) of 1,5- $(\text{Ph}_3\text{PN})_2\text{S}_4\text{N}_4(\text{III})$  and 1,5- $[(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{PN}]_2\text{S}_4\text{N}_4(\text{IV})$  which could not be separated. The filtrate was concentrated and passed through a silica gel column using  $\text{CH}_2\text{Cl}_2$  as eluant and the eluate on working up gave  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{P}(\text{S})$  (0.21 g).

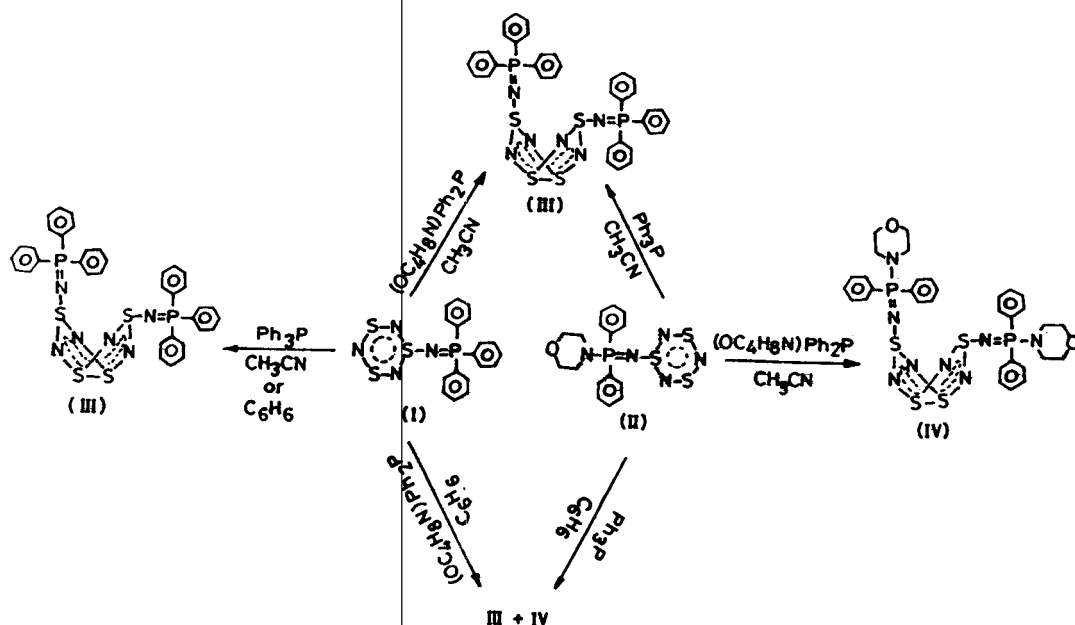
#### Results and Discussion

The results obtained in this study have been summarised in Scheme 2. Contrary to the previous observation<sup>6</sup>, we find that  $\text{Ph}_3\text{PN-S}_3\text{N}_3(\text{I})$  reacts with  $\text{Ph}_3\text{P}(\text{A})$  in 1:2 molar ratio to give 1,5- $(\text{Ph}_3\text{PN})_2\text{S}_4\text{N}_4(\text{III})$  and  $\text{Ph}_3\text{PS}$ . Reactions are slow at room temperature (ca.  $30^\circ\text{C}$ ) and it takes about 3 days to obtain (III) in ca. 65% yield. Similar yields of (III) can be obtained when the reactions are carried out at  $45^\circ\text{C}$  for about 12 h (Table 1). Still higher temperatures were not tried as the monosubstituted  $-\text{S}_3\text{N}_3$  heterocycles undergo thermal degradation under relatively mild conditions<sup>12</sup>.

(Morpholino)diphenylphosphinesulphide was the only product isolable from the reaction of  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{PN-S}_3\text{N}_3(\text{II})$  with  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{P}(\text{B})$  in  $\text{CH}_3\text{CN}$  at  $45^\circ\text{C}$  (Table 1). However, the same reaction in  $\text{CH}_3\text{CN}$  at lower temperature led to the isolation of 1,5- $[(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{PN}]_2\text{S}_4\text{N}_4$  (see Materials and Methods). This is in accordance with our earlier observation of the facile ring contraction of (IV) to (II) which occurs at room temperature in solution<sup>3</sup> (Scheme 1) in the absence of a phosphine.

Interestingly both the cross reactions—of (I) with B and of (II) with A—in  $\text{CH}_3\text{CN}$  give compound (III) and the sulphide of the attacking phosphine, while an inseparable mixture of (III) and (IV) is obtained from room temperature reactions in benzene. The same reactions when performed at  $45^\circ\text{C}$  yield only 1,5- $(\text{Ph}_3\text{PN})_2\text{S}_4\text{N}_4$  which suggests that compound (IV) is thermally less stable. Although at present it is difficult to comprehend entirely the results observed in this study, it is certain that the nucleophilic attack on  $-\text{S}_3\text{N}_3$  by the phosphine followed by ring opening of  $-\text{S}_3\text{N}_3$  are the essential steps involved in these transformations.

It is noteworthy that in this study, 1,5- $(\text{Ph}_3\text{PN})_2\text{S}_4\text{N}_4$  has been isolated from the reactions performed in benzene as well. Recent studies from our laboratory on the reactions of  $\text{S}_4\text{N}_4$  and phosphines<sup>4, 5, 14</sup> indicate that (phosphiniminio)- $\text{S}_3\text{N}_3$  derivatives are readily isolated from



Scheme 2—Products from the reactions of  $\text{Ph}_3\text{PN-S}_3\text{N}_3(\text{I})$  and  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{PN-S}_3\text{N}_3(\text{II})$  with  $\text{Ph}_3\text{P}$  and  $(\text{OC}_4\text{H}_8\text{N})\text{Ph}_2\text{P}$ .

CH<sub>3</sub>CN medium. The previous study<sup>3, 13</sup> has emphasized the use of CH<sub>3</sub>CN solvent for the isolation of 1,5-(Ph<sub>3</sub>PN)<sub>2</sub>S<sub>4</sub>N<sub>4</sub> and benzene solvent for the isolation of Ph<sub>3</sub>PN-S<sub>3</sub>N<sub>3</sub>. Our results described here and elsewhere<sup>4, 5, 14</sup> seem to suggest that the reaction solvent does not play any critical role in these reactions.

### Conclusion

The monosubstituted cyclotrithiazenes similar to S<sub>4</sub>N<sub>4</sub> are attacked slowly by phosphines to give 1,5-bis(phosphinimino)tetrathiazene derivatives which suggests an additional pathway for their formation. The results help in rationalizing some of the complexities observed in the reactions of S<sub>4</sub>N<sub>4</sub> with phosphines.

### Acknowledgement

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