

Phosphorus(III) reagents in the chemistry of cyclothiazenes

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Cyclic sulphur–nitrogen compounds which have been known for over a century are novel examples of inorganic ring systems due to their variety in structure, bonding and reactivity. Especially in the last two decades, the use of different types of trivalent phosphorus reagents have contributed significantly for developing the chemistry of cyclothiazenes. These aspects are highlighted in this article.

THE field of inorganic heterocycles is an active area of research in the contemporary inorganic chemistry^{1–6}. Cyclothiazenes represent an important and interesting class among inorganic heterocycles. The chemistry of cyclothiazenes is well developed and literature information available on them is fairly extensive^{7–13}. Several members of the cyclothiazene family (e.g. S_4N_4 , $S_3N_3Cl_3$, $S_3N_2Cl_2$, S_4N_3Cl , etc.) are readily synthesizable in a laboratory. It is noteworthy that the progress made in the chemistry of phosphorus has aided substantially to continue and develop the chemistry of cyclothiazenes in different ways. A wide range of both tri- and pentavalent phosphorus compounds where phosphorus is present in different coordination numbers have been used for this purpose^{14,15}. This approach has offered scope to construct and obtain newer variety of heterocyclic systems which contain phosphorus either as an endocyclic member or a stable substituent or a functionality to the ring. Comparatively, a larger variety of phosphorus(III) derivatives have been employed in the study carried out so far which has yielded many notable results.

Since the first report on the reaction of S_4N_4 with PCl_3 in 1962 (ref. 16), it appears that there has been a growing interest in this area. Different types of phosphorus(III) reagents, especially phosphines, chlorophosphines and biphosphines have been reacted with cyclothiazenes which have given rise to a variety of heterocyclic compounds containing phosphorus, sulphur and nitrogen (Figure 1). The details of the earlier studies on this topic have appeared in literature in some of the reviews^{9,10,12,14} and monographs^{1,3,4,13} devoted to inorganic ring systems. More than a decade ago, we began our studies in this area using further examples of

phosphines, aminophosphines, diphosphines, chlorophosphines and some other types of phosphorus(III) reagents. Several interesting results have been obtained which have not only helped in providing clarification to some of the earlier observations but also have highlighted the scope of this area for further research. This article provides an overview of the recent results on this topic with special reference to the contributions made from our own laboratory.

Thiophilic and oxidative sensitivity of trivalent tri-coordinate phosphorus centre to yield stable tetra-coordinate pentavalent phosphorus and the known reactive nature of sulfur–nitrogen bonds of cyclothiazenes have rendered them suitable for exploring their chemical behaviour in reactions. Such phosphorus compounds so far used in reactions with cyclothiazenes, especially S_4N_4 are secondary and tertiary phosphines (R_2PH and R_3P), amino phosphines (symmetrically and unsymmetrically substituted), phosphites, biphosphines, R_2PPR_2 and diphosphines R_2PXR_2 as well as PCl_3 and its substituted derivatives ($RPCl_2$ and R_2PCl).

Phosphines

Reactions of triphenylphosphine with a variety of cyclothiazenes have been investigated by different groups.

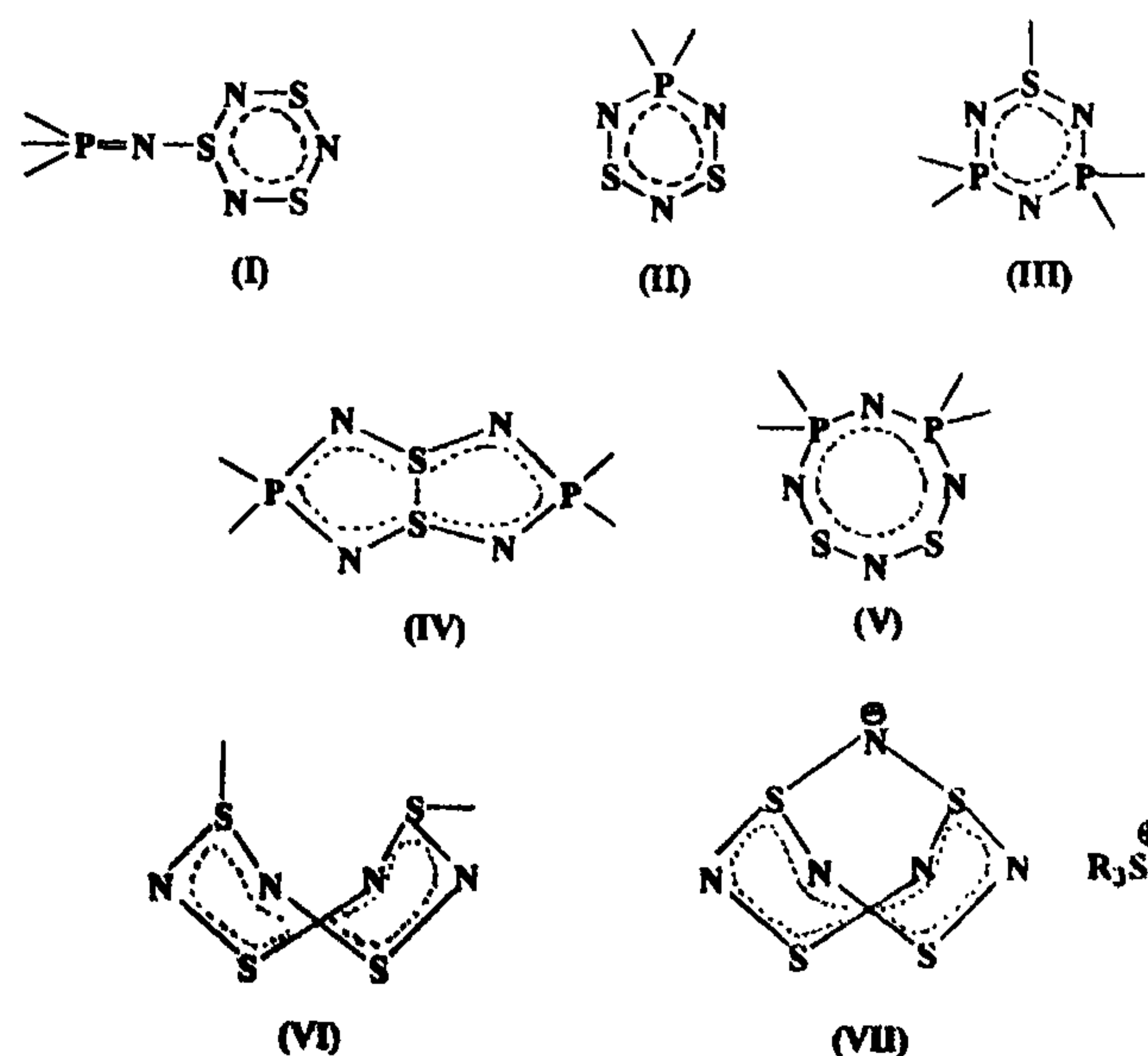


Figure 1. Heterocyclic variety from phosphorus(III) reagents.

This paper is dedicated to Prof. S. S. Krishnamurthy on his 60th birth anniversary.

Kraus and Jung were the first to study the reaction of this phosphine as well as tricyclohexyl phosphine with S_4N_4 in 1961 (ref. 17) and isolate a red coloured mono-substituted cyclotriithiazene, $R_3PN-S_3N_3$ ($R = \text{phenyl}$ and cyclohexyl) in low yield. Prakash and Sisler reported in 1968 (ref. 18) the reaction of S_4N_4 with Ph_3P and isolated only an acyclic product, Ph_3PNH_2Cl . Two other brief studies on the reaction of Ph_3P with $S_4N_4O_2$ (ref. 4) and $Ph_2PN_5S_3$ (ref. 19) are also available. Recently, Mohan *et al.* have successfully isolated $Ph_3PN-S_3N_3$ and 1,5- $(Ph_3PN)_2S_4N_4$ heterocycles by the reaction of Ph_3P with cyclic sulphur-nitrogen chlorides²⁰. In 1981, Bojes *et al.*²¹ reinvestigated the reaction of Ph_3P with S_4N_4 and highlighted the scope of this reaction to obtain different types of heterocyclic products under different conditions (Figure 2). They have also structurally characterized the first example of bis(phosphinimino) cyclotetrathiazene derivative, 1,5- $(Ph_3PN)_2S_4N_4$ (ref. 22) and isolated a bicyclic S_4N_5 anion of a novel sulphonium $(Ph_3PN)_3S^+$ cation. It is the only example of a stable disubstituted S_4N_4 derivative containing two phosphinimino moieties.³¹P NMR spectra reveal the nonequivalence (*exo*- and *endo*-) of the $\rightarrow P=N^-$ groups.

Analogous reactions with several other arylphosphines, $(\text{phenyl})_x(\text{p-tolyl})_{3-x}P$ ($x = 0, 1$ and 2)²³ have been carried out recently and similar results have been obtained. However, other examples of symmetrical phosphines, R_3P [$R =$ i) *t*-butyl, ii) benzyl, iii) cyclohexyl and iv) *p*-methoxyphenyl] gave only the corre-

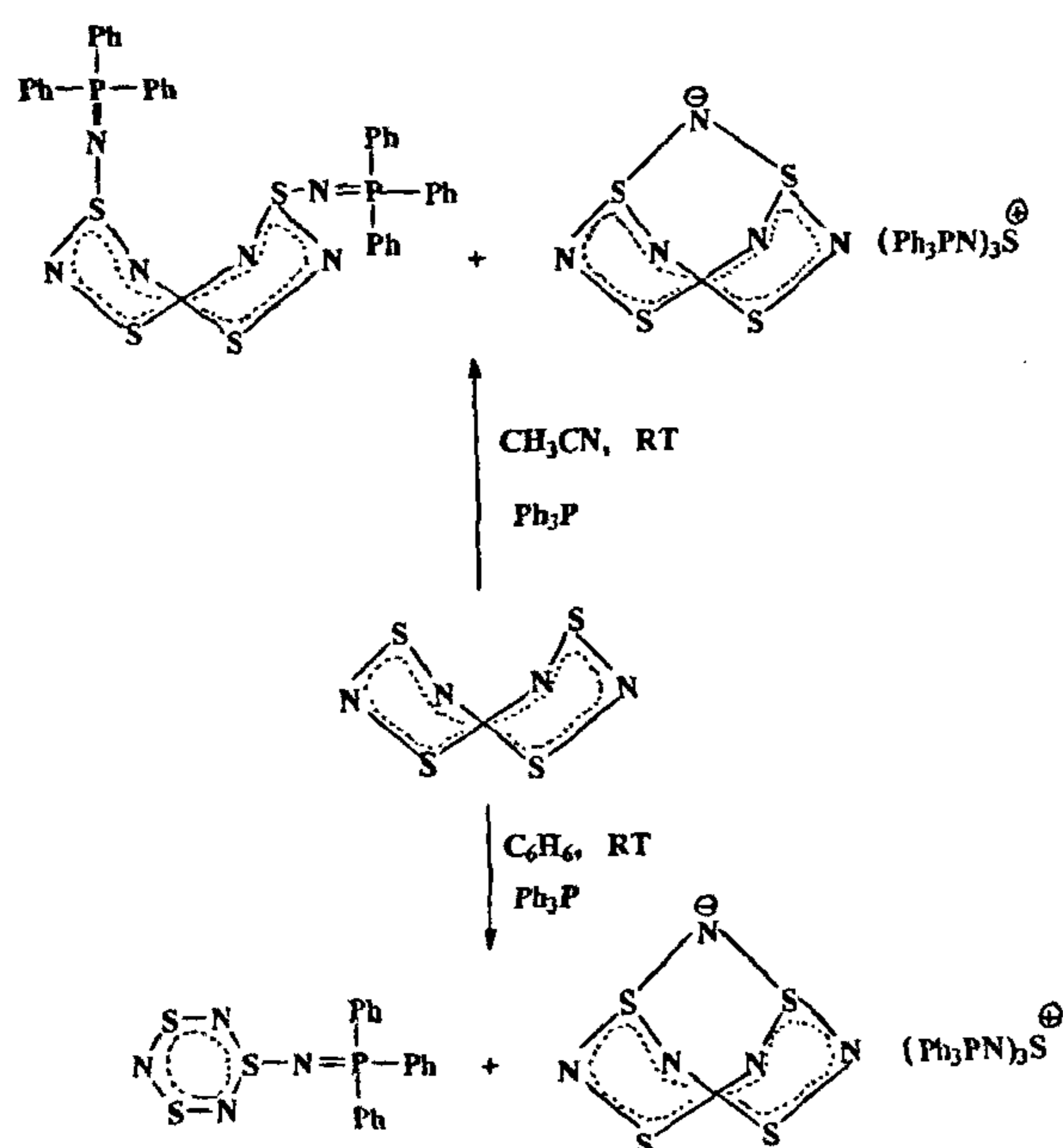


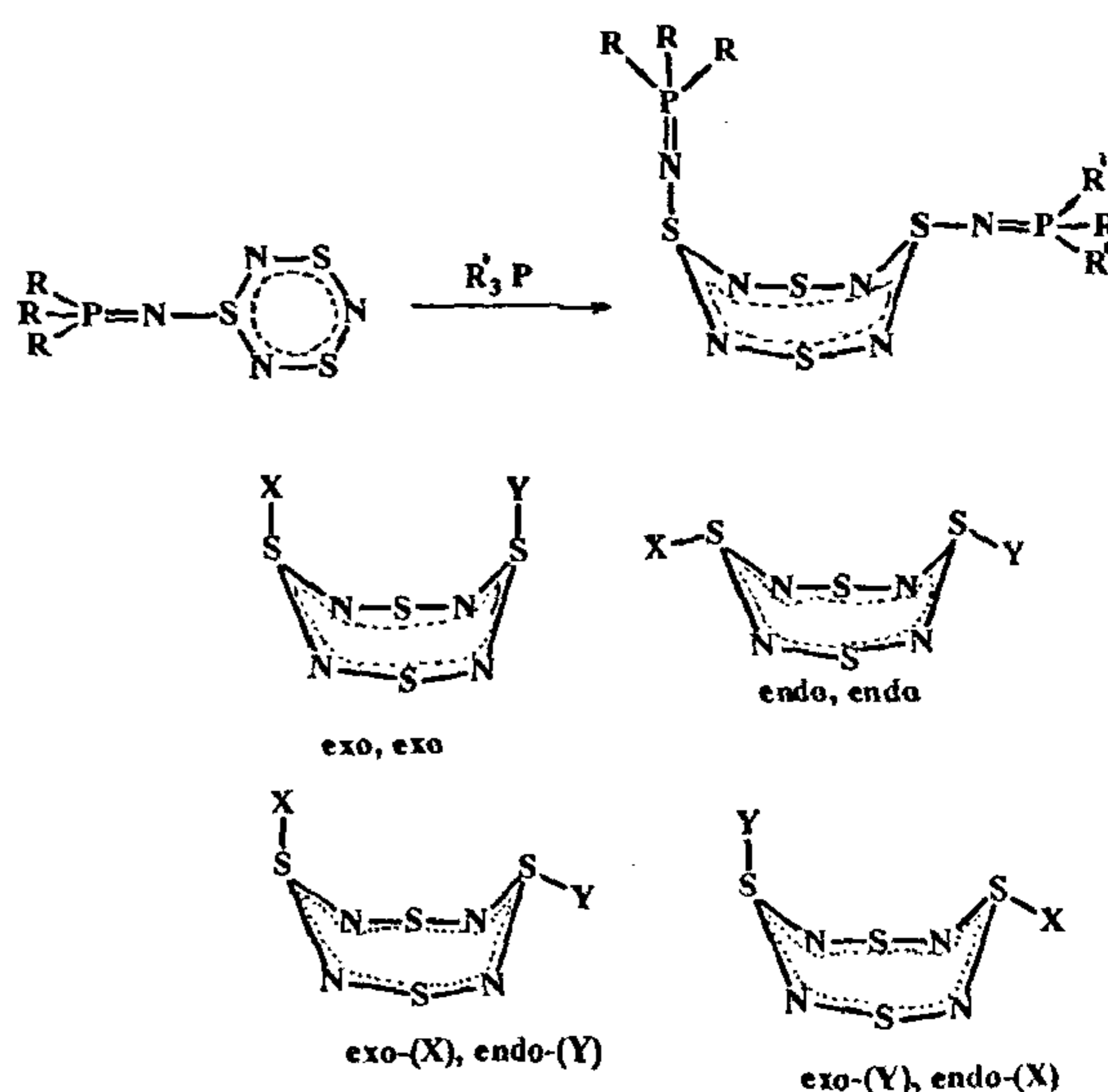
Figure 2. Cyclotriithiazene derivatives from Ph_3P and S_4N_4 under different conditions (solvent dependence).

sponding cyclotriithiazene derivative²⁴. Only the phosphine, $(p\text{-ClC}_6\text{H}_4)_3P$ gave 1,5- $[(p\text{-ClC}_6\text{H}_4)_3PN]_2S_4N_4$ compound in moderate yield. Another interesting 1,5-disubstituted cyclotetrathiazene 1,5- $[(Ph_3PN)(Ph_2(p\text{-tolyl})PN)]S_4N_4$ (ref. 25) was obtained when for the first time S_4N_4 was reacted with two different phosphines, Ph_3P and $Ph_2(p\text{-tolyl})P$. Compounds of this type which exhibit structural isomerism were not known earlier and were subsequently prepared by a ring expansion reaction of $PN-S_3N_3$ with nucleophiles²⁶ (Scheme 1). These reactions have helped in establishing the inter ring relationships among the known PSN heterocycles.

For the first time, Chivers *et al.* showed that when secondary phosphine Ph_2PH (ref. 27) was used in the reaction with S_4N_4 , cyclophosphathiazenes, II, IV, and V could be isolated. These pi-electron rich heterocycles are separated by gel permeation chromatography. Roisky *et al.* obtained the perfluoromethyl and perfluoroethyl analogues of the heterocycle II by reacting the silylated phosphines, $R_2PN(SiMe_3)_2$ [$R = CF_3$ and C_2F_5] with the cyclic sulphur-nitrogen chloride, $S_3N_2Cl_2$ (ref. 28).

Aminophosphines (symmetrical and unsymmetrical)

The adjacent nitrogen atom(s) enhances the versatility of aminophosphines as they offer the possibility of manipulating substituents both on phosphorus and nitrogen in addition to the nucleophilic activity of the trivalent nitrogen itself. The only study of aminophosphine to be reported in literature was that of *tris*(dimethylamino) phosphine and S_4N_4 which gave only an acyclic deriva-



Scheme 1. Isomeric possibilities of 1,5-(X)(Y) S_4N_4 derivatives (X and Y are different phosphinimino groups).

tive²⁹. A detailed study carried out in our laboratory has revealed that the symmetrical and unsymmetrical environment of substituents around phosphorus plays a crucial role on the course of the reaction as well as on products. Several examples of aminophosphines (symmetrical and unsymmetrical) tried so far^{23,30,31}, indicate that they react readily with S₄N₄ in an analogous manner to produce the corresponding (phosphinimino) cyclotrithiazene derivative in varying yield:



For example, (C₆H₅)(OC₄H₈N)₂PN-S₃N₃ is obtained only in 25% yield while (Ph)(DCA)(Mp)PN-S₃N₃ (DCA: dicyclohexylamino and Mp: morpholino) is isolated almost quantitatively³¹. These heterocycles with amino substituents are found to exhibit much higher thermal and solution state instabilities. (C₆H₅)(DCA)(C₅H₁₀N)PN-S₃N₃ was found to be most stable in solution. First examples of phosphiniminocyclotrithiazenes containing primary amino substituent³² and chiral phosphorus³¹ centre have also been isolated and structurally characterized. 1,5-*bis*(phosphinimino) cyclotetrathiazenes and the S₄N₅ anion derivatives could not be isolated from any of the reactions of tertiary amino phosphines. However, 1,5-(\rightarrow PN)₂S₄N₄ are isolated in relatively moderate yield from the reactions of phenyl amino phosphines, Ph₂(amino)P³⁰ and Ph(DCA)(amino)P³¹. Even in those cases, the 1,5-disubstituted derivative is found to undergo a ring contraction³³ in solution to afford the mono substituted heterocycle. This behaviour observed for the first time from such heterocycles has led to identifying the relationship between the mono- and *bis*(phosphinimino) cyclotrithiazenes (Scheme 2).

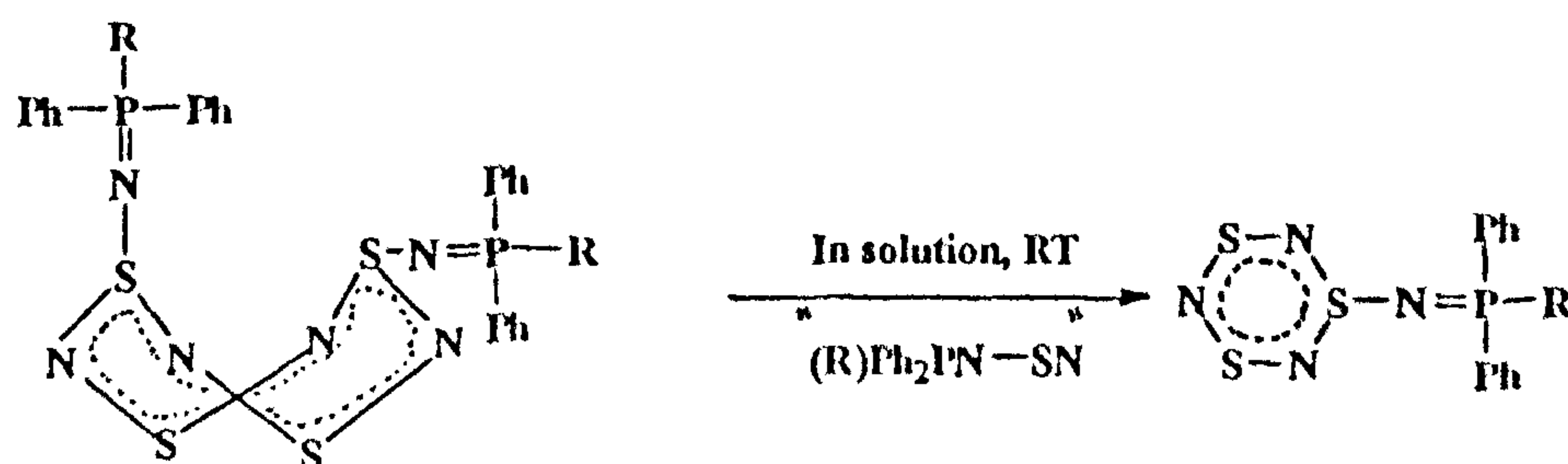
Another interesting type of ring conversion reaction which was not known before has been observed in this study. Thomas and Rao^{30,34} found for the first time that the phosphinimino cyclotrithiazene containing 2-aminopyridyl group expels a 'NSX' moiety (X is phosphinimino) slowly in solution and converts itself to a phosphathiazene (PSN) heterocycle (Scheme 3). The conversion was revealed by the change of colour of the solution from orange red to dark purple. Expectedly, the results of the reaction of S₄N₄ with the phosphine,

Ph₂P(2-aminopyridyl) showed both time and temperature dependence. This important observation has been pursued further to isolate the first example of a phosphadithiatriazene heterocycle containing dissimilar substituents (phenyl and an amino) as a dark blue crystalline solid which has been structurally characterized^{35,36} (Figure 3).

In all these reactions, phosphorus centre which becomes a part of the heterocycle is found to be in the stable oxidized (pentavalent tetracoordinate) state. This oxidation is accompanied with the formation of phosphinesulphide which may be regarded as the reduced product. A mechanistic proposal²¹ to understand the formation of such diverse type of heterocycles has also been attempted (Scheme 4). Nucleophilic degradation of S₄N₄ by the phosphine is said to have been the first step which leads to the formation of thiazene chain bound to phosphine. It has been proposed³¹ that this key intermediate (a) is likely to react in various modes with different species present in the system to afford products isolated. This offers scope to relate preferences of pathways leading to products as substituents on phosphorus vary.

A number of \rightarrow P=N-S₃N₃ derivatives which are rare and novel examples of 8- π heterocycles have been structurally characterized^{35,37-40}. Figure 4 shows the X-ray structures of a few representative examples of \rightarrow P=N-S₃N₃ heterocycles which include a chiral phosphorus centre as well as a primary amino group present on phosphorus. A comparison of their bonding parameters reveals that the two endocyclic S-N bonds of the tri-coordinate sulfur are slightly longer (1.62-1.65Å) compared to the remaining four S-N bonds (1.58-1.61Å) which are almost identical. The S-N ring assumes a half chair conformation in majority of the cases. Interestingly, exocyclic bonds (P-N and S-N) and the angle at imino nitrogen vary noticeably with the change in the substituents attached to phosphorus.

Various types of novel and structurally interesting heterocyclic derivatives obtained from the reactions of S₄N₄ and phosphorus reagents have also been subjected to different types of theoretical analysis⁴¹⁻⁴⁵ with a view to understand their electronic structure, reactivity and spectral features. For example, the conclusions drawn



Scheme 2. Ring conversion of 1,5-(\rightarrow PN)₂S₄N₄ to \rightarrow PN-S₃N₃ systems.

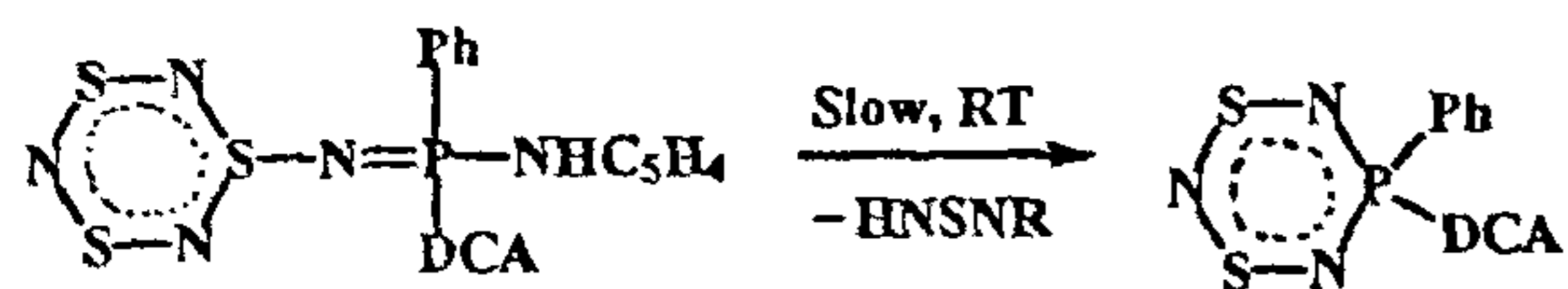
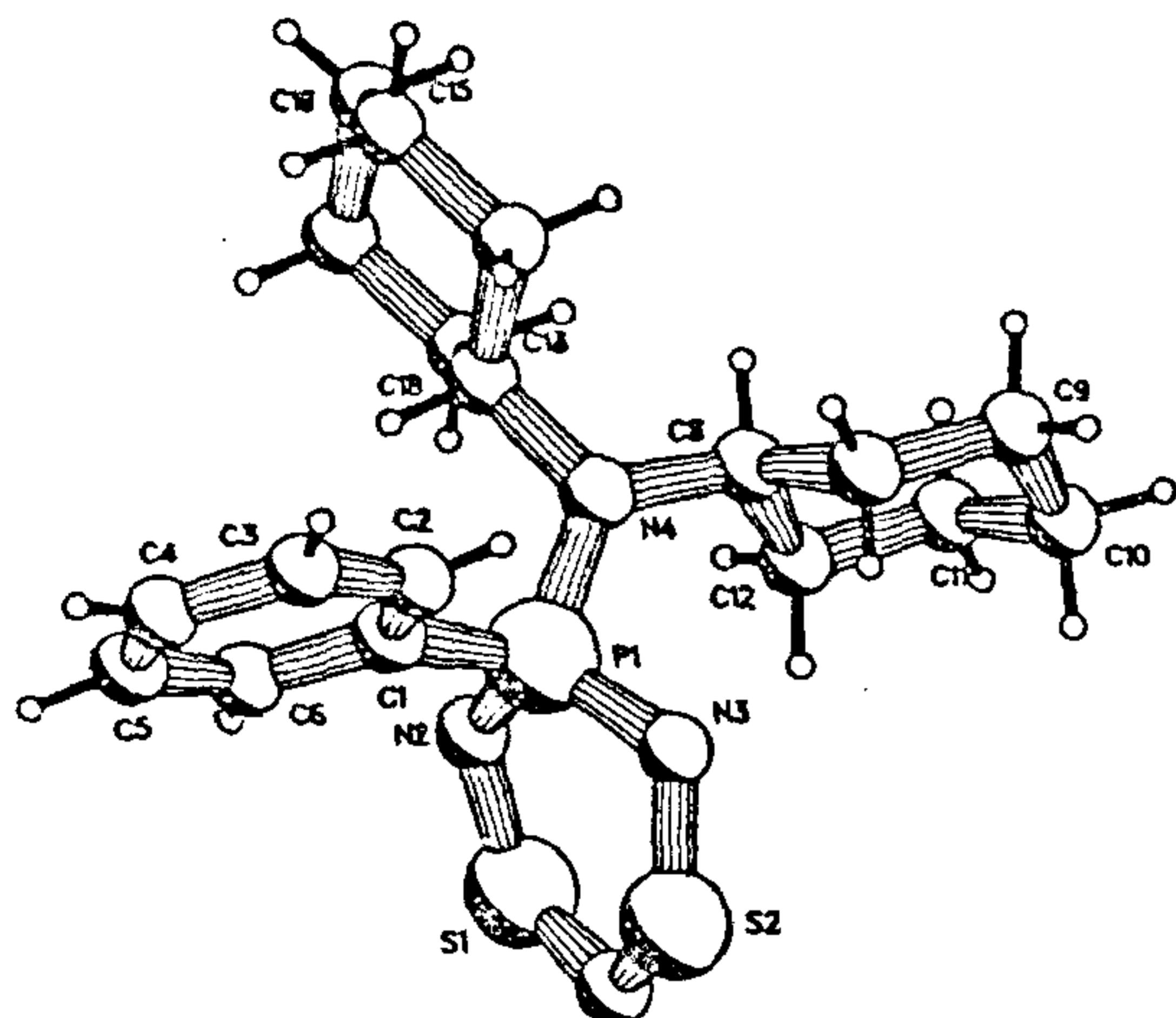
Scheme 3. $>PS_2N_3$ heterocycle from $\rightarrow PNS_3N_3$ ring system.

Figure 3. X-ray crystal structure of 1-phenyl-1-(dicyclohexylamino)cyclo-1-phospha-3,5-dithia-2,4,6-triazene.

from *ab initio* calculations on $>PS_2N_3$ (ref. 43) ring system are found to be in good agreement with the measured uv-visible spectral data. Similarly, it is found that the uv-visible spectra of $\rightarrow PN-S_3N_3$ derivatives show two characteristic absorptions^{10,14,31} at around 330 and 480 nm.

Significant differences observed in the structural features of these otherwise, analogous $\rightarrow PN-S_3N_3$ heterocycles having different substituents on phosphorus render them attractive for studies on their chemical and thermal behaviour. Recently, Swarnalatha⁴⁶ has addressed this issue and found many unexpected results. For example, $(R_2N)_3PN-S_3N_3$ (ref. 47) ring systems show different thermal stabilities and mode of decomposition. A rather general behaviour observed with these $\rightarrow PN-S_3N_3$ heterocycles is that i) they readily add a molecule of the diene^{34,48}, norbornadiene at room temperature and ii) they undergo pyrolysis under reflux acetonitrile condition to afford an acyclic derivative, $\rightarrow PN-S_3N$ (refs 23, 49).

Biphosphines and diphosphines

Biphosphines, R_2PPR_2 and diphosphines, R_2PXPR_2 by definition possess dual nucleophilic sites as they are characterized by the presence of two phosphorus(III) centres with a lone pair of electron on each. This offers an interesting possibility of obtaining products containing ring skeleton at either or both the P(III) centres as well as a compound having both ring and the sulphide

on the same bi- or diphosphine example (Figure 5). Only two biphosphines, R_2PPR_2 ($R = \text{phenyl and methyl}$)^{50,51} have been studied so far with S_4N_4 under reflux toluene conditions to isolate three types of cyclophosphathiazene products (II, IV and V in Figure 1). Interestingly, all are examples of pi-electron-rich heterocycles. Besides, IV and V are isomeric derivatives.

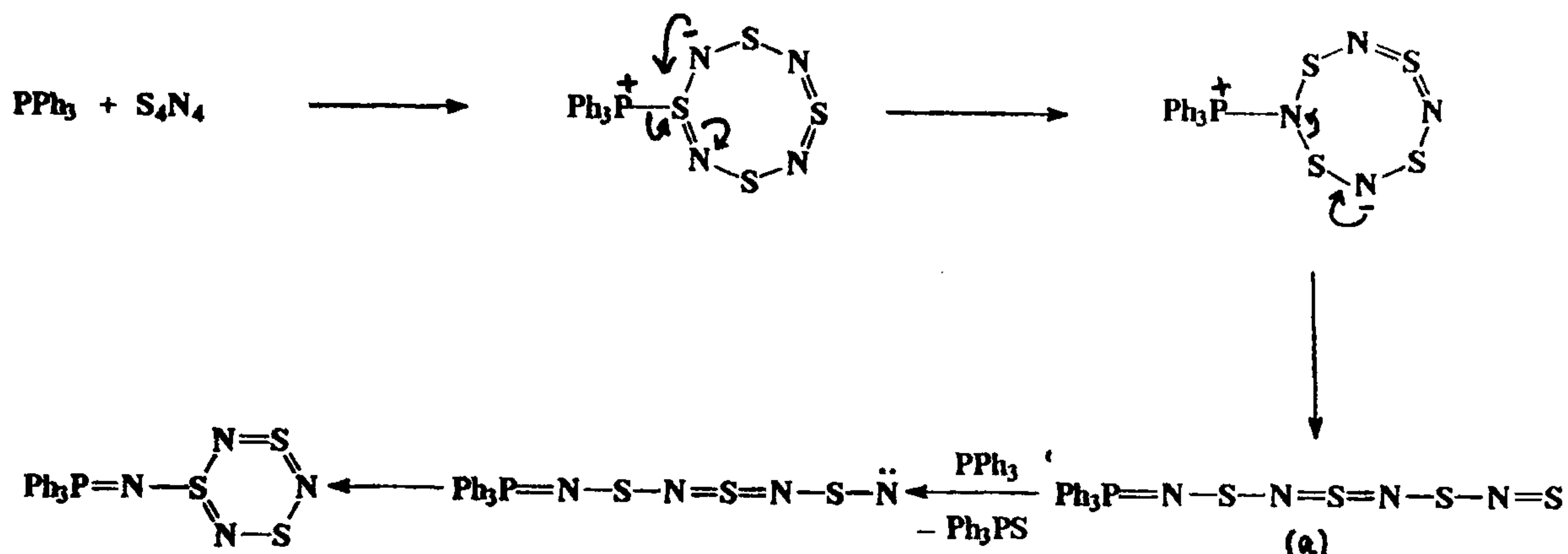
Thomas and Rao⁵² have reported the first study on the reactions of S_4N_4 with five examples of diphosphines, Ph_2PXPh_2 [$X = \text{i) } CH_2, \text{ ii) } CH_2CH_2, \text{ iii) } CH_2CH_2CH_2, \text{ iv) } CH_2CH_2CH_2CH_2 \text{ and v) } NC_4H_8N$] and novel products of the type VIII and IX in Figure 5 have been isolated. Number of methylenes are found to exert an influence on the reaction and in general, isolation of pure products containing cyclotriazene was significantly more difficult. The isolation of mixed derivative of the type IX from an equimolar reaction provide further support to the fact that in these reactions, phosphinesulphide is the by-product.

Chlorophosphines, R_2PCl , $RR'PCl$, $RPCl_2$ and PCl_3

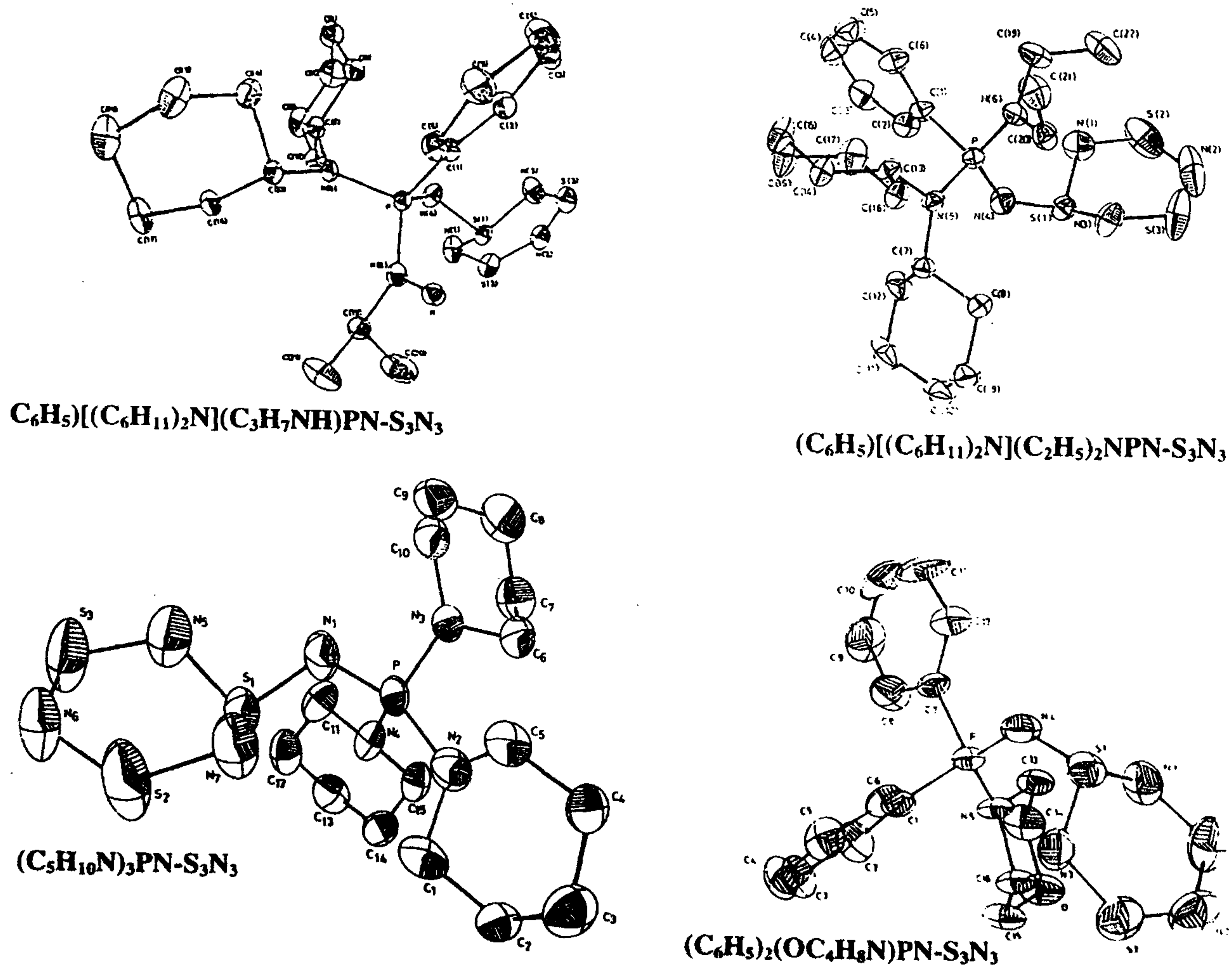
Chivers and Rao⁵³ reinvestigated the reaction of PCl_3 with S_4N_4 and extended it for Ph_2PCl and $PhPCl_2$ as well. These chlorophosphines reactions gave scope to isolate diphosphamonothiazene ring systems, $(\rightarrow PN)_2(NSCl)$ [III in Figure 1]. The 6-pi phosphathiazene heterocycle, $(Ph_2PN)_2NSCl$ obtainable in good yield has been structurally characterized and used to demonstrate its rich chemical behaviour. The same authors found that the reaction of Ph_2PCl and CsS_3N_3 (ref. 54) was very complex which afforded a variety of heterocyclic systems (II, III, IV, and V in Figure 1) including cyclophosphazenes. Very recently, Janarthanan⁵⁵ studied the reactions of S_4N_4 with several aminochloro phosphines, $Ph(R_2N)PCl$, $(R_2N)_2PCl$ and $(R_2N)(R'_2N)PCl$ and obtained a surprising result. The reactions produced highly coloured 8-pi $>PS_2N_3$ heterocyclic product of the corresponding phosphine (II in Figure 1) instead of the expected $>P_2SN_3$ ring system (III in Figure 1). Accordingly, $Ph(DCA)PCl$ gave the heterocycle $(Ph)(DCA)PS_2N_3$ which was first made by Mohan *et al.*,³¹ by a different approach. These results seem to indicate that the aminochlorophosphines have a general behaviour and the amino substituent affects the course of the reaction. This synthetic strategy has given way for the first time, to introduce newer variety of this class of novel cyclophosphathiazene derivatives (Figure 6).

Other phosphorus(III) reagents

Burford *et al.*⁵⁰, in 1982 have reported that a phosphite such as $(PhO)_3P^{50}$ reacts with S_4N_4 to afford the $>PS_2N_3$



Scheme 4. Mechanistic proposal for the formation of diverse type of heterocycles.

Figure 4. X-ray structures of $\rightarrow\text{P}=\text{NS}_3\text{N}_3$ heterocycles.

heterocycle. Isolation of the product was difficult due to the complex nature of the reaction mixture. No other

example of this kind has so far been reported to the best of our knowledge.

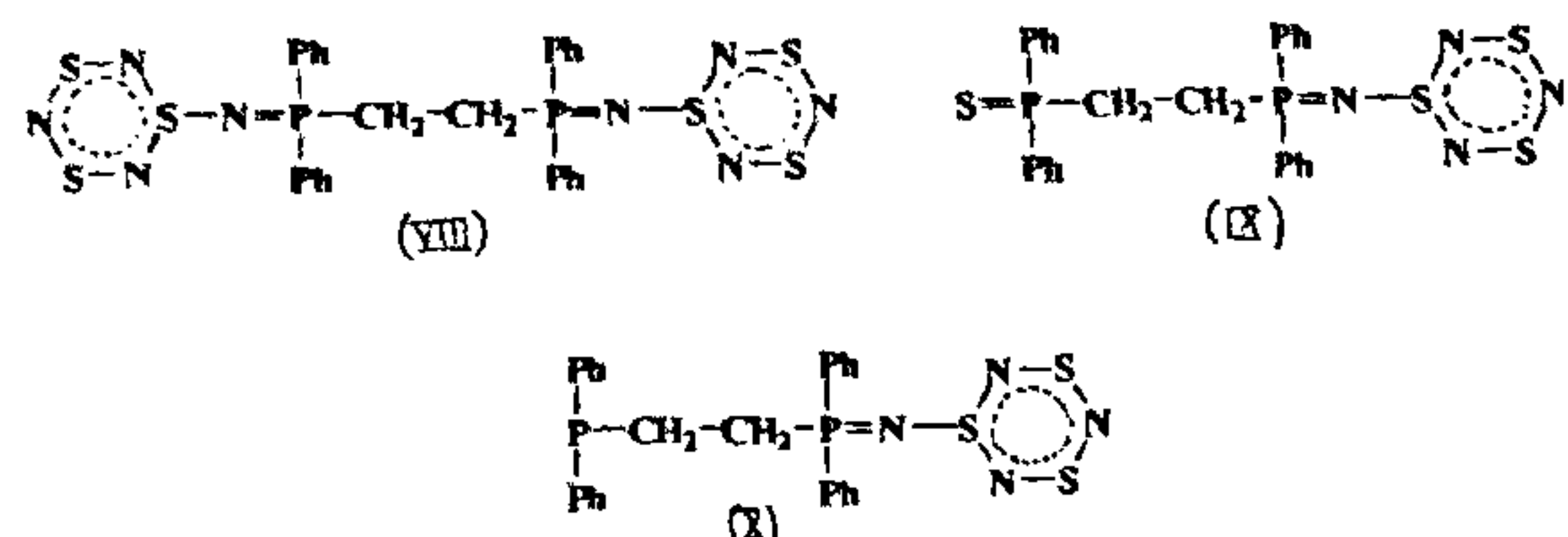


Figure 5. Cyclotrithiazene products(s) possibility from diphosphines.

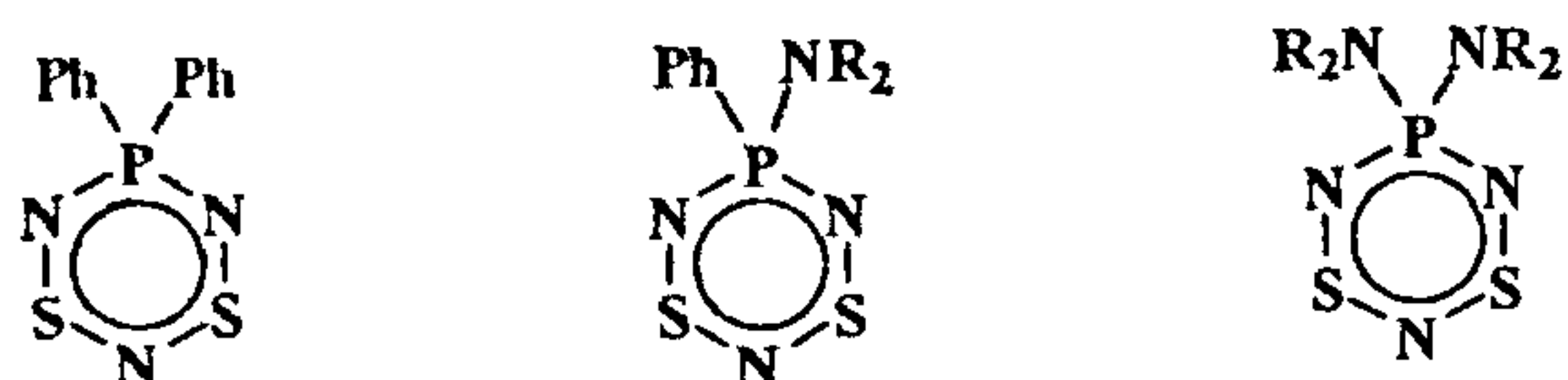


Figure 6. Types of $>PS_2N_3$ heterocycles obtained from our recent study.

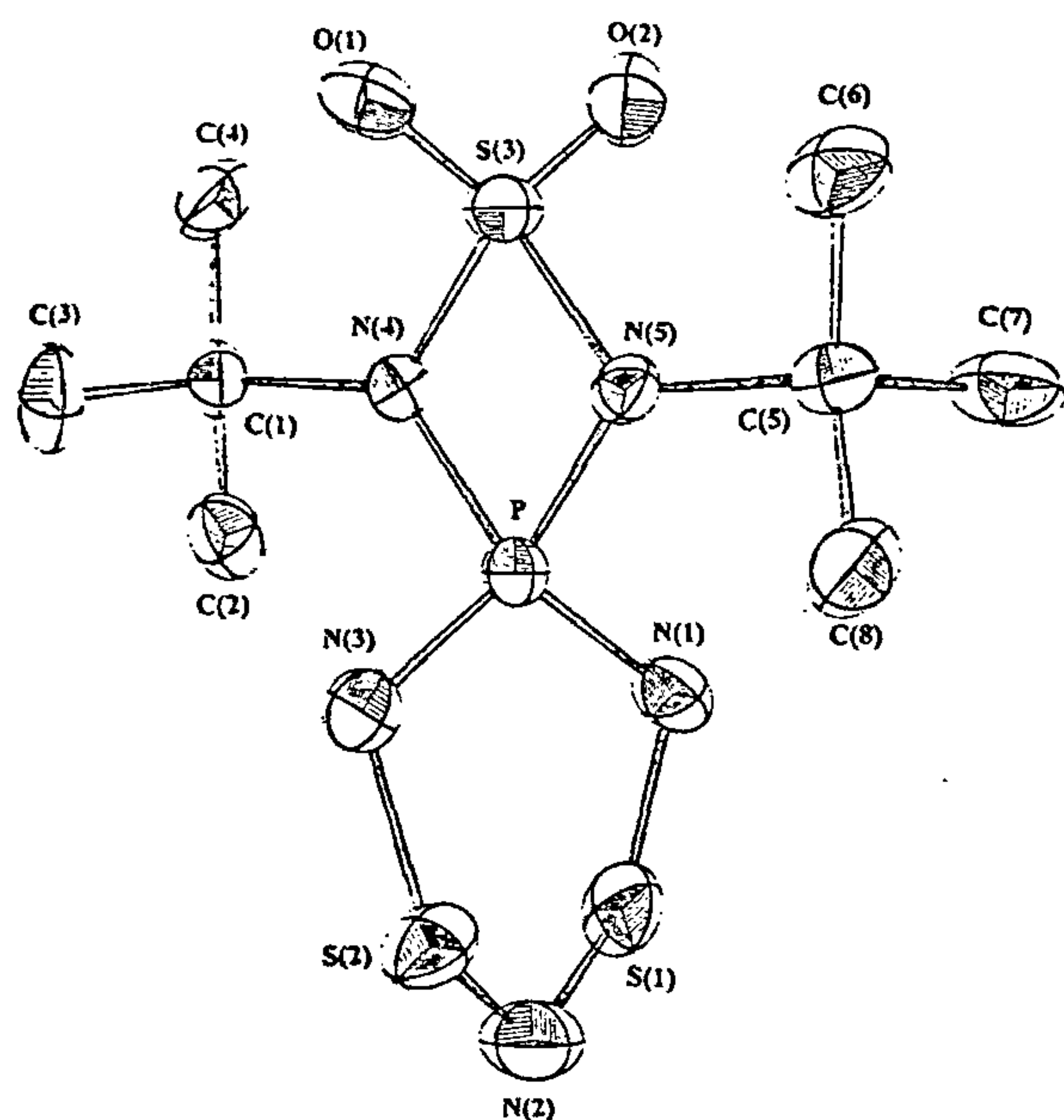


Figure 7. X-ray structure of PSN spirocycle.

Janarthanan has considered recently to explore the possible reaction of chlorophosphetidines⁵⁵ such as $E(t\text{-BuN})_2\text{PCl}$ [$E = i) \text{SO}_2$ and $ii) \text{P}(\text{NH}t\text{-Bu})$] and cyclic chlorophosphines, $(o\text{-C}_6\text{H}_4\text{O}_2)\text{PCl}$ and $(\text{CH}_2)_3(t\text{-BuN})_2\text{PCl}$ with S_4N_4 . The reactions proceed slowly at room temperature but rigorously under reflux condition in benzene or acetonitrile and give rise to intensely coloured complex reaction mixtures which pose formidable difficulties for isolation of products.

A major highlight of this work is the successful isolation of the first example of a novel spirocyclic compound from the reaction of thiaphosphetidine⁵⁶ which has been structurally characterized (Figure 7). This dark

blue black air stable crystalline solid is the first of its kind to be isolated and has its visible absorption at ca. 600 nm. X-ray structure clearly reveals that the phosphorus atom is the spiro centre which subtends on either side of it a saturated 4-membered PN_2S ring and an unsaturated (8- π) 6-membered PN_3S_2 ring. The structure provides additional interesting features.

Recently, Senthivel⁵⁷ carried out the reaction of S_4N_4 with a special type of phosphorus(III) reagent, $\text{Ph}_2\text{P}=\text{N}=\text{PPh}_3$ and observed that the reaction affords both kinds of six-membered heterocycles, I and II which suggests the cleavage of P–N single bond.

Concluding remarks

Recent studies on this topic have unfolded a number of novel findings and several of them are first time observations. Substituent chemistry of phosphorus(III) has paid noteworthy dividends. Methodologies for obtaining different types of phosphorus containing cyclic products whose chemistry is little known have become available. The results presented here have clearly demonstrated the high capability of phosphorus(III) reagents to react with a selected few cyclotrithiazenes to afford new kinds of results and heterocyclic products. Further efforts especially to develop the chemistry of novel spirocyclic compounds, substituted cyclotrithiazene of diphosphines as well as arsines and the unsymmetrically disubstituted cyclotetrathiazenes merit due consideration. The fact that a large number of such sulphur–nitrogen heterocycles as well as phosphorus(III) reagents can be readily accessed in a laboratory suggests that this fertile area offers tremendous scope for continued and worthwhile research activity for obtaining many more exciting results. It is hoped that more will be heard about them in the near future.

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