

THE UNIVERSITY OF CALGARY

**SYNTHETIC APPROACHES TO FIVE- AND SEVEN-MEMBERED
CYCLOPHOSPHATHIAZENES**

BY

JOSEPH R. MICHAUD

**A THESIS SUBMITTED TO
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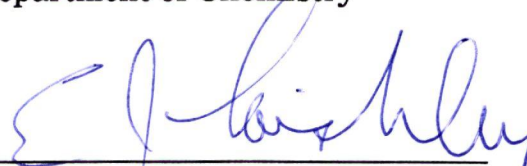
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Abstract

This thesis describes two approaches which have been investigated as potential means of preparing the five- and seven-membered cyclophosphathiazenes $\text{Ph}_2\text{PN}_2\text{S}_2^+$ (phosphadithiadiazolium) and $\text{Ph}_2\text{PN}_3\text{S}_3$ (phosphatrithiatiazepine), respectively.

The first route involves the use of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ as a template for building these species. Its reactions with $(\text{NSCl})_3$ lead to a number of six- and eight-membered cyclophosphathiazenes including $\text{Ph}_2\text{PN}_3\text{S}_2$, 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ and $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$. The former two are proposed to be the result of the decomposition of a thermally unstable cyclophosphatrithiatiazepine $\text{Ph}_2\text{PN}_3\text{S}_3$, which is formed by means of a cyclocondensation of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with two equivalents of NSCl . The unsymmetrical sulphur diimide $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ may also be isolated in low yield from these reactions.

The preparation of the unsymmetrical sulphur diimides $\text{Ph}_2\text{P}(\text{S})\text{NSNEMe}_3$ ($\text{E} = \text{Si}, \text{Sn}$) has been achieved by the reaction of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ with $\text{K}[\text{NSNSSiMe}_3]$ and $\text{Me}_3\text{SnNSNSnMe}_3$, respectively. The silicon derivative has not been obtained pure due to contamination by oily by-products. The tin derivative, however, has been obtained as an analytically pure solid and fully characterized.

Preliminary attempts to prepare the phosphadithiadiazolium and phosphatrithiatiazepine ring systems by the reaction of the unsymmetrical

sulphur diimides with SO_2Cl_2 and NSCl , respectively, indicated that these reactions are not as straightforward as anticipated, providing a variety of unidentified species as evidenced by ^{31}P nmr spectroscopy.

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**To my parents,
who encouraged me to achieve my goals
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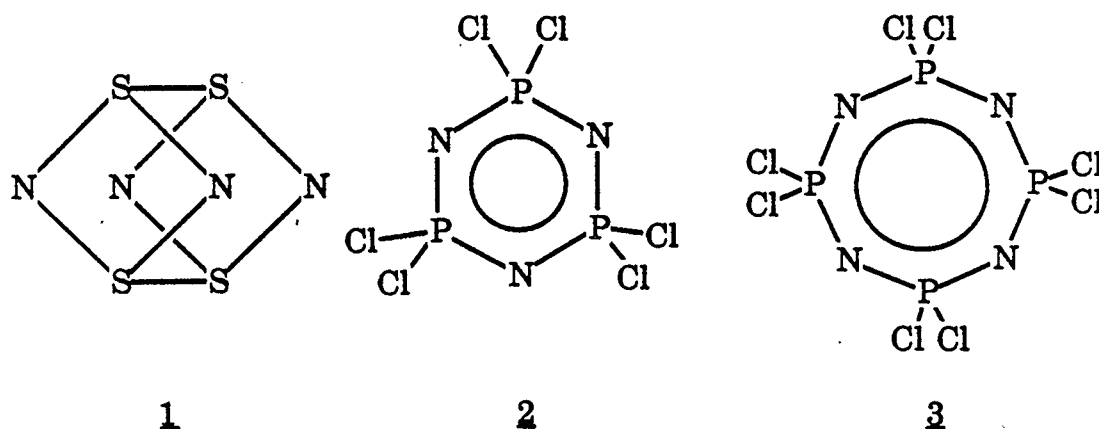
1.1 General Introduction

A number of different classes of inorganic heterocycles of the main group elements are known, including borazenes, siloxanes, thiazenes, and phosphazenes. The interest in these species is due to their molecular and electronic structures and also as sources of linear polymers with unusual properties.

The earliest reported preparation of a binary sulphur nitride was that of cyclotetrathiazene, more commonly known as tetrasulphur tetranitride (1), in 1835^[1]. Over a century after this initial discovery the structure of S_4N_4 was determined by gas phase electron diffraction studies^[2] and later by X-ray crystallography^[3,4]. In 1975 the superconducting properties of poly (sulphur nitride) (9) were discovered^[5,6] sparking a dramatic increase in research in the field of sulphur - nitrogen chemistry, which can be seen by the number of recent reviews in the area^[7-17].

In 1834, Lieberg and Woehler^[18] and, independently, Rose^[19] isolated the first phosphazenes from the reaction of PCl_5 with NH_4Cl . It was much later before the composition^[20-22], $(NPCl_2)_x$, and molecular weights [$x=3$ (2), 4 (3)] were determined^[23-25]. Stokes was the first to show the cyclic nature of these compounds in 1895^[26-31].

The phosphazenes consist of a backbone of alternating nitrogen and pentavalent phosphorus atoms with each phosphorus having two exoskeletal substituents. These substituents may vary to a great extent and include halogens as well as several organic and organometallic groups. Heterocyclic species with up to 40 phosphazene units are known in addition to the high polymers which have demonstrated considerable technologically appealing properties^[32].



1.2 Binary Sulphur-Nitrogen Compounds

Not only was S_4N_4 the first binary sulphur-nitrogen compound produced, it has also been one of the principal starting materials for the production of a variety of other binary species. This is due, in large part, to the ease of preparation from sulphur monochloride and gaseous ammonia^[33,34], and its air stability. It is, however, very sensitive to shock and will explode if ground or struck suddenly.

The thermochromic nature of S_4N_4 (it loses its dark orange colour on cooling)^[35] has led to a recent report of a low temperature crystallographic study which showed no significant change in its structure on cooling^[36]. The cage-like structure may be described as a planar arrangement of nitrogen atoms superimposed on a tetrahedron of sulphur atoms (1). The S-N bond lengths are equal (1.61 Å), and shorter than a normal single bond^[37]. The S-S bond lengths of 2.6 Å are less than the sum of the Van der Waals' radii (3.64 Å)^[38], yet considerably greater than a normal S-S single bond of 2.05 Å^[39].

The binary sulphur-nitrogen compounds display an incredible diversity in their structures ranging from simple chains such as the cations NS^+ ^[40] and S_2N^+ (4) to $(NS)_x$ (5)^[5,6], from four-^[6,41-44] to ten-membered rings^[45-48], as well as fused rings and cages (such as S_4N_4) of up to 11 atoms^[49-52] (Figure 1.1).

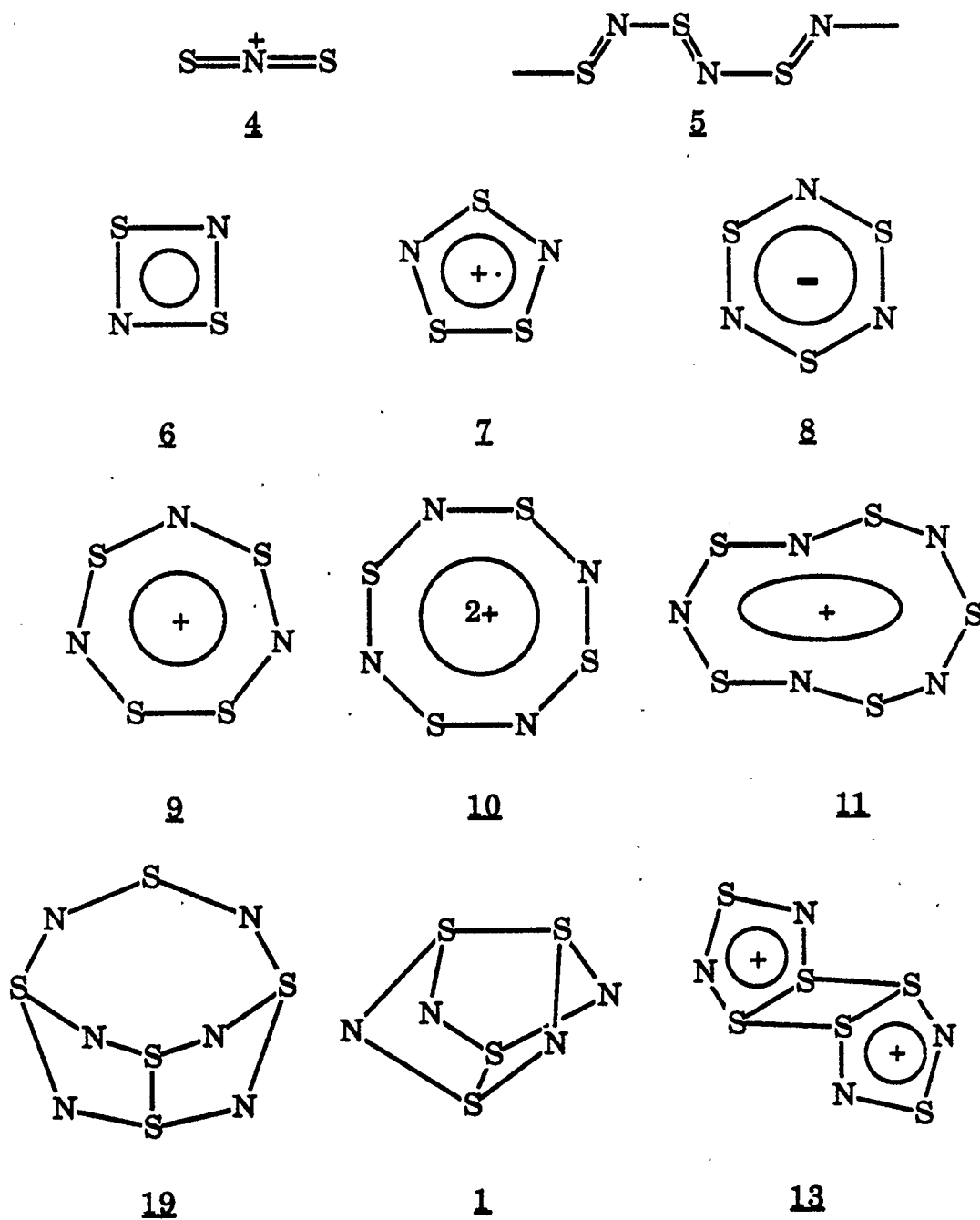


Figure 1.1 Binary sulphur nitrides

1.2.1 Bonding and Electronic Structures

Planar binary sulphur-nitrogen heterocycles are representative of "electron-rich aromatics" in that they conform to the Hückel $(4n+2)$ π -electron rule and the number of π -electrons exceeds the number of ring atoms^[53]. The assumption is that two of the six valence electrons of sulphur are contributed to the σ bonds and two are non-bonding, leaving two to be contributed to the π system. In a similar manner, nitrogen donates one of its five valence electrons to the π -system. Thus S_2N_2 (6), $S_3N_3^-$ (8) and $S_5N_5^+$ (11), are considered to be 6-, 10-, and 14- π -electron systems, respectively. The excess π -electrons are usually accommodated in antibonding (π^*) orbitals, often giving rise to intra- or inter-molecular S-S bonds.

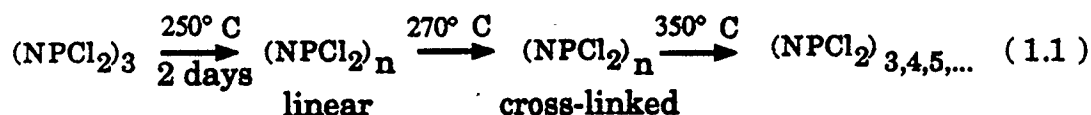
Various theoretical studies of planar thiazenes have been carried out at the simple Hückel level (HMO)^[54], extended Hückel level (EHMO)^[55], and recently at the ab initio level by Laidlaw and Trsic^[56].

Organic systems typically accommodate the same number of π electrons as ring atoms. The S-N analogs, however, contain more π electrons, the most extreme example being $S_3N_3^-$ (8), which is a 10 π -electron system according to Banister's electron counting scheme. The organic analog, benzene, in contrast, is a 6 π -electron ring. The tetraanion $C_6H_6^{4-}$ would also be a 10 π -electron system but is unstable relative to $S_3N_3^-$ because of its higher ionic charge and the inability of carbon to handle the excess negative charge, which nitrogen is effectively able to handle. Also, the S-N distances in $S_3N_3^-$ (1.6 Å)^[57] are greater than the C-C distances in benzene (1.4 Å), thus reducing the repulsion of the lone pairs.

1.3 Cyclic and Linear Phosphazenes

In a similar manner to the dependence of much of thiazene chemistry on S_4N_4 , the major part of phosphazene research is based on the chemistry of hexachlorocyclotriphosphazene (2) and octachlorocyclotetraphosphazene (3) mentioned in the introduction to this chapter. In a review in 1972, Allcock reported that more than 1000 compounds have been prepared through routes involving the use of the trimer or tetramer^[58] and the pace of research in this field has not slowed in recent years.

The chemistry of phosphazenes expanded rapidly following the development of techniques for the replacement of the halogens by organic groups in the late 1950's and early 1960's. This allowed a wide range of compounds to be prepared and studied. Polyphosphazenes may be prepared by heating the trimer or tetramer to 250° C, however, above 350° C cyclic species are again formed [Equation (1.1)]^[59]



1.3.1 Bonding in Cyclophosphazenes

A number of bonding schemes for cyclophosphazenes have been proposed^[60] and to date there is no consensus as to the extent of participation of the d-orbitals on phosphorus in the bonding.

Each nitrogen atom has a lone pair occupying an sp^2 orbital in the local PNP plane. Two bonding patterns have been proposed involving the d-orbitals of phosphorus (figure 1.2). The π' system results from overlap of the doubly occupied sp^2 orbital with the vacant $d_{x^2-y^2}$ and d_{xy} orbitals on

phosphorus. The singly occupied p_z orbital on nitrogen may overlap with the out-of-plane d_{xz} ["pseudoaromatic" heteromorphic (N-P) $p\pi-d\pi$ bonding] or d_{yz} [homomorphic (N-P) $p\pi-d\pi$ bonding] orbitals. Equal contribution of the latter two π systems would result in 3 center- 2 electron PNP bonds.

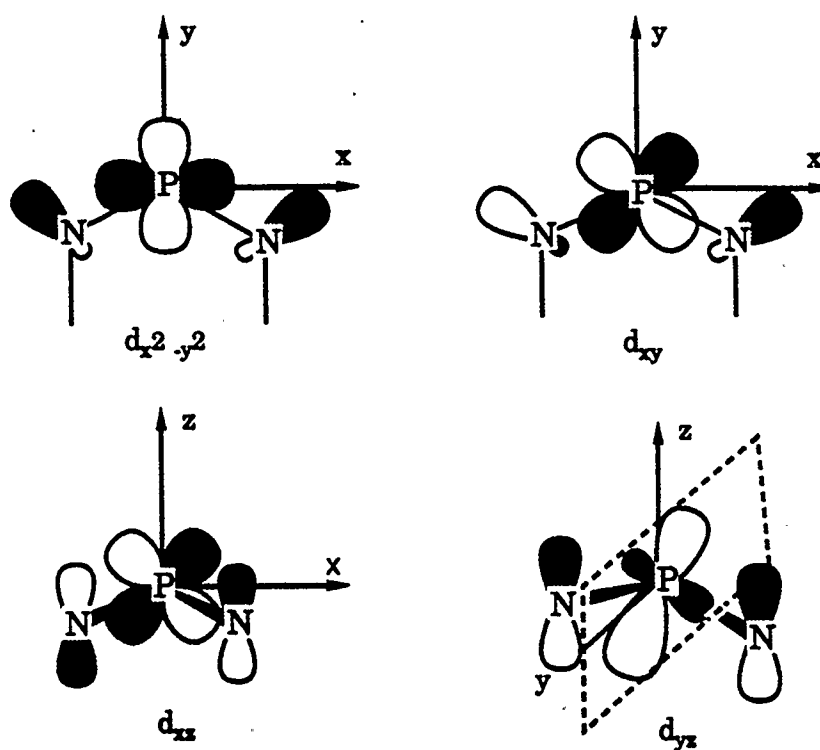


Figure 1.2. Bonding in cyclophosphazenes

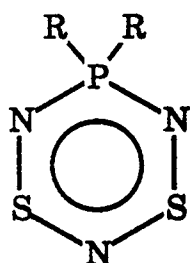
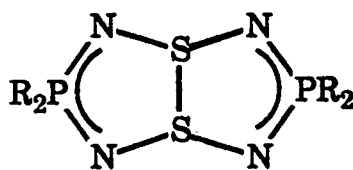
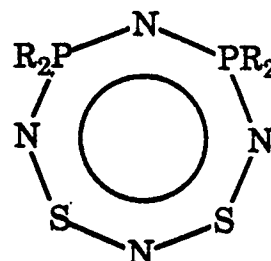
1.4 Cyclophosphathiazenes

Cyclophosphathiazenes may be considered as hybrids of the binary thiazenes and the cyclophosphazenes by incorporating the monomers R_2PN and NS (or NSX for three coordinate sulphur) to provide an extensive series

of compounds of general formula $(R_2PN)_a(NSX)_b$, $a=1$ to 4, $b=1$ to 2. This section will be divided into two parts, the first dealing with two-coordinate sulphur [S(II)], and the second with three-coordinate sulphur [S(IV)].

1.4.1 Cyclophosphathiazenes Containing Two-coordinate Sulphur

The first example of this class of compounds was the six-membered ring $R_2PN_3S_2$ (**14**) ($R = Me_3SiNH$)^[61,62], a deep blue species prepared by the reaction of S_4N_4 with $(Me_3Si)_2NP(NSiMe_3)_2$. The phenyl or methyl derivatives may be prepared by the reaction of tetraphenyl- or tetramethyl-diphosphine^[63,64] or diphenylphosphine^[65] with S_4N_4 in toluene under reflux giving dark purple compounds. Perfluoroalkyl derivatives of **14** ($R = CF_3$, C_2F_5) have also been prepared by the reaction of $R_2PN(SiMe_3)_2$ ($R = CF_3$, C_2F_5) with $S_3N_2Cl_2$ and isolated as the norbornadiene adduct^[66].

**14****15****16**

The phenyl derivative of **14** consists of a planar NSNSN chain attached to a phosphorus atom which is 0.28 \AA out of the plane, contrasting significantly with the puckered ring of the (Me_3SiNH) derivative^[62]. The S-N bond lengths in **14** ($R = Ph$) range from 1.56 to 1.58 \AA , slightly shorter than those found in $S_3N_3^-$ (1.60 \AA)^[57], due to lower occupation of the π^* orbitals ($R_2PN_3S_2$ is an

8π - electron system whereas $S_3N_3^-$ is a 10π electron system), resulting in an increase in bond order.

Two isomers of the eight-membered cyclophosphathiazene $R_4P_2N_4S_2$ are possible (15 and 16) and are known for $R=Me, Ph$. They were initially isolated in low yield via column chromatography from the reaction of tetraphenyl- or tetramethyl diphosphine with S_4N_4 ^[67]. An alternative syntheses for the 1,5 isomer 15 is the slow thermal decomposition of the corresponding six membered ring 14^[68,69], and the 1,3 isomer 16 ($R=Ph$) may be prepared by the reaction of $Ph_2PN(H)PPh_2$ with S_4N_4 ^[69]. After several days a solution of 14 ($R=CF_3$) provides crystals of the perfluoromethyl derivative of 16^[68].

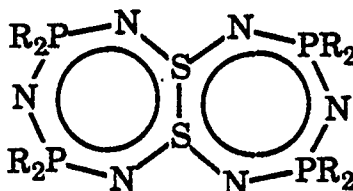
The yield of 16 ($R=Ph$) is increased to 50% in the reaction of $Ph_4P_2N_3H_4^+Cl^-$ with S_4N_4 in a 2:1 molar ratio in chloroform in the presence of triethylamine^[70]. Compound 15 may also be prepared in 50% yield by the reaction of $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ with SCl_2 in a 3:2 molar ratio in CH_2Cl_2 . The 1,3 isomer 16 is related to 14 in that there is a planar NSNSN unit with similar bond lengths and the phosphorus atoms lie out of and on opposite sides of the plane, one by 0.2\AA , and the other by 0.5\AA ^[67].

The 1,5 isomer 15 ($R=Ph, Me$) has a folded structure with a transannular S-S linkage. Alternatively, it may be considered as two $R_2PN_2S_2$ rings sharing an S-S bond. The N_2S_2 units of each ring are planar and the phosphorus atoms lie 0.21\AA below their respective planes ($R=Ph$). For $R=Me$, one P atom lies 0.19\AA above and the other 0.48\AA below their respective planes.

A related species is the larger twelve-membered ring $Ph_8P_4N_6S_2$ (17) prepared by the reaction of the six-membered ring $Ph_4P_2N_3SCl$ with 1/2 molar equivalent of triphenylstibine. The S-N bond lengths (ave. 1.60\AA) are

similar to those in the 1,5 eight-membered ring and the P-N bond lengths [1.58Å(internal) and 1.62Å(terminal)] are almost identical to those in the 1,3 eight-membered ring (1.59 and 1.61Å, respectively). Unlike the 1,5 isomer, however, the two seven-membered rings adopt a highly puckered geometry about the S-S bond due to the incorporation of an additional R₂PN unit into each ring.

Oakley has shown that the conversion of the six- to twelve-membered ring occurs via a Ph₄P₂N₃S• radical^[71] giving an esr spectrum consisting of a quintet of triplets with a g value of 2.0058, indicating significant localization of the lone electron on the sulphur atom.



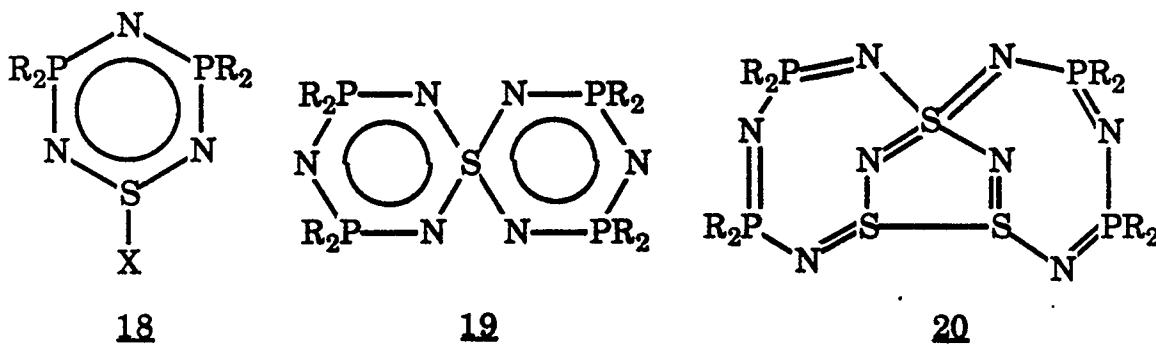
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1.4.2 Cyclophosphathiazenes Containing Three-coordinate Sulphur

The first species of this type, Cl₅P₂N₃S (**18**) (R=Cl, X=Cl), was originally prepared by Roesky in the reaction of S(NSO)₂ with PCl₅^[72] and later by the reaction of Me₃SiNSNSiMe₃ with PCl₅^[73]. The crystal structure of **18** (R=Ph, X=Cl)^[74] (prepared by the reaction of Ph₂PCl with S₄N₄ in a 2:1 molar ratio under reflux in toluene) shows a planar NPNPN unit with the sulphur atom 0.31Å out of the plane. The S-N bonds are 1.56Å, shorter than those in S₃N₃Cl₃ [d(S-N) = 1.60Å^[75]] and the P-N distances in the PNP unit are 1.58Å, comparable to those found in phosphazenes^[59]. The other PN distances are

significantly longer indicating localized π -bonding at either end of the ring. The S-Cl distance is 2.36Å, longer than in (NSCl)₃ (2.08, 2.15Å)^[76] indicating some ionic character.

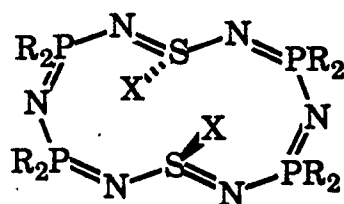
Chivers and coworkers have shown that **18** [R=Ph, X=I, prepared by reacting Ph₄P₂N₃SCl with KI^[77]; R=Ph, X=NMe₂, prepared by reacting Ph₄P₂N₃SCl with Me₃SiNMe₂ in a 3:2 molar ratio^[78]] undergoes thermolysis at 150°C to give the spirocyclic species **19**^[77]. The structure consists of two almost planar P₂N₃S rings sharing a common sulphur atom, which is of approximate tetrahedral geometry with equal N-S bond lengths. The P-N bond lengths are all approximately equal (1.60Å) and the same as those found in (Ph₂PN)₃^[79] so that each ring may be considered to be a 6 π system with S donating one electron to each ring.



Another spirocyclic species, **20**, has been prepared in 20% yield by the reaction of two equivalents of Ph₄P₂N₃SCl with Me₃SiNSNSiMe₃ in CH₂Cl₂^[74]. The structure consists of two eight-membered rings fused at a common sulphur atom, which, like its smaller analogue, is almost tetrahedral. In addition, there is a weak S-S interaction of 2.37Å [cf. S₈(2.05 Å)] between the eight-membered rings resulting in a tricyclic structure. The P-N bond lengths of 1.60 Å and the NPN angles of 120.5° are approximately

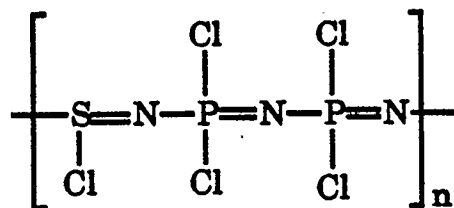
the same as those found in cyclophosphazenes.

A solution of **18** ($R=Ph$, $X=NMe_2$) after several days at room temperature provided crystals of a twelve-membered ring, **21**, which has been shown to be a precursor to the spirocycle **19**. The structure of **21** consists of a twelve-membered ring with trans dimethylamino substituents on the sulphur atoms. The S-N bond lengths to the substituents are 1.70 Å, suggesting single-bonding character, which is also supported by the pyramidal geometry of the exocyclic nitrogen atoms.



21

Very recently, Allcock and coworkers have reported the preparation of the first poly(phosphathiazene)^[80]. Heating **18** ($R=Cl, X=Cl$) to 90°C in a sealed Pyrex tube provides the moisture-sensitive polymer **22** in 90% yield. Treatment of the polymer with sodium o-phenylphenoxide results in the replacement of ~65% of the chlorine atoms by aryloxy substituents, imposing considerable hydrolytic stability to the polymer.



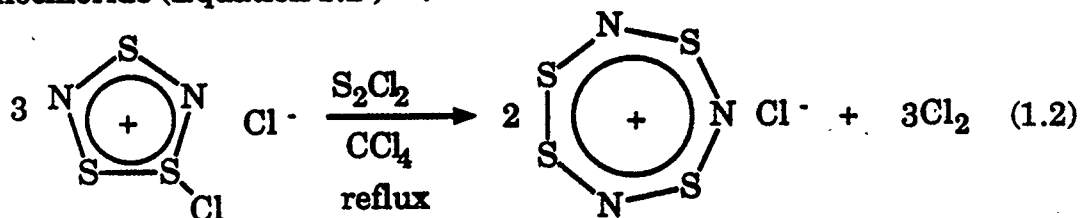
22

1.5 Preparation of Binary Five- and Seven-membered Cyclothiazenes

The radical cation 1,3,4-trithia-2,5-diazolium, $S_3N_2^{\bullet+}$ (7) may be prepared in solution by the reaction of S_4N_4 with a variety of oxidizing agents, but it is only isolable as the AsF_6^- salt using $(Te_6^{4+})(AsF_6^-)_4$ ^[81,82] as the oxidant. Other oxidizing agents, such as arsenic pentafluoride, perfluoromethylsulphonic acid, fluorosulphonic acid, $FeCl_3$, and $(S_8^{2+})(AsF_6^-)$ produce dimeric salts of formulae $(S_6N_4^{2+})(X)_2$ (13), $X = AsF_6^-$ ^[81,82], $CF_3SO_3^-$ ^[83,84], $S_2O_2F^-$ (and SO_3F^-)^[82], $FeCl_4^-$ ^[85] and AsF_6^- ^[86], respectively.

$S_3N_2^+$ is essentially a planar ring with an average S-N bond distance of 1.58 Å, comparable to other SN compounds (eg. $S_3N_3Cl_3$, $d(S-N) = 1.61$ Å^[75]), indicating considerable double bond characteristics in the SN linkages. The S-S bond (2.15 Å) is slightly longer than that found in S_8 , and thus may be considered to be a single bond.

The 1,2,4,6-tetrathia-3,5,7-triazepinium cation $S_4N_3^+$ (9) was one of the first sulphur-nitrogen heterocycles to be prepared^[87] and is isolable as a number of salts. A high yield synthesis of the chloride salt is the reaction of S_4N_4 with thionyl chloride or sulphur monochloride in refluxing carbon tetrachloride or, alternatively, the reaction of $S_3N_2Cl^+Cl^-$ with sulphur monochloride (Equation 1.2)^[88].

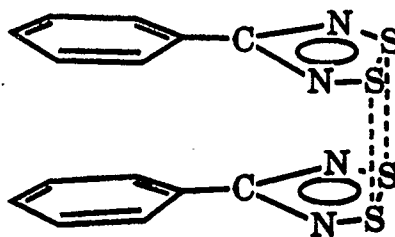


Like its smaller analogue, $S_4N_3^+$ is essentially a planar ring with approximately equal S-N bonds lengths (ave. 1.55 Å) and a sulphur-sulphur linkage of 2.09 Å^[89], once again suggesting a single S-S bond and multiple bonding in the remainder of the cation.

1.6 Five-Membered CNS Heterocycles

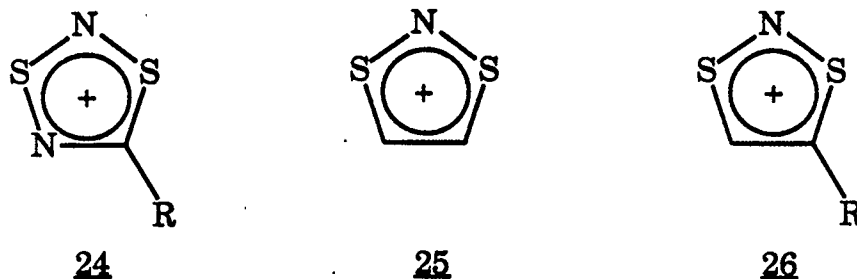
The radical 4-phenyl-1,2-dithia-3,5-diazole $PhCN_2S_2^\bullet$, isoelectronic to $S_3N_2^+$, was first prepared by the reduction of 4-phenyl-1,2-dithia-3,5-diazolium chloride with sodium thiocyanate^[90]. Like $S_3N_2^+$, it crystallizes as a dimer $(PhCN_2S_2)_2$ (23), but it is not a stepwise linkage of monomer units but a cofacial arrangement of almost parallel S_2N_2C units (dihedral angle $\sim 7^\circ$) and phenyl groups. The average S-N bond distances (1.62 Å) are comparable to those in $S_3N_2^+$ (1.58 Å)^[81]. The endocyclic S-S bond length of 2.09 Å is almost identical to the S-S bond lengths in S_8 ^[39].

Passmore and coworkers have demonstrated the use of $(S_2N^+)(AsF_6^-)$ (4) as a building block for the preparation of the five-membered cations (24), (25), and (26). Compound (24) ($R=CH_3$) is prepared quantitatively by the reaction



23

of S_2N^+ with neat acetonitrile^[91]. The reaction with a slight excess of ethyne or propyne in liquid SO_2 generates (25) or (26), respectively^[91,92]. The crystal structures of both (24) and (26) show planar rings including the exocyclic carbon atoms.



Two very interesting examples of five-membered CNS heterocycles are the thermally stable 7π paramagnetic liquids (27) and (28) ($R=tBu$)^[93] which interconvert by means of a cofacial association of two radicals as shown in figure 1.3.

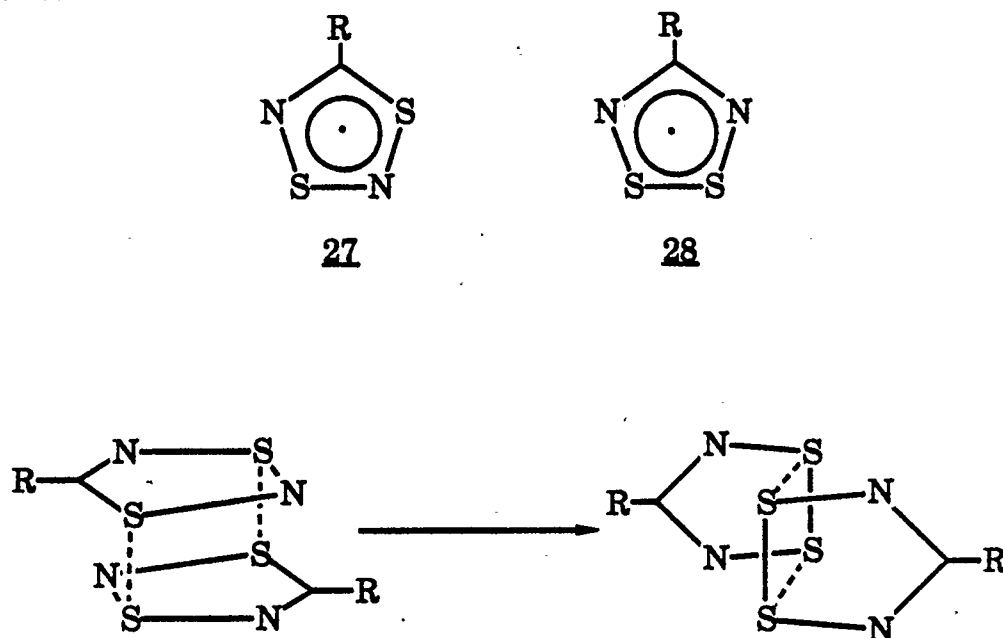
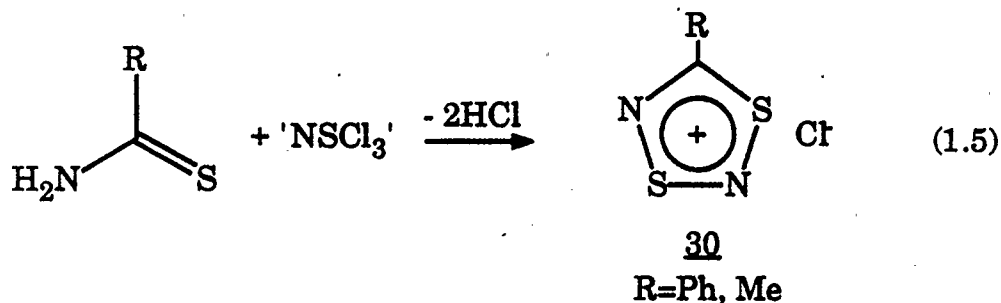
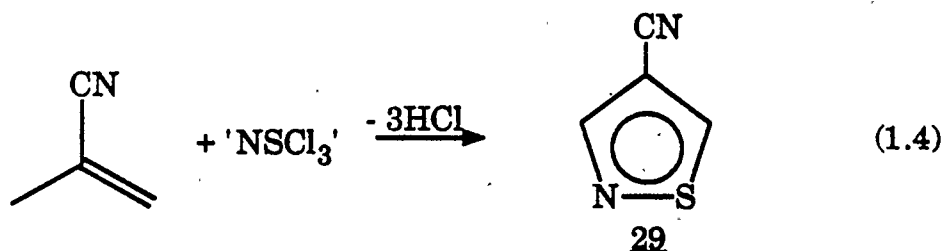
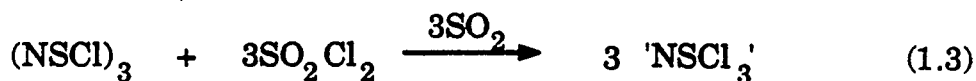


Figure 1.3. Isomerization of dithiadiazole radicals

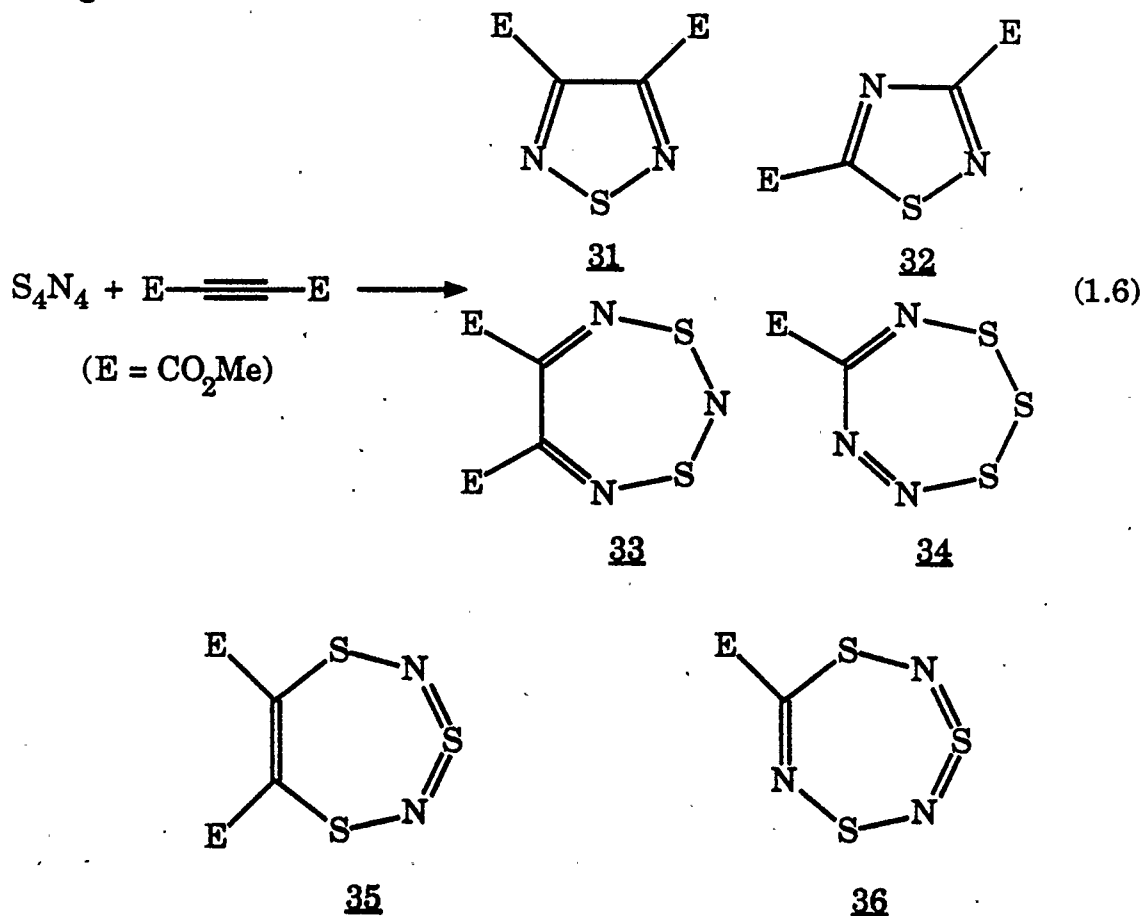
Chivers and coworkers have recently shown that a solution of $S_3N_3Cl_3$ treated with a large excess of sulphuryl chloride behaves as if the reagent "NSCl₃" [Equation (1.3)] is present and may be used for the production of CNS heterocycles (29) and (30) (Equations 1.4 and 1.5) [94].



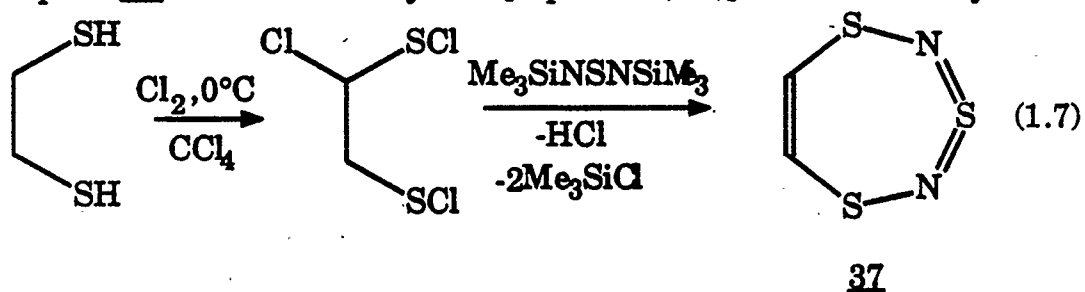
1.7 Seven-Membered CNS Heterocycles

Seven-membered CNS rings were first reported by Tashiro and coworkers^[95] from the reaction of S_4N_4 and dimethylacetylenedicarboxylate (DMAD) [Equation (1.6)]. It was later shown by X-ray crystallography that 5,6-diphenyl-1,3-dithia-2,4,7-triazepine (33) and 6-phenyl-1,2,3-trithia-4,5,7-triazepine (34) are actually 6,7-diphenyl-1,3,5-trithia-2,4-diazepine (35) and 7-phenyl-1,3,5-trithia-2,4,6-triazepine (36)^[96], respectively. Both (35) and (36) are planar species with S-N bond lengths of 1.54 to 1.60 Å, slightly less than

those in $(\text{NSCl})_3$ (1.60 \AA)^[75] indicating some delocalized character in the ring. A result of the planarity of the rings is enlarged angles of $135\text{-}141^\circ$ at the nitrogen atoms.

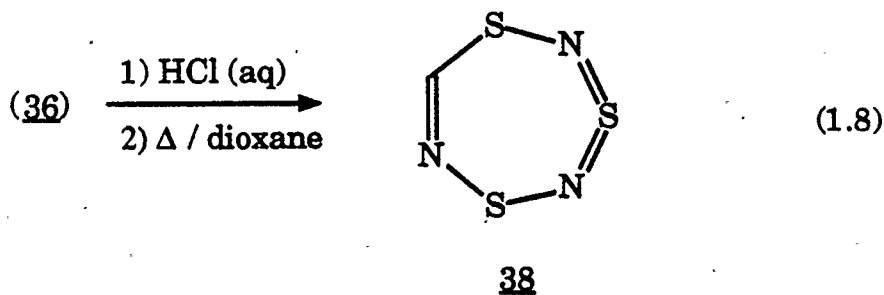


Rees and coworkers have prepared the parent species 1,3,5-trithia-2,4-diazepine (**37**) as colourless crystals [Equation (1.7)]^[97]. The heterocyclic ring



is planar, again resulting in large angles at the nitrogen atoms (137 and 138°)^[98], similar to the diphenyl derivative. The S-N bond distances of 1.56 to 1.69 Å indicate multiple bonding character in the ring system.

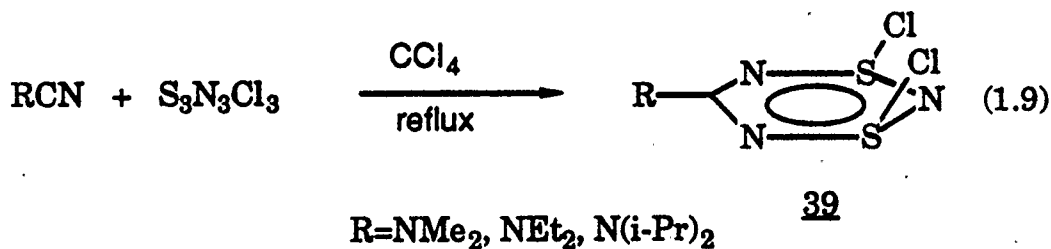
As indicated earlier in the discussion of the trithiadiazepines, the reaction of S₄N₄ with DMAD also produces methyl-1,3,5,2,4,6-trithiatriazepine-7-carboxylate as a minor product (36)^[96], which may then be hydrolyzed and decarboxylated to produce the parent species (38) as colourless crystals:^[99]



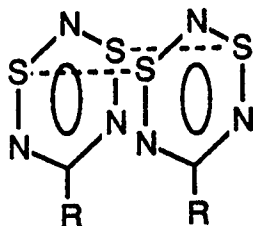
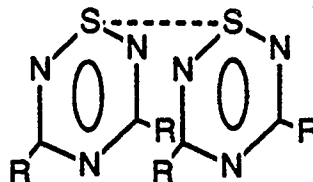
1.8 Six- and Eight-Membered CNS Heterocycles

Chivers and coworkers have shown the versatility of a variety of dialkyl cyanamides in the preparation of 5-amino-1,3-dichloro-1,3-dithia-2,4,6-triazines (39) [equation (1.9)]^[100]

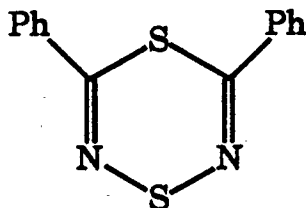
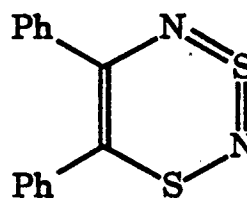
Mews and coworkers have found that 39 (R=CF₃), when reduced by Zn, gives the dechlorinated species RCN₃S₂^[101]. The reduction of 39 (R=Ph) by



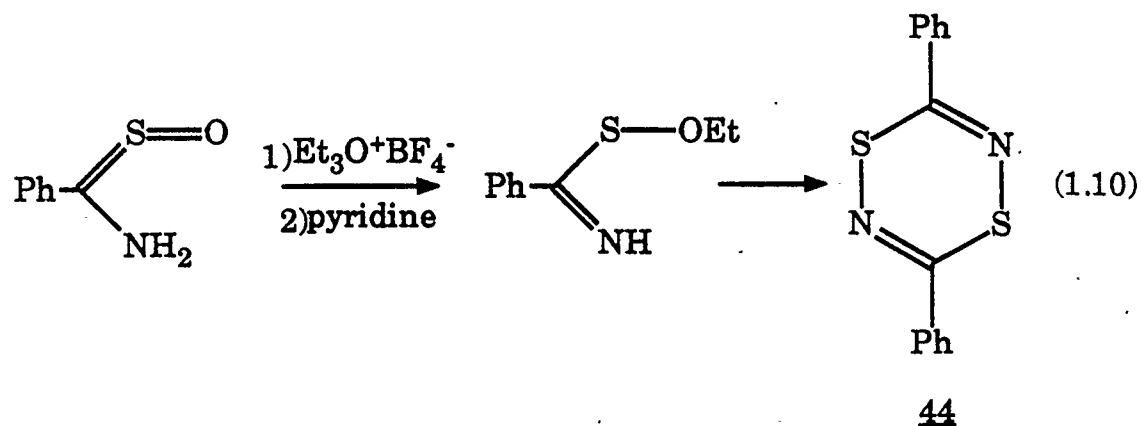
Ph_3Sb provides the cofacial dimer **40**^[102], which is related to 3,5-diphenyl-1-thia-2,4,6-triazine which also crystallizes as a dimer (**41**)^[103]. The intermolecular S-S linkages in **40** and **41** are 2.53 and 2.67 Å, respectively, considerably less than the sum of the van der Waals radii of 3.6 Å^[104].

**40****41**

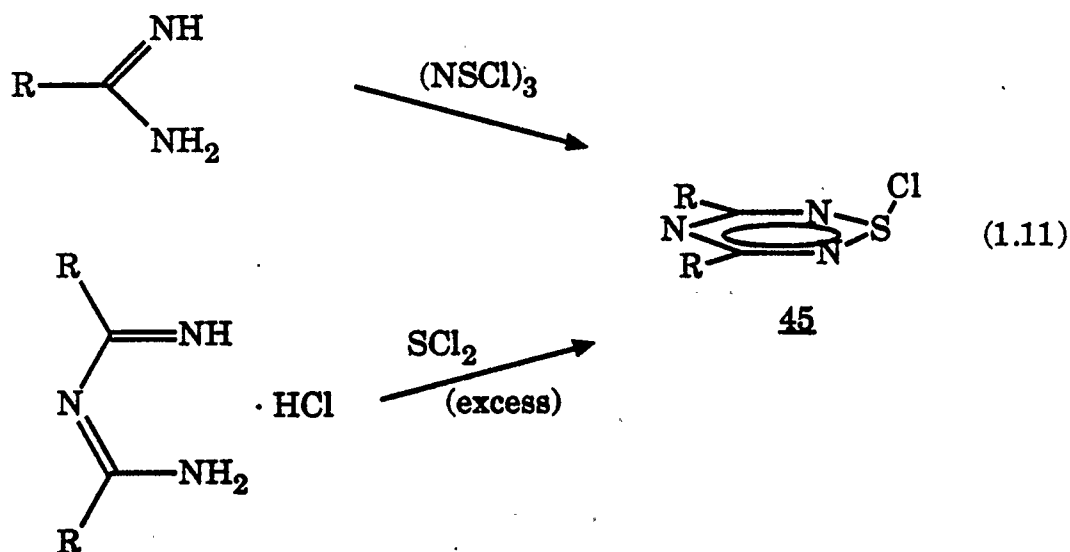
The reagent S_4N_4 has also been used as a precursor for six-membered CNS rings. The reaction of diphenylacetylene with S_4N_4 gives rise to 3,5-diphenyl-1,4-dithia-2,6-diazine (**42**)^[105], which was originally reported to be (**43**)^[106]. Heterocycle (**42**) is not a planar ring, but exists in a boat conformation with short C-N bond lengths (1.27 Å), indicating no delocalization of the π electrons in the ring.

**42****43**

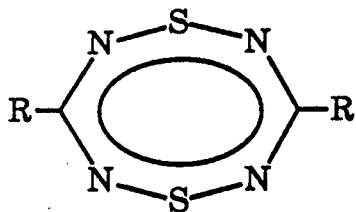
Another CNS ring containing two carbon atoms is 3,6-diphenyl-1,4-dithia-2,5-diazine (**44**) prepared according to the route shown in equation (1.10)^[107].



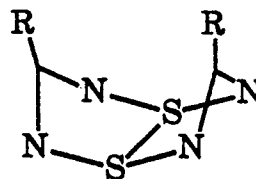
Two methods are available for the preparation of 1-chloro-1-thia-2,4,6-thiatriazines (45)^[108,109] and these are indicated in equation (1.11).



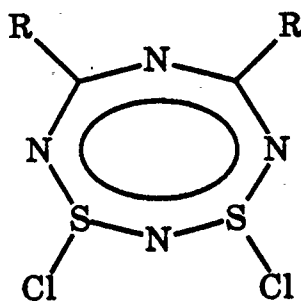
The reaction of substituted amidines with sulphur dichloride yields the eight-membered rings 46 and 47. The difference in the structures of these two derivatives is due to the π -donor ability of the exocyclic dimethylamino groups weakening the π -system, causing a distortion to the folded structure^[69].



46 R=Aryl

47 R=NMe₂

Treatment of thiazyl chloride with an excess of dimethyl cyanamide results in the production of 48 (R=Me₂N), the first example of a 1,3-isomer of a CNS heterocycle. It is interesting to note that the reduced form of 48, (ie. the carbon-containing analogue of 16) is unknown.



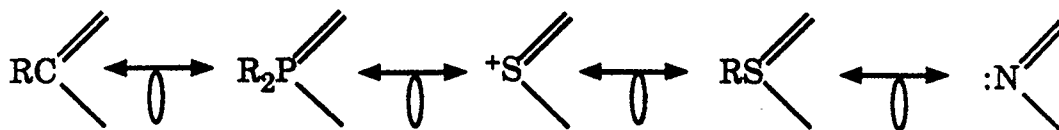
48

1.9 Objectives and Preparative Strategy

As discussed in sections 1.4 and 1.5, the primary synthon for five- and seven-membered binary thiazenes as well as a number of cyclophosphathiazenes is tetrasulphur tetranitride. However, in all reports of reactions of S₄N₄ with phosphorus-containing reagents no characterization of five- or seven-membered cyclophosphathiazenes was achieved. Rather than relying on this "hit-and-miss" approach, the preparation of CNS rings focused on "building-blocks" (sections 1.6 and 1.7) as precursors to the desired species

as did later work in the synthesis of cyclophosphathiazenes.

Qualitatively, the cyclothiazenes may be considered to be made up of isolobal "fragments":



Replacement of one of these fragments by another gives a series of isoelectronic heterocycles, as indicated in figure 1.4 for a variety of rings with from five to eight endocyclic atoms. The obvious absences in figure 1.4 are the five- and seven-membered cyclophosphathiazenes.

The objective of this thesis research, then, was to investigate routes to these unknown cyclophosphathiazenes, which, like their binary and carbon-containing analogs, would be expected to be 6π - or 10π - Hückel-type aromatic systems, respectively.

The preparative strategy for these heterocycles, as was the case for the CNS rings, will focus on a "building-block" approach in which precursors to the desired ring systems with appropriate substituents will be prepared and induced to cyclize.

Two main preparative routes will be investigated and these are discussed in the following chapters. The first involves the use of bis-(trimethylsilyl)amino-diphenylphosphine sulphide, $Ph_2P(S)N(SiMe_3)_2$ **49**, and the second involves the preparation of unsymmetrical sulphur diimides of the type $Ph_2P(S)NSNEMe_3$ ($E=Si, Sn$) as precursors to the desired species.

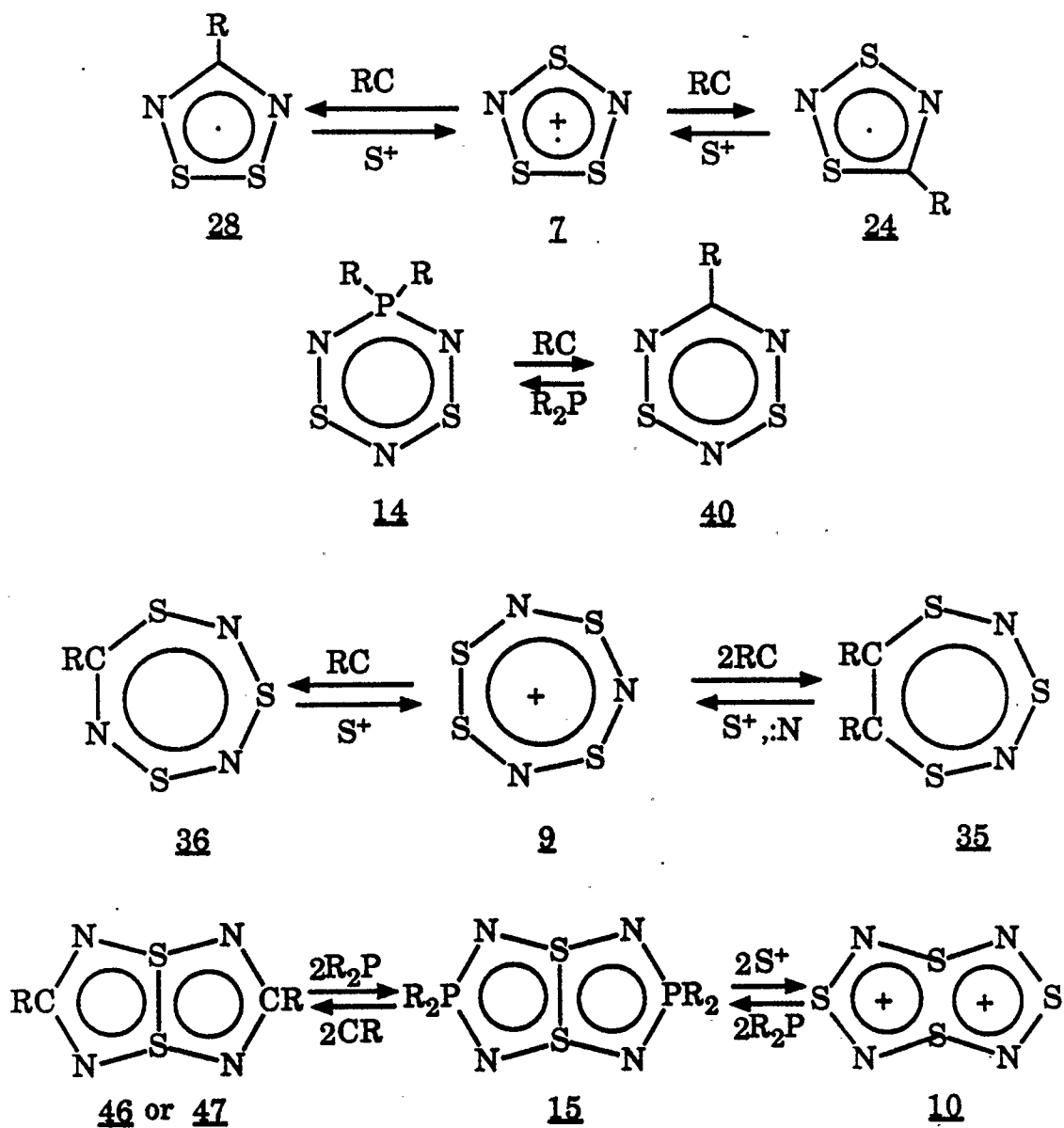


Figure 1.4. Isolobal Relationships Among Various Heterocyclothiazenes

Chapter 2

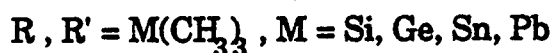
Ph₂P(S)N(SiMe₃)₂ and Ph₂PN(SiMe₃)₂ as Synthons for Cyclophosphathiazenes

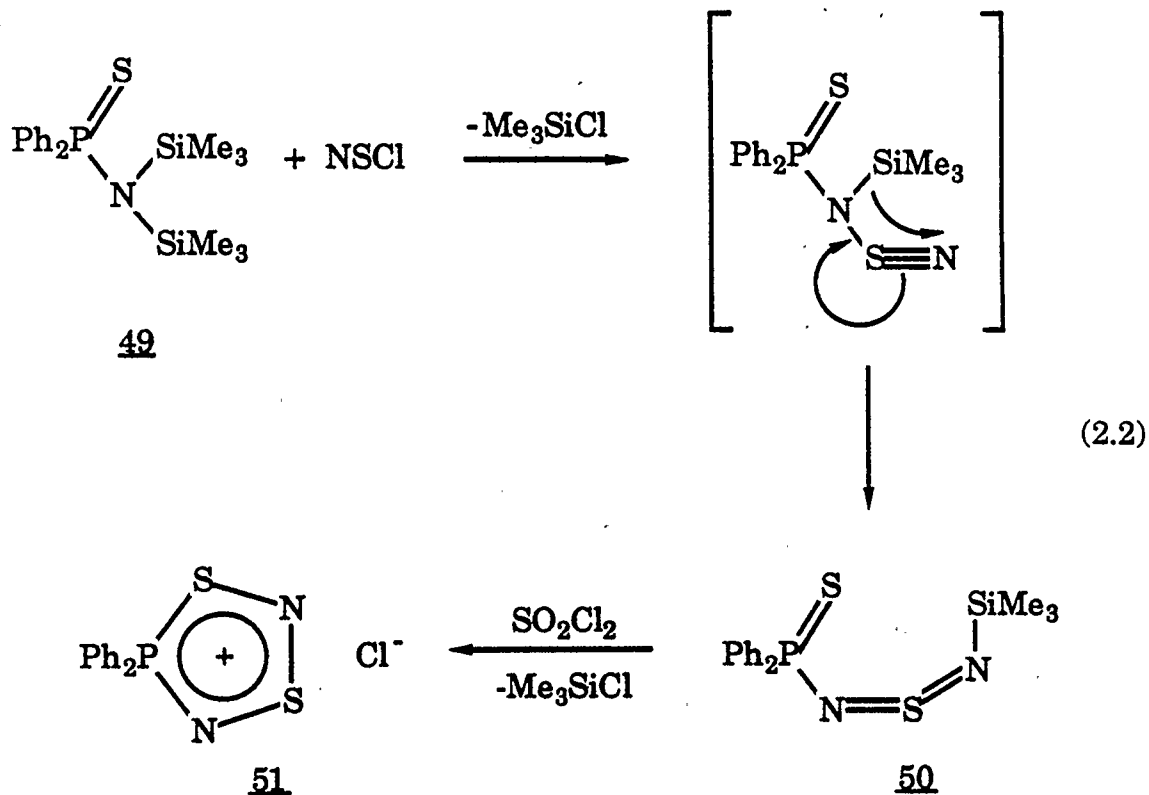
2.1 Introduction

As discussed in Chapter One, the absence of five- and seven- membered cyclophosphathiazenes is perplexing in light of the existence of CNS and NS analogues of both ring sizes.

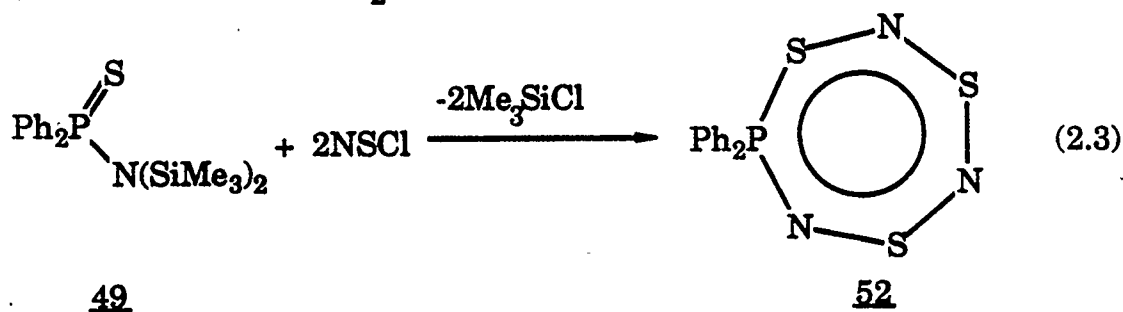
This chapter discusses investigations carried out toward the synthesis of these elusive species using Ph₂P(S)N(SiMe₃)₂ **49** as a synthon by making use of the SPN fragment as a template and the Me₃Si- substituents as labile leaving groups in order to avoid possible complications arising from the production of HCl^[110].

It was anticipated that the reaction of Ph₂P(S)N(SiMe₃)₂ with one equivalent of thiazyl chloride would generate the unsymmetrical sulphur diimide as was the case in the work of Brands and Golloch with secondary and tertiary amines of elements of group 14 (Equation 2.1)^[111]. This species could then be induced to cyclize, thus generating the diphenylphosphadithiadiazolium cation (Equation 2.2).





The reaction with two equivalents of thiazyl chloride was expected to generate the diphenylphosphatrithiazepine (Equation 2.3), a 10π -electron system which would be formally related to the well known $S_4N_3^+$ by replacement of S^+ by a Ph_2P fragment.



As well, the reaction of $Ph_2PN(SiMe_3)_2$ with $(NSCl)_3$ was investigated as a means of preparing known cyclophosphathiazenes. The results of this study

are presented and compared to those obtained for the $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ reactions.

General experimental procedures and specific details for the various reactions are described in section 2.8 .

2.2 Preparation and Characterization of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$, $\text{E}=\text{S}, \text{Se}$

Oxidative addition of sulphur or selenium to $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ results in the production of the new compounds $\text{Ph}_2\text{P}(\text{E})\text{N}(\text{SiMe}_3)_2$ ($\text{E}=\text{S}, \text{Se}$).

The procedure used for the production of the sulphide is almost identical to that reported by Roesky^[112] and coworkers during the course of this research, with slight differences in the work-up. In their report, only the molecular ion (mass spectrum) and ^{31}P nmr chemical shift are reported. Herein is the infrared spectrum (Figure 2.1) as well as ^1H nmr data. The ^{31}P nmr chemical shift is in agreement with the reported value (Table 2.1).

The reaction of sulphur with $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$, as is the case with many phosphines^[113] is very exothermic and care must be taken, especially in larger scale preparations.

The reaction with selenium is much less vigorous. Indeed, for many aromatic substituted tertiary phosphines, the oxidative addition of selenium requires different approaches such as : a) fusion of the phosphine with elemental selenium in the absence of solvent, b) heating with selenium in a high-boiling solvent, or c) reacting the phosphine with potassium selenocyanate in acetonitrile according to equation (2.4)^[113].



In the present case, the oxidation occurred at room temperature with elemental selenium. The spectroscopic data for $\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{SiMe}_3)_2$ are presented in Figure 2.2 and Table 2.1, respectively. The difference in the ^{31}P

 Table 2.1. Nuclear Magnetic Resonance Data for $\text{Ph}_2\text{P}(\text{E})\text{N}(\text{SiMe}_3)_2$
 ^1H nmr Spectrum (in CDCl_3 solution):

Chemical Shift (ref. CDCl_3 7.27 ppm)	Integration	Assignment
<u>E=S</u>		
7.95 ppm (multiplet)	2	Ph-
7.43 (multiplet)	3	Ph-
0.17 (singlet)	8.9	$\text{Me}_3\text{Si-}$
<u>E=Se</u>		
7.85 (multiplet)	2	Ph-
7.32 (multiplet)	3	Ph-
0.22 (singlet)	8.9	$\text{Me}_3\text{Si-}$

 ^{31}P nmr Spectrum (in CHCl_3 solution / D_2O lock):
(ref. external 85% H_3PO_4)E=SSinglet at 60.6 ppm (cf. literature ^{31}P $\delta=61$ ppm^[112])E=Se

Singlet at 55.8 ppm

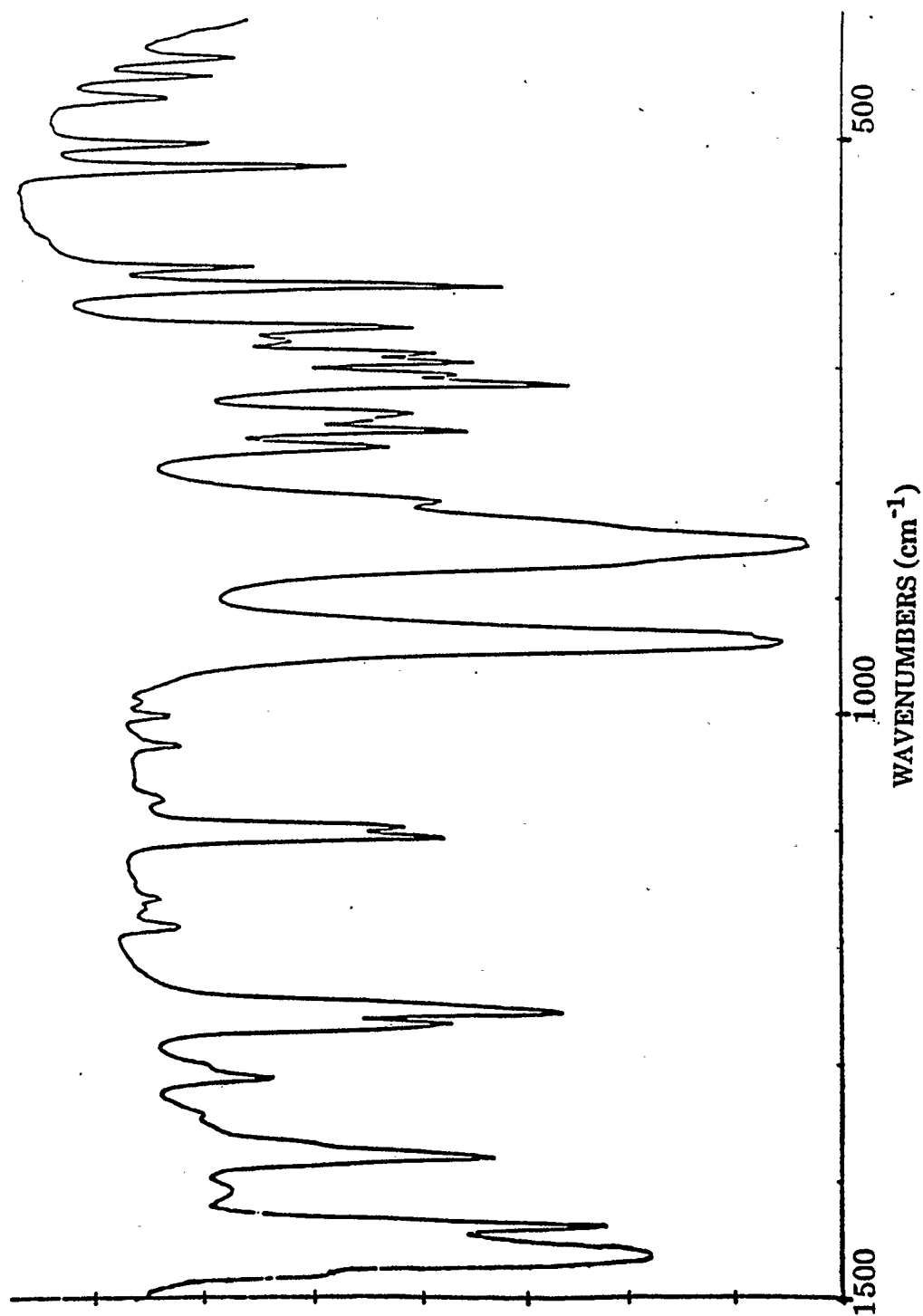


Figure 2.1 Infrared Spectrum of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ (as Nujol mull)

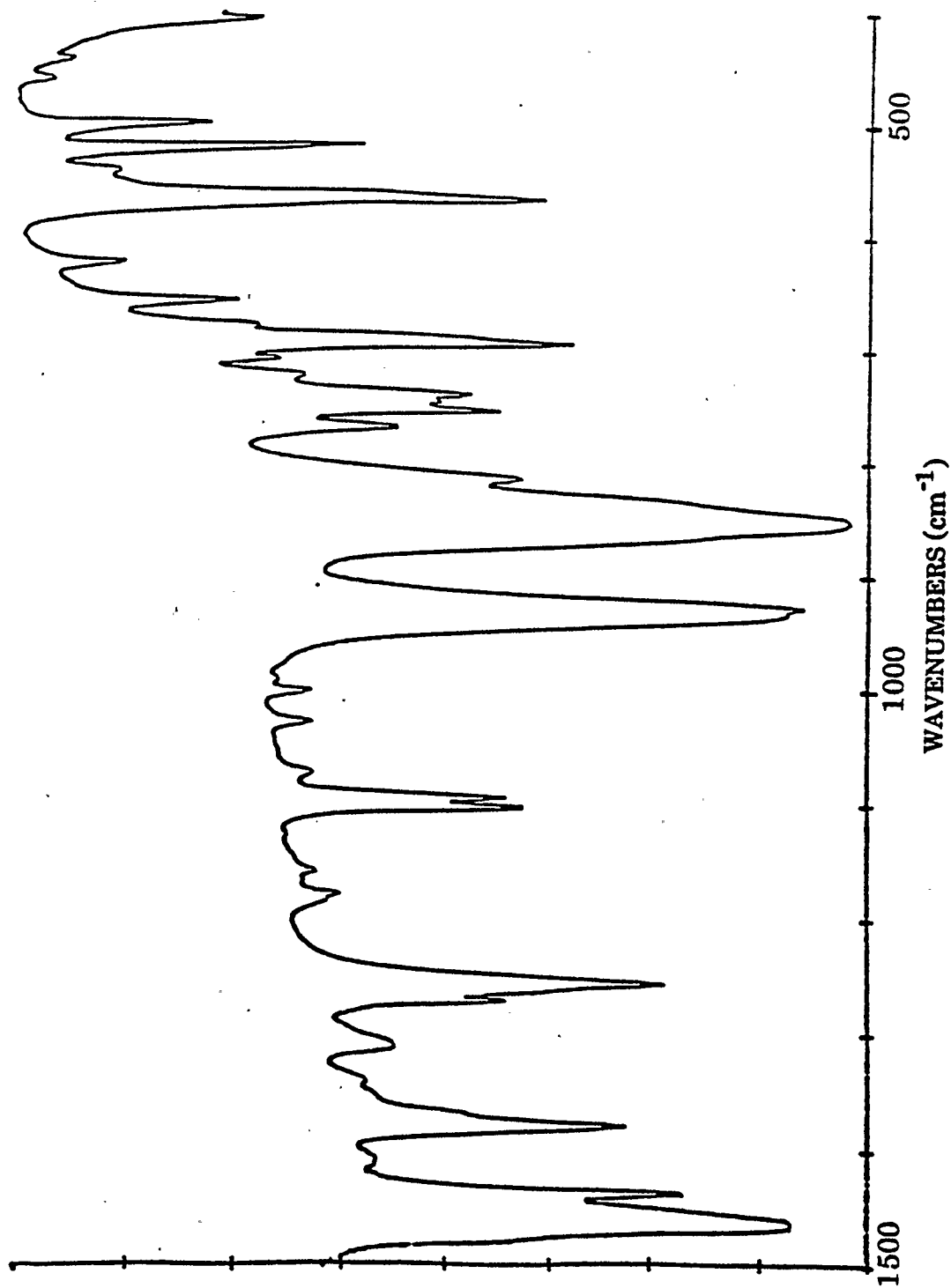


Figure 2.2 Infrared Spectrum of $\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{SiMe}_3)_2$ (as Nujol mull)

chemical shift of the two phosphine chalcogenides is similar to values reported in the literature (cf. Ph_3PS , $\delta^{31}\text{P}=42.6$ ppm and Ph_3PSe , $\delta^{31}\text{P}=35.0$ ppm)^[113]

Comparison of the infrared spectra of $\text{Ph}_2\text{P}(\text{E})\text{N}(\text{SiMe}_3)_2$ (E = S, Se) allows the assignment of the $\nu(\text{P}=\text{S})$ and $\nu(\text{P}=\text{Se})$ bands at 631 and 567 cm^{-1} , respectively. This is consistent with values reported in the literature for a number of tertiary phosphine chalcogenides such as triphenylphosphine sulphide ($\nu(\text{P}=\text{S}) = 627$ cm^{-1}) and triphenylphosphine selenide [$\nu(\text{P}=\text{Se}) = 560$ cm^{-1}].^[114]

2.3 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with NSCl in a 1:1 Molar Ratio

The reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with one equivalent of NSCl at room temperature in chloroform solution results in the production of a number of phosphorus-containing species. A ^{31}P nmr spectrum obtained four days after mixing the two reagents shows several known and unknown species in the reaction mixture (Figure 2.3). The species at 114.1 ppm may be assigned to 1,5-diphosphadithiatetrazocine, $\text{Ph}_4\text{P}_2\text{S}_2\text{N}_4$ (15), on the basis of its chemical shift (cf. literature (^{31}P) $\delta = 113.9$ ppm^[67]) and the resonance at 60.7 is due to the starting material $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$. The minor product at -21.3 ppm is the six-membered ring $\text{Ph}_2\text{PN}_3\text{S}_2$ (14).

There are three resonances that may be resolved at 53.0 , 53.4 , and 54.6 ppm and attempts have been made to separate these products. The species responsible for the singlet at 53.0 ppm may be removed along with 23, because of its solubility in acetonitrile. Recrystallization from $\text{CHCl}_3/\text{CH}_3\text{CN}$

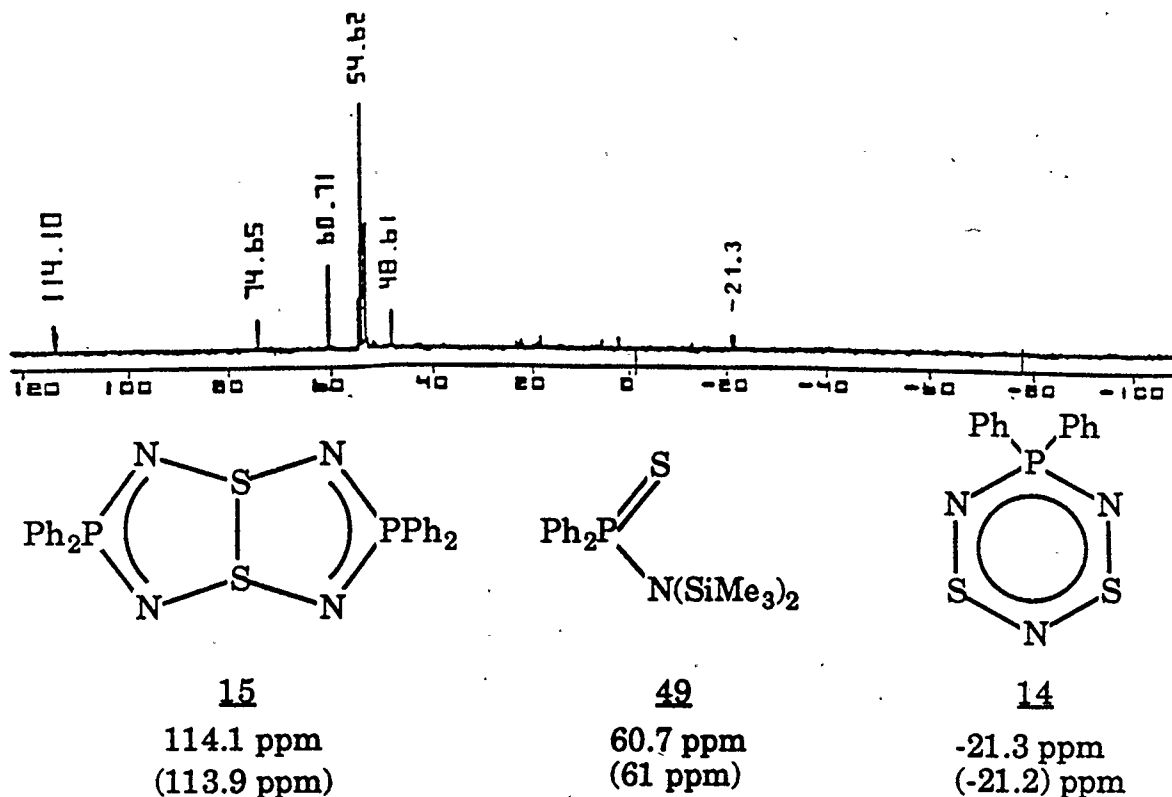


Figure 2.3 ^{31}P nmr spectrum for reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with 1NSCl (literature chemical shifts are indicated in parentheses)

provided a small amount of a bright yellow solid [$\lambda_{\text{max}}(\text{CHCl}_3 \text{ solution}) = 451\text{nm}$] for which consistent analyses for C,H,N,S, and Cl could not be obtained.

Sublimation of the resulting residue at 80°C and 0.2 torr onto a water-cooled cold finger results in the growth of both colourless and purple crystals with ^{31}P nmr chemical shifts of 55.5 and 54.6 ppm, respectively. Pentane extraction of the sublimate, followed by slow cooling does produce a small amount of colourless crystals with a ^{31}P chemical shift of 55.5 ppm. The ^1H nmr spectrum of a CDCl_3 solution of the colourless crystals indicated two

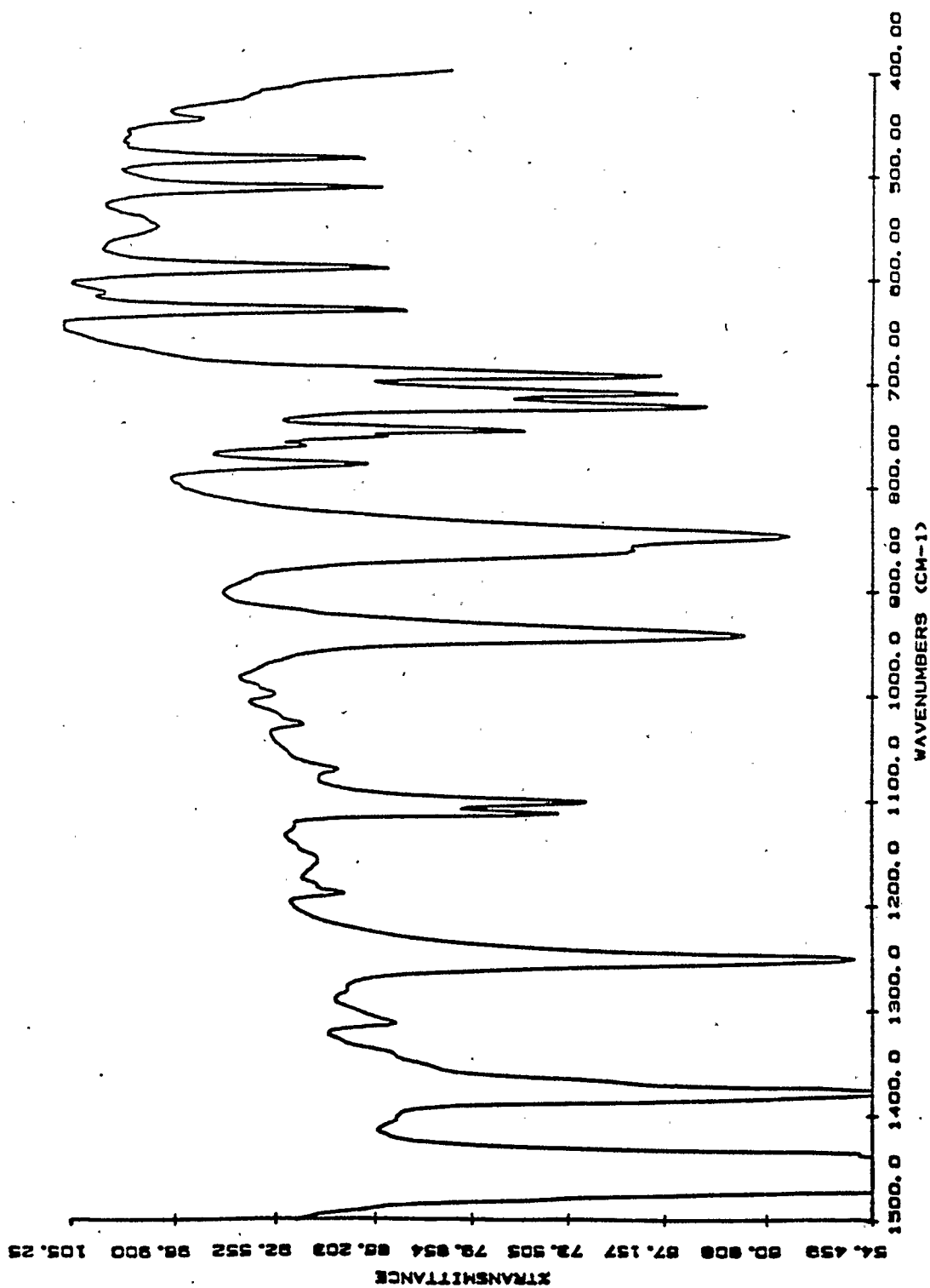


Figure 2.4 Infrared spectrum of colourless crystals obtained from the reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with 1 NSCl (as Nujol mull)

phenyl substituents for each trimethylsilyl group.

The infrared spectrum (Figure 2.4), aside from a weak N-H absorption at 3300 cm^{-1} due to slight hydrolysis, is remarkably similar to that of the starting material $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$. In addition, two strong broad absorbances are found at $1100\text{-}1110$ and $1250\text{-}1260\text{ cm}^{-1}$, which may be assigned to ν_{sym} and ν_{asym} ($\text{N}=\text{S}=\text{N}$), respectively (see section 3.4). In $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ sharp absorbances occur at 1096 and 1104 cm^{-1} for C-H in plane bending and at 1252 and 1265 cm^{-1} for Me_3Si deformations. The broadening of these absorbances in the infrared spectrum of the colourless crystals is due to overlap of these modes with the $\text{N}=\text{S}=\text{N}$ stretching modes. The similarity of the two spectra supports the formation of the acyclic sulphur diimide 50.

The purple material, which is difficult to purify due to contamination by the unsymmetrical sulphur diimide, is suggested to be one of the five-membered rings 53 or 54 (Figure 2.5), which may isomerize by means of a 1,3

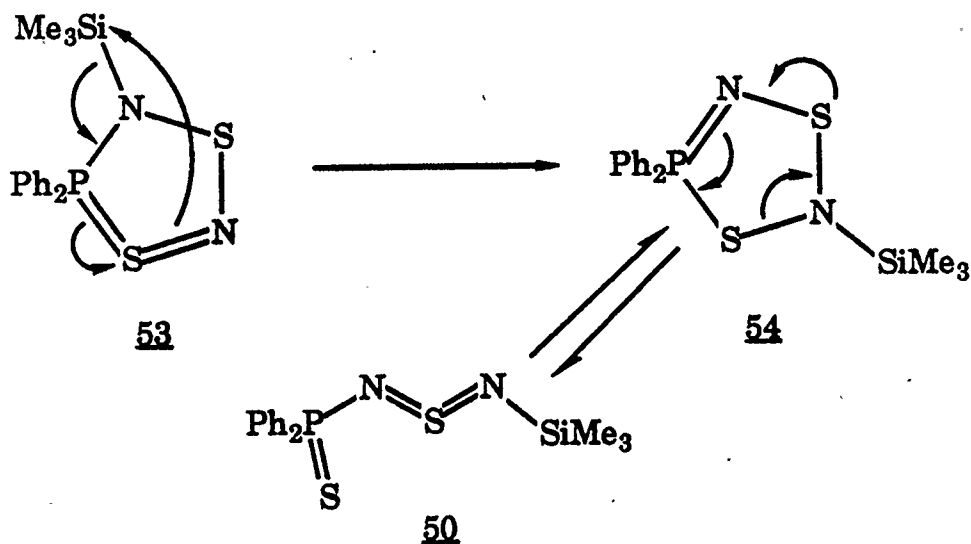
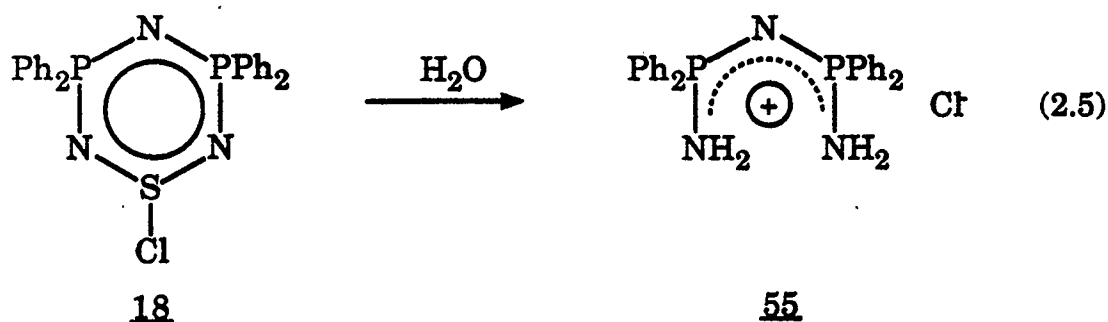


Figure 2.5 Isomerization of $\text{Ph}_2\text{PS}_2\text{N}_2\text{SiMe}_3$

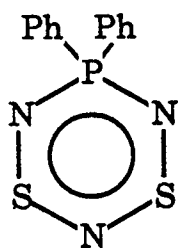
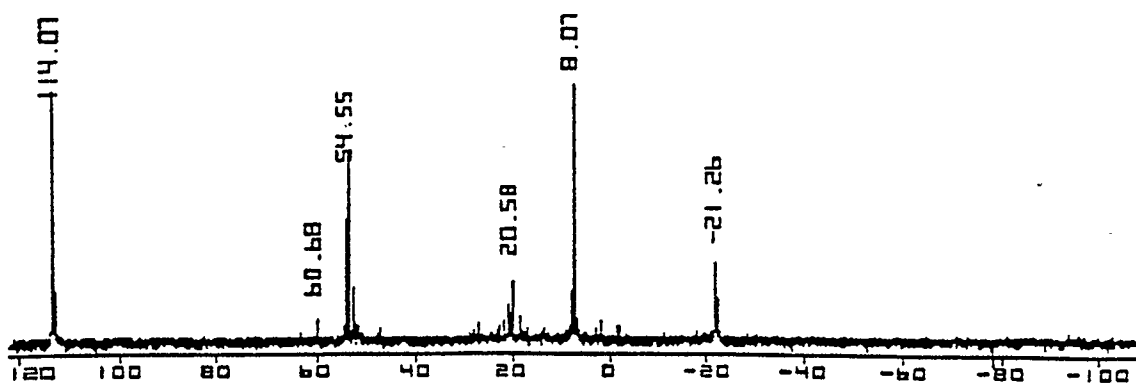
shift of the trimethylsilyl group. There is no evidence to allow a distinction between the two isomers, however **54** is more likely. Upon sublimation, a ring opening of **54** may result in the production of the acyclic sulphur diimide as illustrated in Figure 2.5.

2.4 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ With NSCl in a 1:2 Molar Ratio

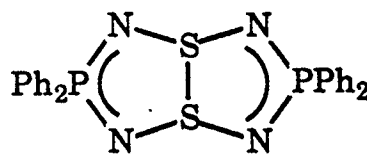
The ^{31}P nmr spectrum of the 2:1 reaction mixture reveals a number of compounds, many of which, not surprisingly, are the same as in the case of the 1:1 reaction, although their relative yields have changed significantly (Figure 2.6). In particular, the yields of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (**15**) and $\text{Ph}_2\text{PN}_3\text{S}_2$ (**14**) are much higher than in the 1:1 reaction. In addition, a new major product, identified as $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$ (**18**) on the basis of its ^{31}P nmr chemical shift, is formed. The weak signal at 20 ppm may be assigned to either 1,3- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (**24**) or more likely, $\text{Ph}_4\text{P}_2\text{N}_3\text{H}_4^+$ (**55**). The presence of $\text{Ph}_4\text{P}_2\text{N}_3\text{H}_4^+$ (**55**) would not be surprising in that it is easily produced from $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$ upon hydrolysis (equation 2.5)^[94].



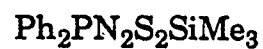
It is noteworthy that most of the major reaction products do not retain the phosphorus-sulphur bond of the starting material (**49**). The 1:2 reaction mixture exhibits a ^{31}P nmr resonance at 54.6 ppm, which was attributed to



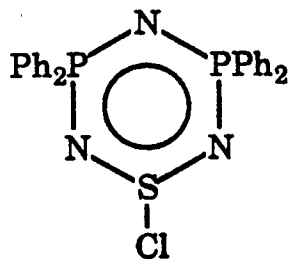
14
-21.2 ppm
(-21.2 ppm)



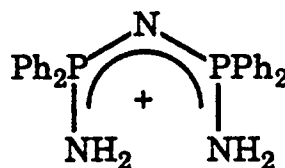
15
114.1 ppm
(113.9 ppm)



53 or 54
54.6 ppm



18
8.1 ppm
(7.8 ppm)



55
20.6 ppm
(20.3 ppm)

Figure 2.6. ^{31}P nmr spectrum for the reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with 2 NSCl (literature chemical shifts are indicated in parentheses)

one of the five-membered rings $\text{Ph}_2\text{PN}_2\text{S}_2\text{SiMe}_3$ (53 or 54) in the 1:1 reaction.

It is suggested, therefore, that 54 reacts with a second mole of NSCl to give a thermally unstable intermediate which decomposes to give the observed products. As indicated in Figure 2.7, this intermediate is tentatively proposed to be the seven-membered ring $\text{Ph}_2\text{PN}_3\text{S}_3$, which decomposes by loss of sulphur to generate $\text{Ph}_2\text{PN}_3\text{S}_2$ (14) or by dimerization and elimination of sulphur and nitrogen to produce 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (15). An explanation for the formation of $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$, with juxtaposed Ph_2PN units, is not evident.

2.5 Reaction of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ With NSCl in a 1:2 Molar Ratio

Since the majority of phosphorus-containing compounds in the $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ / NSCl reactions do not retain the phosphorus-sulphur bond, the reaction of the precursor to the sulphide, $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$, with NSCl in a 1:2 molar ratio was studied.

The reaction of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ with NSCl in chloroform solution is very rapid at room temperature, running to completion within four hours with no further change after 24 hours. The ^{31}P nmr spectrum of the reaction mixture obtained four hours after mixing the reagents reveals a number of similarities to the reaction of NSCl with the P(V) reagent (Figure 2.8). It is of interest to note that the phosphine sulphide, $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ is a minor product in the reaction due to oxidative addition of sulphur to $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$. The major products in the reaction are the eight-membered ring, 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$, the six-membered rings $\text{Ph}_2\text{PN}_3\text{S}_2$, and, in smaller amounts, $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$, and one of the five-membered rings (53 or 54), which is presumably formed by the reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with NSCl.

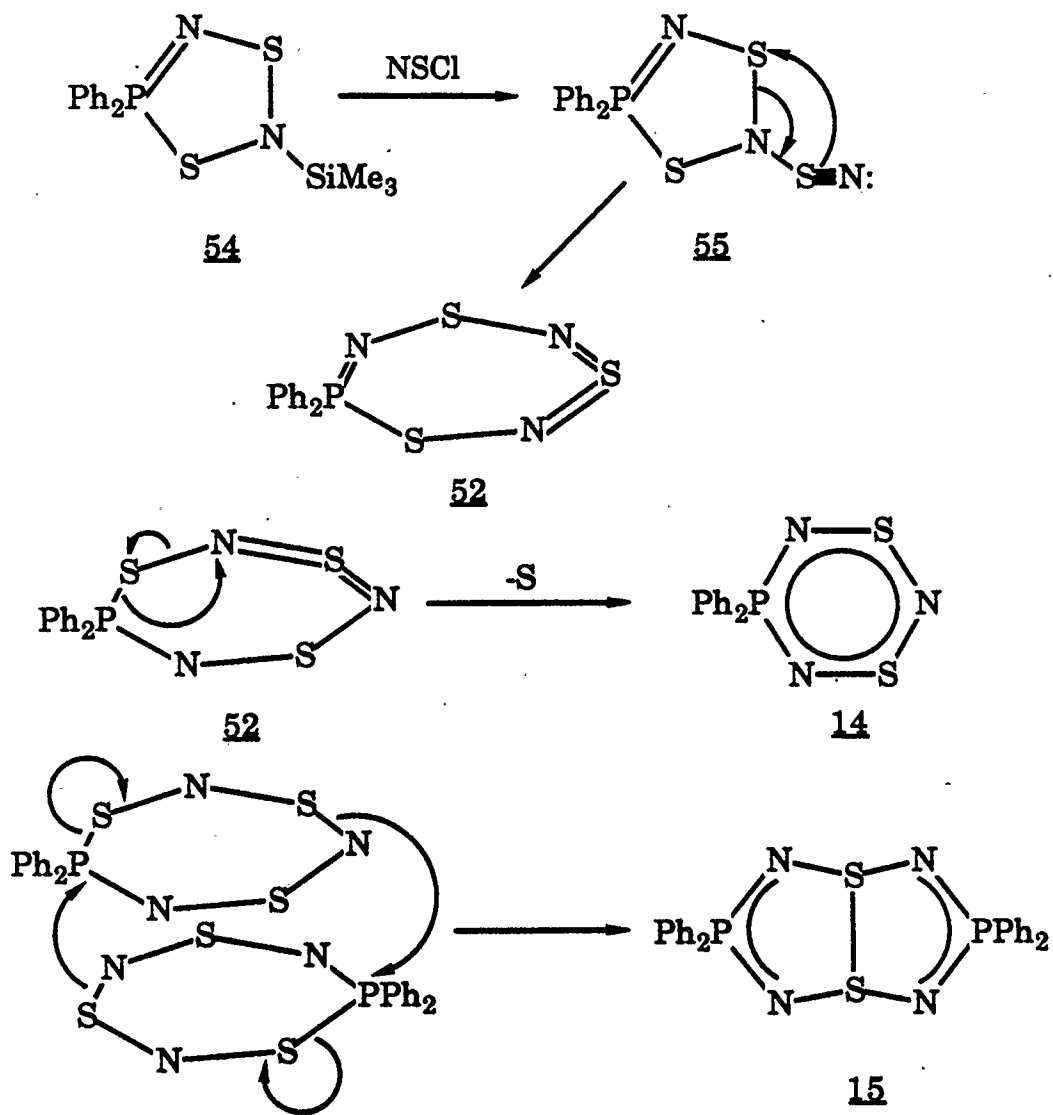
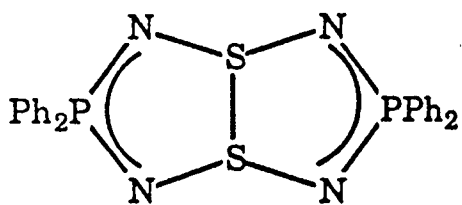
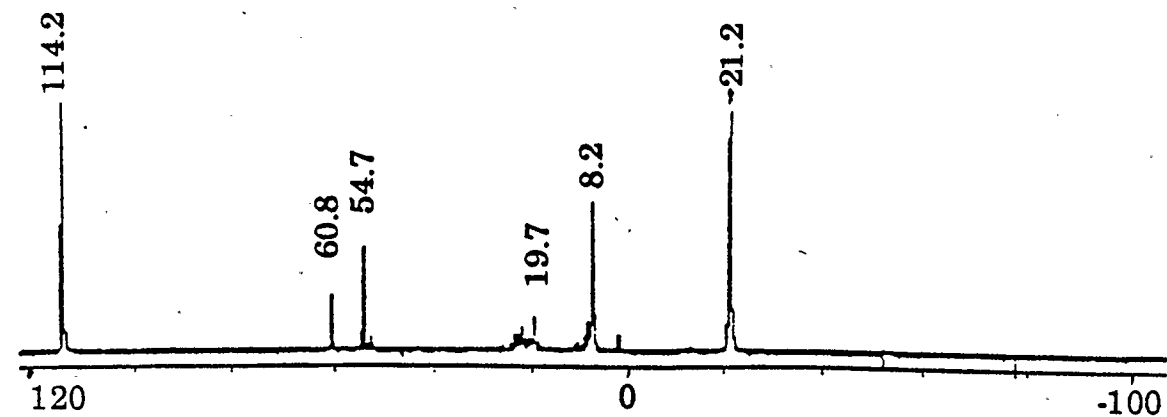
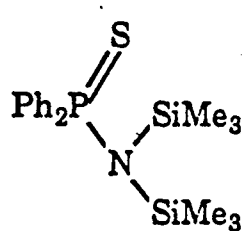


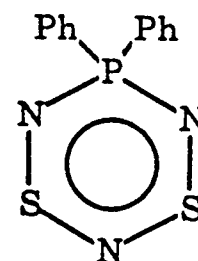
Figure 2.7 Proposed pathway for the formation of $\text{Ph}_2\text{PN}_3\text{S}_3$, $\text{Ph}_2\text{PN}_3\text{S}_2$, and $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ produced in the reactions of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with NSCl



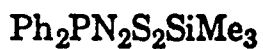
15

114.2 ppm
(113.9 ppm)

49

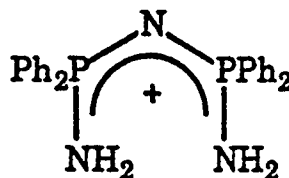
60.8 ppm
(61 ppm)

14

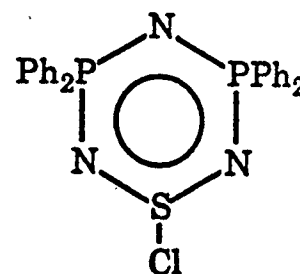
-21.2 ppm
(-21.2 ppm)

53 or 54

54.6 ppm



55

8.2 ppm
(8.1 ppm)

18

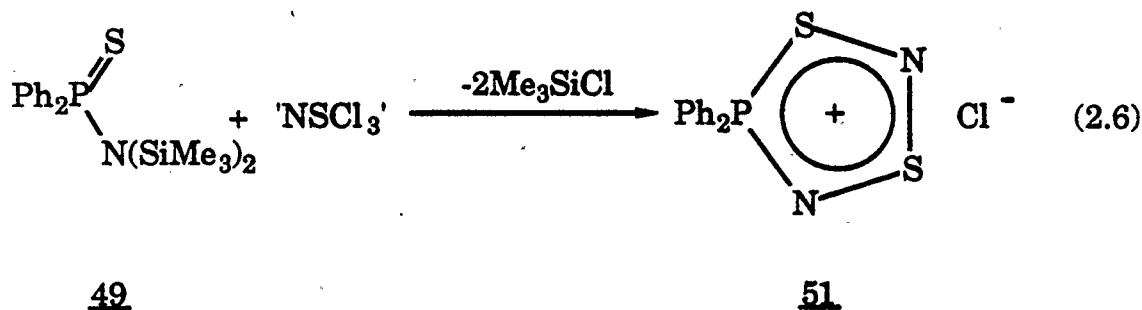
19.7 ppm
(20.3 ppm)

Figure 2.8. ^{31}P nmr spectrum for the reaction of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ with 2 NSCl (Literature chemical shifts are in parentheses.)

This reaction provides an alternative to known methods for the preparation of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (15) and $\text{Ph}_2\text{PN}_3\text{S}_2$ (14) (see section 1.4.1), but the recent procedures described for the synthesis of these individual rings yield more easily purifiable products (see section 1.4.1).

2.6 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ With 'N SCl_3 '

As discussed in section 1.6, a solution of $(\text{NSCl})_3$ in the presence of a large excess of sulphuryl chloride behaves as if the reagent 'N SCl_3 ' is present^[95]. The reaction of such a solution with $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ was expected to generate the phosphadithiadiazolium cation $\text{Ph}_2\text{PN}_2\text{S}_2^+$ (Equation 2.6).



The reaction, however, was complex and the major products appear to result from the reaction SO_2Cl_2 with $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ as they were also obtained in the absence of $(\text{NSCl})_3$ (Figure 2.9). These species were not isolated and no attempt was made to characterize them.

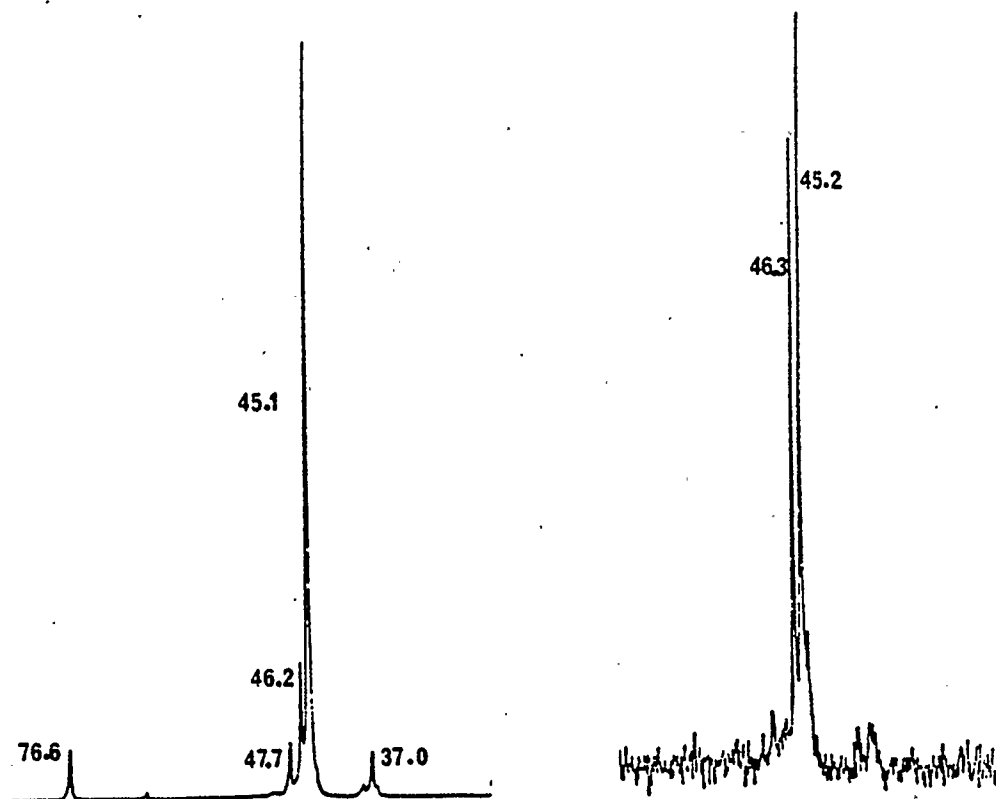


Figure 2.9 ^{31}P nmr spectra for the reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with SO_2Cl_2 : a) with NSCl , b) without NSCl

2.7 Conclusions

With the synthesis of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ and $\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{SiMe}_3)_2$, new synthetic reagents for the preparation of heterocyclophosphathiazenes or their selenium analogues have been obtained.

The reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with thiazyl chloride in a 1:1 molar ratio has proven to be more complex than anticipated. Small amounts of the expected product $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ as well as the known cyclophosphathiazenes 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ and $\text{Ph}_2\text{PN}_3\text{S}_2$ are produced along with the major product, a purple species, tentatively identified as one of two isomers of a five-membered ring $\text{Ph}_2\text{PN}_2\text{S}_2\text{SiMe}_3$.

The reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with two equivalents of thiazyl chloride results in the production of significant amounts of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$, $\text{Ph}_2\text{PN}_3\text{S}_2$, and $\text{Ph}_4\text{P}_2\text{N}_3\text{S}\text{Cl}$ as well as the purple compound obtained in the 1:1 reaction. The intermediate formation and subsequent decomposition of the seven-membered ring $\text{Ph}_2\text{PN}_3\text{S}_3$ (from $\text{Ph}_2\text{PN}_2\text{S}_2\text{SiMe}_3$ and NSCl) is proposed to account for the formation of $\text{Ph}_2\text{PN}_3\text{S}_2$ and 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$, which do not retain the P-S bond of the starting material.

The reaction of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ with thiazyl chloride has been shown to be an alternative route for the preparation of the known cyclophosphathiazenes 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ and $\text{Ph}_2\text{PN}_3\text{S}_2$ and may prove to be a useful means of preparing derivatives which have substituents other than Ph on the phosphorus centre. The specific procedures described in 1.4.1, however, are likely to be preferable for the synthesis of individual PNS ring systems.

2.8 Experimental

2.8.1 General

All distillations and reactions were carried out under an atmosphere of nitrogen gas, dried by passing through phosphorus pentoxide or Sicapent (E. Merck Darmstadt), a commercial drying agent containing phosphorus pentoxide with a moisture indicator.

Manipulation of all solid products, as well as air/moisture-sensitive solid reagents was carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Corporation glove box fitted with a dry train. Transferral of liquids and solutions was carried out by means of syringes or transfer needles.

2.8.2 Instrumentation

Infrared spectra were obtained as Nujol mulls or thin films on potassium bromide plates using a Nicolet 5DX Fourier transform spectrometer. A Bruker ACE-200 spectrometer was used to collect ^1H nmr spectra. ^{31}P nmr spectra were collected either on a Bruker AM-400 operating at 162 MHz or on a Varian XL-200 operating at 81 MHz. Samples were locked by using sealed D_2O inserts and were referenced to external 85% H_3PO_4 . UV-Vis spectra were obtained by using a Cary 219 spectrophotometer and cuvettes sealed with rubber septa.

2.8.3 Solvents

The solvents used for reactions and recrystallizations were of reagent grade and were dried prior to use. Diethyl ether (Na and benzophenone), chloroform (phosphorus pentoxide), toluene (Na and benzophenone), hexanes

Hexamethyldisilazane (60.45 g, 374 mmol) was dissolved in 200ml of hexanes in a 1000 ml three neck round bottom flask equipped with a nitrogen inlet, a dropping funnel and a rubber septum. The dropping funnel was charged with a 2.5M solution of n-BuLi (150 ml, 375 mmol) which was added over 2 hrs at room to the stirring solution of $(\text{Me}_3\text{Si})_2\text{NH}$ at 0°C . After stirring overnight at room temperature the reaction mixture was again cooled to 0°C and the dropping funnel charged with Ph_2PCl (83.01 g, 376 mmol) which was added with stirring to the $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ solution over the course of one hour. After warming to room temperature a ^{31}P nmr spectrum of the reaction mixture showed the product at 50.2 ppm with a minor product at -5 ppm. Stirring was discontinued and the resulting LiCl was allowed to settle. The supernatant solution was decanted to another 1000ml flask and the precipitate washed with hexanes (3 x 100 ml), with the washings added to the supernatant solution. The solvent was removed in vacuo leaving an orange solid which was distilled to give 72 g of a white solid (bp $148\text{-}152^\circ\text{C}$ at 0.4- 0.5 torr) (yield 56%).

A procedure very similar to that reported by Roesky and coworkers^[118] during the course of this research was used for the preparation of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$. A suspension of elemental sulphur (1.99 g, 7.75 mmol S_8) in toluene (75 ml) was added under nitrogen via transfer needle to a stirring solution of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ (21.50 g, 62.2 mmol) in 75 ml of toluene over a period of 1.5 hours. After stirring overnight at room temperature a ^{31}P nmr spectrum of the pale yellow reaction mixture showed only a singlet at 60.6 ppm. The solution was concentrated to 100 ml and approximately 25 ml of pentane was added before cooling overnight at 10°C . Decanting the supernatant solution through a filter needle allowed the isolation of 12.20 g of long, needle-like crystals. Concentration of the supernatant solution, followed by further cooling allowed the isolation of another 5.68 g of product (total 17.88 g, 76% yield) . Analytical data are presented in Table 2.2.

The phosphine selenide was prepared in a similar manner to its sulphur analogue. Gray selenium (1.11 g, 14.06 mmol) was added as a single aliquot to a stirred solution of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ (4.85 g, 14.05 mmol) in toluene (70 ml) under nitrogen. After stirring vigorously for two days to maintain a suspension of selenium, a ^{31}P nmr spectrum showed only a singlet at 55.8 ppm. At this point a small amount of unreacted selenium remained which was removed by first concentrating the solution to 50 ml and then filtering it through a fine filter needle. Cooling of the solution to 10°C allowed isolation of 4.11 g (9.68 mmol, 69 % yield based on Ph_2PCl) of $\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{SiMe}_3)_2$ as cubic crystals. Analytical data for the selenide are presented in Table 2.2.

Table 2.2. Analytical Data for $\text{Ph}_2\text{P}(\text{E})\text{N}(\text{SiMe}_3)_2$

	<u>E=S</u>		<u>E=Se</u>	
	Calculated	Found	Calculated	Found
C	57.25%	57.25%	50.93	51.16
H	7.47%	7.24%	5.78	6.65
N	3.71%	3.71%	3.82	3.30

2.8.6 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ With NSCl in a 1:1 Molar Ratio

The reaction between $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ and NSCl in a 1:1 molar ratio may be carried out by one of two procedures, both of which result in a similar distribution of products. In a typical reaction a dropping funnel was charged with a solution of $(\text{NSCl})_3$ [0.89 g, 3.64 mmol] in 30 ml of CHCl_3 , which was

added to a stirred solution of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ [4.14 g, 10.96 mmol] in 70 ml of CHCl_3 in a 250 ml three neck round bottom flask over a period of three to four hours at room temperature resulting in the production of a wine-red-coloured solution. The reaction flask may be fitted with a reflux condenser and heated to 60°C for 36 hours or maintained at room temperature for a period of five to six days.

The solvent was then removed in vacuo with no external heating leaving a dark red tarry residue, which was extracted repeatedly with acetonitrile to remove $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ ($\delta^{31}\text{P} = 114.1$ ppm) and an unidentified yellow product. The residue was then sublimed onto a water-cooled cold finger resulting in the formation of purple ($\delta^{31}\text{P} = 54.6$ ppm) and colourless crystals ($\delta^{31}\text{P} = 55.5$ ppm). Pentane extraction of the sublimate followed by cooling resulted in the formation of a very small amount of colourless crystals. Attempts at separating the two species from the supernatant solution were unsuccessful.

Attempts at separating the products in the crude reaction mixture via gel permeation chromatography on a Biobeads S-X8 column resulted in a colour change from wine-red to yellow, likely due to hydrolysis of the products on the column.

2.8.7 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ With NSCl in a 1:2 Molar Ratio

A greenish-yellow solution of $(\text{NSCl})_3$ [1.12 g, 4.58 mmol] in 50 ml of CHCl_3 was added from a dropping funnel over the course of 1.5 hours at 20°C to a stirred solution of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ [2.57 g, 6.80 mmol] in 100 ml of chloroform in a 250 ml round bottom flask. The reaction mixture proceeded through a number of colours over the course of the addition: bronze, orange,

red, and eventually a persistent wine-red-coloured solution. The reaction was monitored by ^{31}P nmr spectroscopy which showed that the starting material had been consumed within two hours of completing the addition. Solvent was removed in vacuo and 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ and $\text{Ph}_4\text{P}_2\text{N}_3\text{H}_4^+$ were removed by washing the residue with acetonitrile and identified by their characteristic ^{31}P nmr^[67] and infrared data^[119], respectively. Cooling of the acetonitrile extract resulted in the precipitation of crude $\text{Ph}_4\text{P}_2\text{N}_3\text{H}_4^+$. Attempts at separating the other components were unsuccessful.

2.8.8 Reaction of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ With NSCl in a 1:2 Molar Ratio

In a typical reaction, a solution of $(\text{NSCl})_3$ [1.12 g, 4.58 mmol] in 100 ml of CHCl_3 was added to a rapidly stirring solution of $\text{Ph}_2\text{PN}(\text{SiMe}_3)_2$ [2.57 g, 6.8 mmol] in 100 ml CHCl_3 over a period of 3.5 hours at room temperature giving rise to a deep purple-coloured solution. A ^{31}P nmr spectrum showed significant amounts of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (114.1 ppm), $\text{Ph}_2\text{PN}_3\text{S}_2$ (-21.2 ppm), $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$ (8.1 ppm), and its hydrolysis product $\text{Ph}_4\text{P}_2\text{N}_3\text{H}_4^+$ (20.6 ppm). Removal of the solvent in vacuo followed by acetonitrile extraction allows removal of a mixture of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ and $\text{Ph}_4\text{P}_2\text{N}_3\text{H}_4^+$. Pentane extraction of the residue allows removal of $\text{Ph}_2\text{PN}_3\text{S}_2$ and small amounts of the other products, which could not be separated from one another.

2.8.9 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ With NSCl
in the presence of SO_2Cl_2

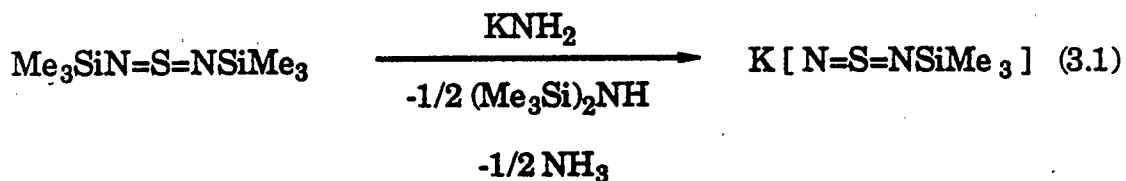
In a typical reaction, a solution of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ (3.82 g, 10.1 mmol) in chloroform was added over 1.5 hours to a mixture of $(\text{NSCl})_3$ (0.83 g, 3.4 mmol) and SO_2Cl_2 in chloroform at 0°C , resulting in a slight darkening of the yellow solution. It was noticed that the $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ solution was reacting with the vapours of SO_2Cl_2 before coming into contact with the $(\text{NSCl})_3$ solution. For this reason and the large number of products, there was no attempt made to separate the components of the reaction mixture.

Chapter 3

The Synthesis of Unsymmetrical Sulphur Diimides: Potential Synthons for Cyclophosphathiazenes

3.1 Background

Bis(trimethylsilyl)sulphurdiimide, $\text{Me}_3\text{SiNSNSiMe}_3$ (54), was first prepared and characterized in 1962^[120] and almost immediately its synthetic utility was realized. It has proven invaluable as a means of incorporating an NSN unit into a variety of open chain and cyclic species. The reaction of bis(trimethylsilyl)sulphurdiimide with potassium tertiary butoxide and potassium amide, respectively, gives the salts $\text{K}_2\text{N}_2\text{S}$ (54)^[121] and KNSNSiMe_3 (55)^[122] (Equation 3.1), which have been found useful in the



synthesis of a number of species including unsymmetrical sulphur diimides of the type RNSNSiMe_3 (56)^[122]. The tin analogue $\text{Me}_3\text{SnNSNSnMe}_3$ (57) was first reported in 1973 as an intermediate in the reaction of S_4N_4 with tris(trimethylstannyl)amine leading to the five-membered ring $\text{Me}_2\text{SnN}_2\text{S}_2$ (58)^[123] (Equations 3.2 and 3.3). It may also be prepared from the reaction of $\text{Me}_3\text{SnNMe}_2$ with S_4N_4 ^[124].



In 1982 Brands and Golloch reported its synthesis from tris(trimethylstannyl)amine and $(\text{NSCl})_3$ (Equation 3.4) [111], which was an improvement as it avoided the use of explosive S_4N_4 .



This section will provide a brief overview of the use of these sulphur diimide reagents in the synthesis of sulphur-nitrogen heterocycles. Information regarding their application in the preparation of linear and polymeric compounds may be found elsewhere. [69]

The reactions of bis(trimethylsilyl)sulphur diimide with a number of halogenated species proceeds as expected with elimination of chlorotrimethylsilane and addition of a NSN bridge as illustrated in Figure 3.1.

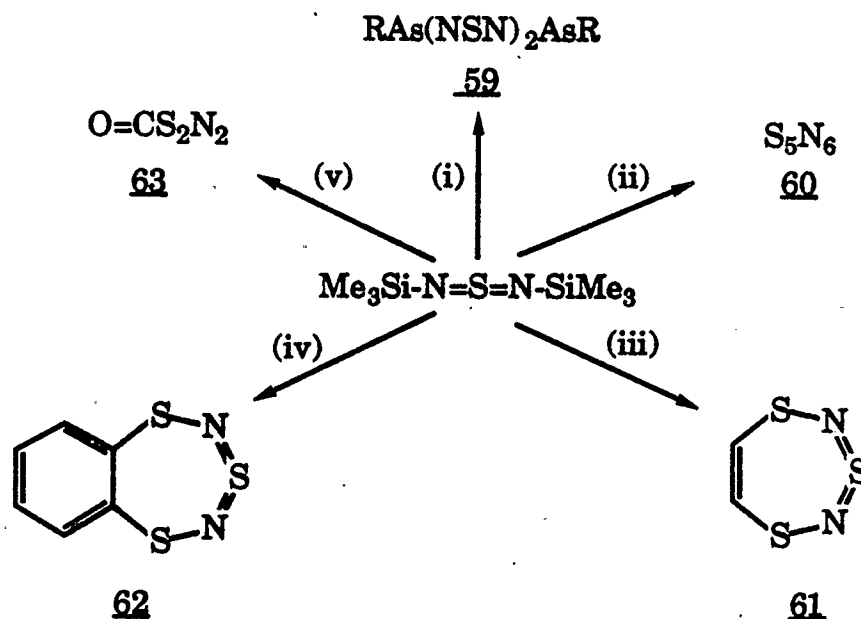
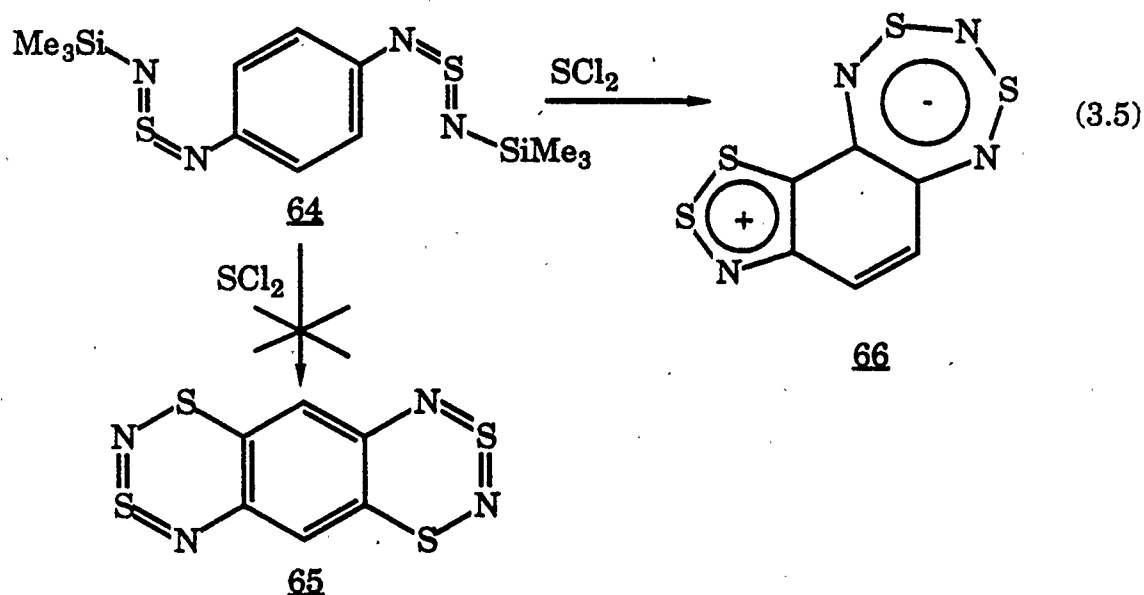


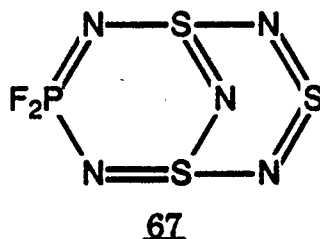
Figure 3.1 $\text{Me}_3\text{SiNSNSiMe}_3$ as a synthetic reagent for SN heterocycles:

- (i) RAsCl_2 , (ii) $1,5\text{-Cl}_2\text{S}_4\text{N}_4$, (iii) chloro-bis(chloromercapto)ethane,
(iv) bis(chloromercapto)benzene, and (v) $\text{O}=\text{C}(\text{Cl})\text{SCl}$

In several cases, however, the predicted reactions do not occur. In an attempt to prepare the tricyclic species **65** from **64** the azulene-like molecule **66** resulted^[125].

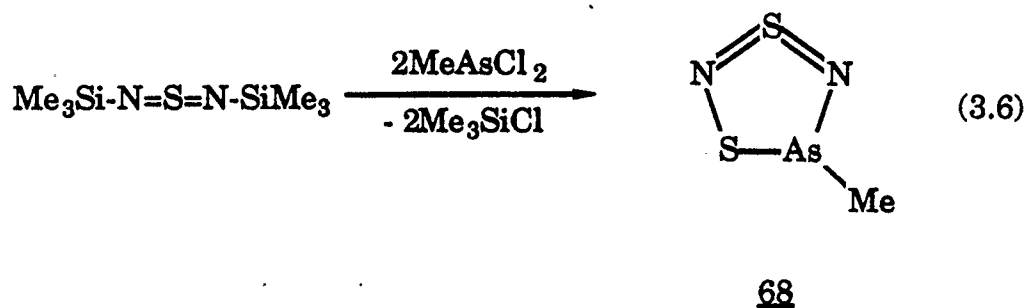


The reactions of PCl_5 and PF_5 with $\text{Me}_3\text{SiNSNSiMe}_3$ also illustrate a departure from anticipated reactions. In the former case the six-membered ring $\text{Cl}_5\text{P}_2\text{N}_3\text{S}$ [(18), $\text{R}=\text{Cl}$, $\text{X}=\text{Cl}$] is the product^[128]. In the reaction with PF_5 , however, the bicyclic species **67** is formed^[127].



The reaction of CH_3AsCl_2 with $\text{Me}_3\text{SiNSNSiMe}_3$ in a 1:1 molar ratio provides, not surprisingly, the eight-membered ring **59** (Figure 3.1)^[128]. The *t*-Bu derivative may be prepared by the reaction of the K_2SN_2 with *t*-

BuAsCl_2 ^[129]. The reaction of CH_3AsCl_2 with $\text{Me}_3\text{SiNSNSiMe}_3$ in a 2:1 molar ratio, however, results in the production of the five-membered ring **68** in low yield (Equation 3.6)^[130].



3.2 Objective

It was anticipated that the preparation of unsymmetrical sulphur diimides **50** would allow the use of the SPNSN unit as a building block for five- and seven-membered rings when cyclized with sulphuryl chloride or NSCl , respectively (Figure 3.2).

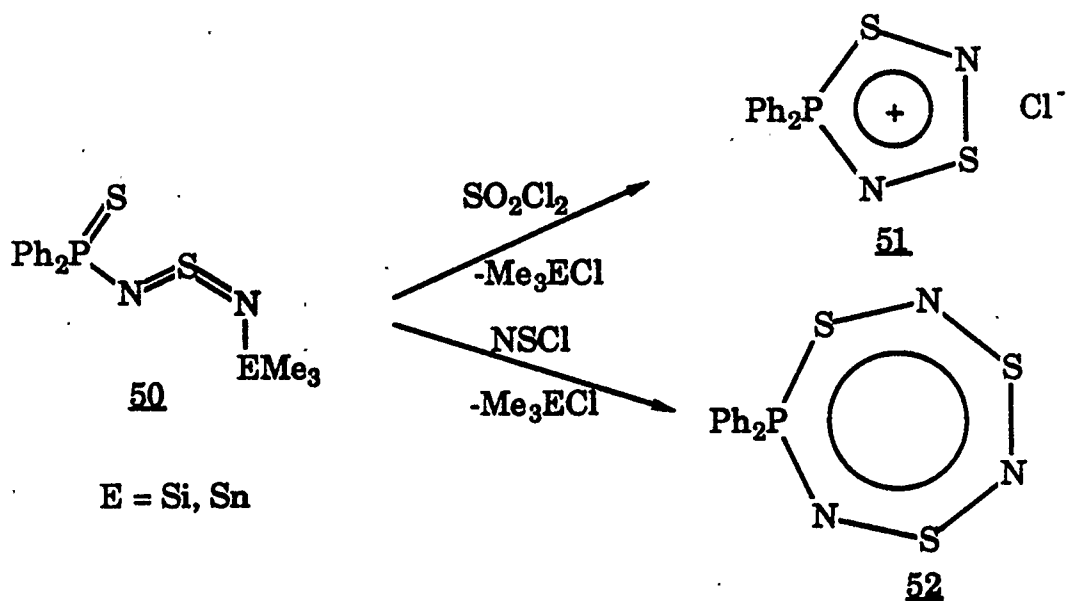
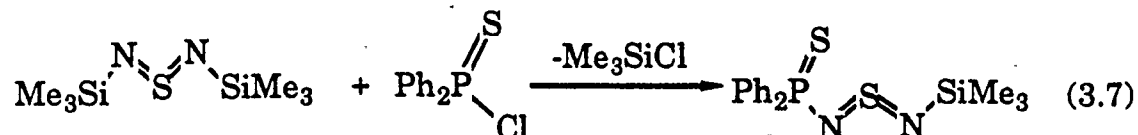


Figure 3.2 Desired cyclization reactions of unsymmetrical sulphur diimides

This chapter discusses approaches used for the synthesis of these sulphur diimides and preliminary results of their reactions with sulphuryl chloride and thiazyl chloride.

3.3 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ with $\text{Me}_3\text{SiNSNSiMe}_3$

The desired reaction involving the substitution of one trimethylsilyl group by $\text{Ph}_2\text{P}(\text{S})$ - (Equation 3.7) did not occur to any great extent. Indeed,



54

49

after three days at reflux in carbon tetrachloride, only 10% of the chlorodiphenylphosphine sulphide had been consumed as shown by ^{31}P nmr spectroscopy (Figure 3.3). After four days it was interesting to observe that a small amount of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ had been produced. Even if the reaction is carried out at 90°C in toluene solution, there is no significant consumption of chlorodiphenylphosphine sulphide.

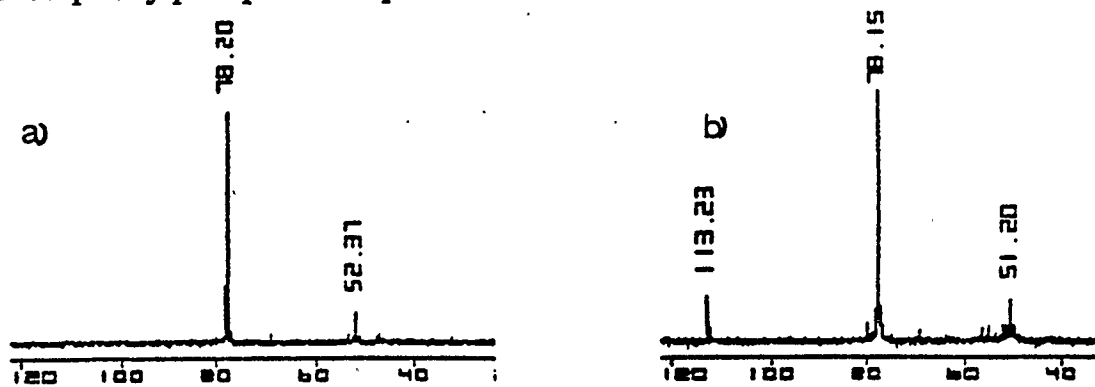
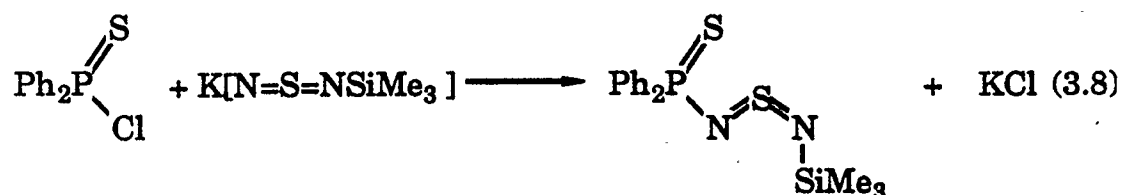


Figure 3.3 ^{31}P nmr spectra of the reaction mixture of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ +

$\text{Me}_3\text{SiNSNSiMe}_3$: a) At 3 days b) At 4 days

3.4 Reaction of K[NSNSiMe₃] With Ph₂P(S)Cl

Due to the slow rate of reaction between Me₃SiNSNSiMe₃ and chlorodiphenylphosphine sulphide, the potassium salt K[NSNSiMe₃] was used to prepare the unsymmetrical sulphur diimide Ph₂P(S)NSNSiMe₃ (Equation 3.8). The addition of a pale yellow solution of Ph₂P(S)Cl to the



bright yellow solution of K[NSNSiMe₃], both in THF, resulted in an immediate colour change to bright red, which became an orange colour within a few minutes.

A ³¹P nmr spectrum obtained immediately after the addition showed that 75% of Ph₂P(S)Cl had been consumed to generate a species with a chemical shift of 52.2 ppm (Figure 3.4). The chemical shift difference (ca. 3.3 ppm) between this product and the compound identified as Ph₂P(S)NSNSiMe₃ in Section 2.3 may be attributed to solvent effects of THF and CHCl₃, respectively. After stirring overnight, a weak signal at 53.7 ppm was also observed, which may be assigned to the symmetrical sulphur diimide Ph₂P(S)NSNP(S)Ph₂ (see section 3.5). The addition of pentane and subsequent cooling of the reaction mixture resulted in a pale yellow oily precipitate, a ¹H nmr spectrum of which showed four signals in the region between 0 and 0.5 ppm in addition to the phenyl protons. As well, a broad peak at 2.9 ppm attributable to N-H is present indicating that some hydrolysis of

the unsymmetrical sulphur diimide to generate $\text{Ph}_2\text{P}(\text{S})\text{NSNH}$ had occurred.

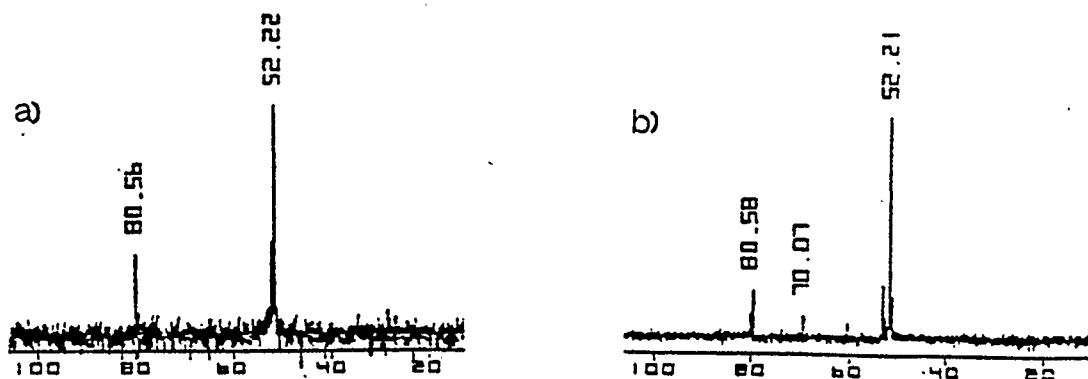


Figure 3.4. ^{31}P nmr spectra of the reaction mixture of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ + $\text{K}[\text{NSNSiMe}_3]$: a) immediately after addition
b) after 24 hours

The infrared spectrum (figure 3.5) of the precipitate supports the assignment of the signal at 2.9 ppm in the ^1H nmr spectrum as there is a broad absorbance at 3300 cm^{-1} , indicative of N-H stretching. As well, two strong broad peaks are found at 1107 and 1250 cm^{-1} , which may be assigned to ν_{asym} and ν_{sym} (N=S=N), respectively, by comparison with the IR spectra of other sulphur diimides (Table 3.2). The reason for the broadness of these bands is due to nearby absorptions from C-H in-plane bending and Me_3Si -stretching vibrations, respectively. The absorption due to the P=S stretching vibration has shifted from 660 cm^{-1} in $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ to 632 cm^{-1} in the unsymmetrical sulphur diimide $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ (**50**) (E = Si).

Repeated attempts at the preparation and isolation of pure **50** (E = Si) were unsuccessful. Some hydrolysis of the desired product was always observed.

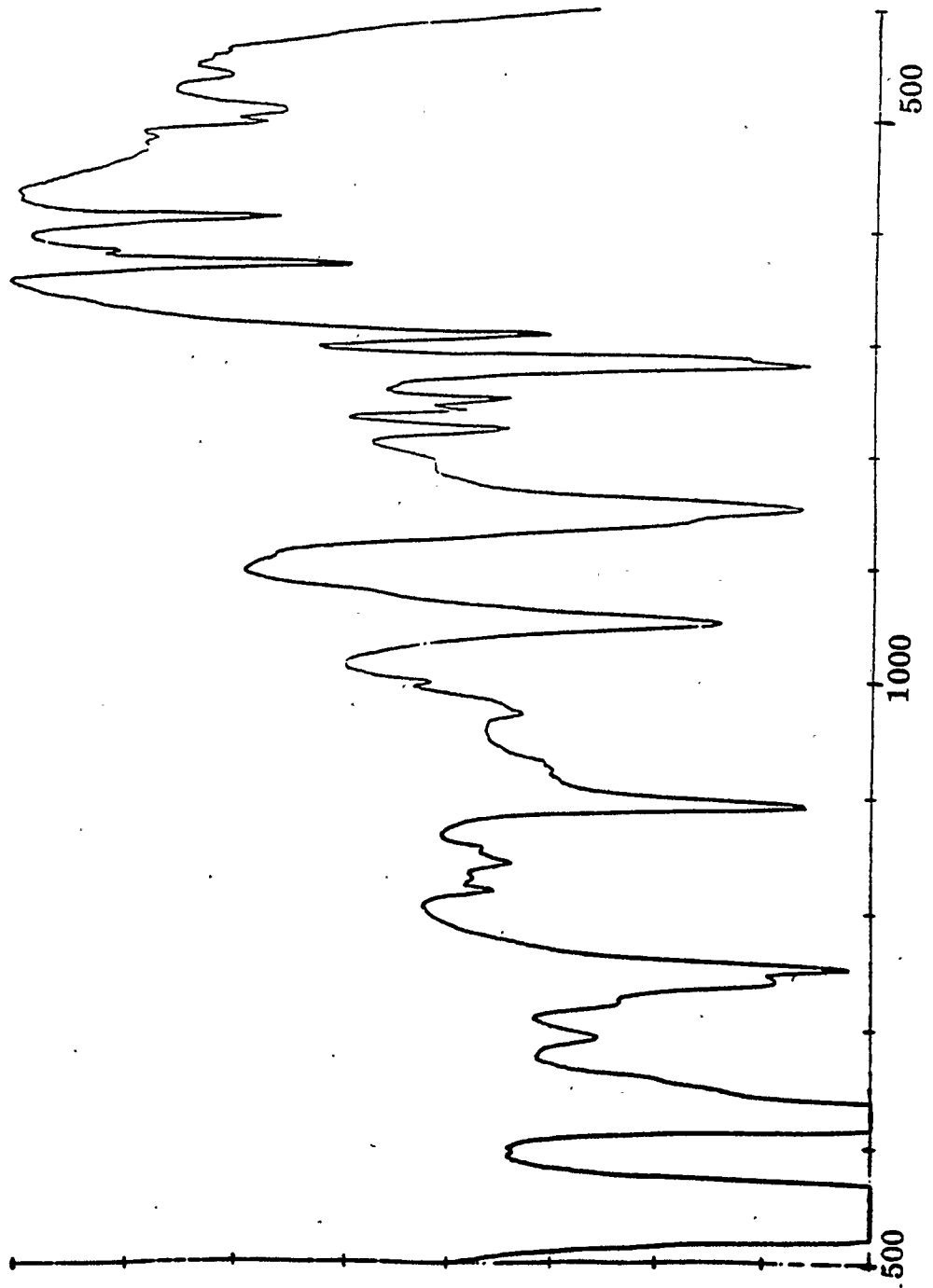


Figure 3.5 Infrared spectrum of impure $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$

3.5 Preparation of $\text{Ph}_2\text{P(S)NSNSnMe}_3$

In view of the difficulties encountered in the purification of the silicon derivative, the reaction of $\text{Ph}_2\text{P(S)Cl}$ with $\text{Me}_3\text{SnNSNSnMe}_3$ was investigated as a means of preparing the unsymmetrical sulphur diimide 50 ($\text{E} = \text{Sn}$).

Unlike the reaction with bis(trimethylsilyl)sulphurdiimide, the addition of a solution of chlorodiphenylphosphine sulphide to the tin derivative in tetrahydrofuran at 20°C resulted in only a slight darkening of the yellow colour upon mixing of the two reagents. Concentration of the reaction mixture and addition of pentane allowed the growth of bright yellow cubic crystals overnight in the refrigerator. Infrared and nmr data (^{31}P and ^1H) are presented in Figure 3.6 and Table 3.1, respectively.

The infrared spectrum shows a strong band at 630 cm^{-1} , which may be assigned to the $\text{P}=\text{S}$ stretching vibration, as well as bands at 1179 and 1060 cm^{-1} due to ν_{asym} and ν_{sym} ($\text{N}=\text{S}=\text{N}$), respectively.

The reaction of two molar equivalents of $\text{Ph}_2\text{P(S)Cl}$ with one mole of $\text{Me}_3\text{SnNSNSnMe}_3$ results in the production of two species according to ^{31}P nmr spectroscopy. The first is $\text{Ph}_2\text{P(S)NSNSnMe}_3$ at 45.1 ppm and the second at 53.7 ppm may be assigned to the symmetrical sulphur diimide $\text{Ph}_2\text{P(S)NSNP(S)Ph}_2$ because of the stoichiometry of the reaction and the fact that it is observed as a minor product in the reaction of $\text{Ph}_2\text{P(S)Cl}$ with $\text{K[NSNSiMe}_3]$ (Section 3.4). The pale yellow colour of both $\text{Ph}_2\text{P(S)NSNSnMe}_3$ and $\text{Ph}_2\text{P(S)NSNP(S)Ph}_2$ contrasts with that of other phosphorus-containing sulphurdiimides such as $[(\text{Bu}^t)_2\text{P(S)N}]_2\text{S}$ and $[(\text{Bu}^t)_2\text{P(Se)N}]_2\text{S}$, which are red compounds^[131].

 Table 3.1 Nuclear Magnetic Resonance Data for $\text{Ph}_2\text{P}(\text{S})\text{NSNSnMe}_3$

^1H nmr spectrum (in CDCl_3 solution):

Chemical Shift (ref CHCl_3 7.27 ppm)	Integration	$^2\text{J}^a$ ($^{117}\text{Sn}-^1\text{H}$) ($^{119}\text{Sn}-^1\text{H}$)		Assignment
multiplet 7.85	4	n/a	n/a	Ph
multiplet 7.43	6	n/a	n/a	Ph
singlet 0.61 (with satellites)	10	56.5Hz	58.8 Hz	$\text{Me}_3\text{Sn}-$

^a(cf. $\text{Me}_3\text{SnNSNSnMe}_3$ $^2\text{J}_{\text{Sn-H}} = 57\text{Hz}^{[132]}$)

^{31}P nmr spectrum (in tetrahydrofuran): singlet 45.0 ppm

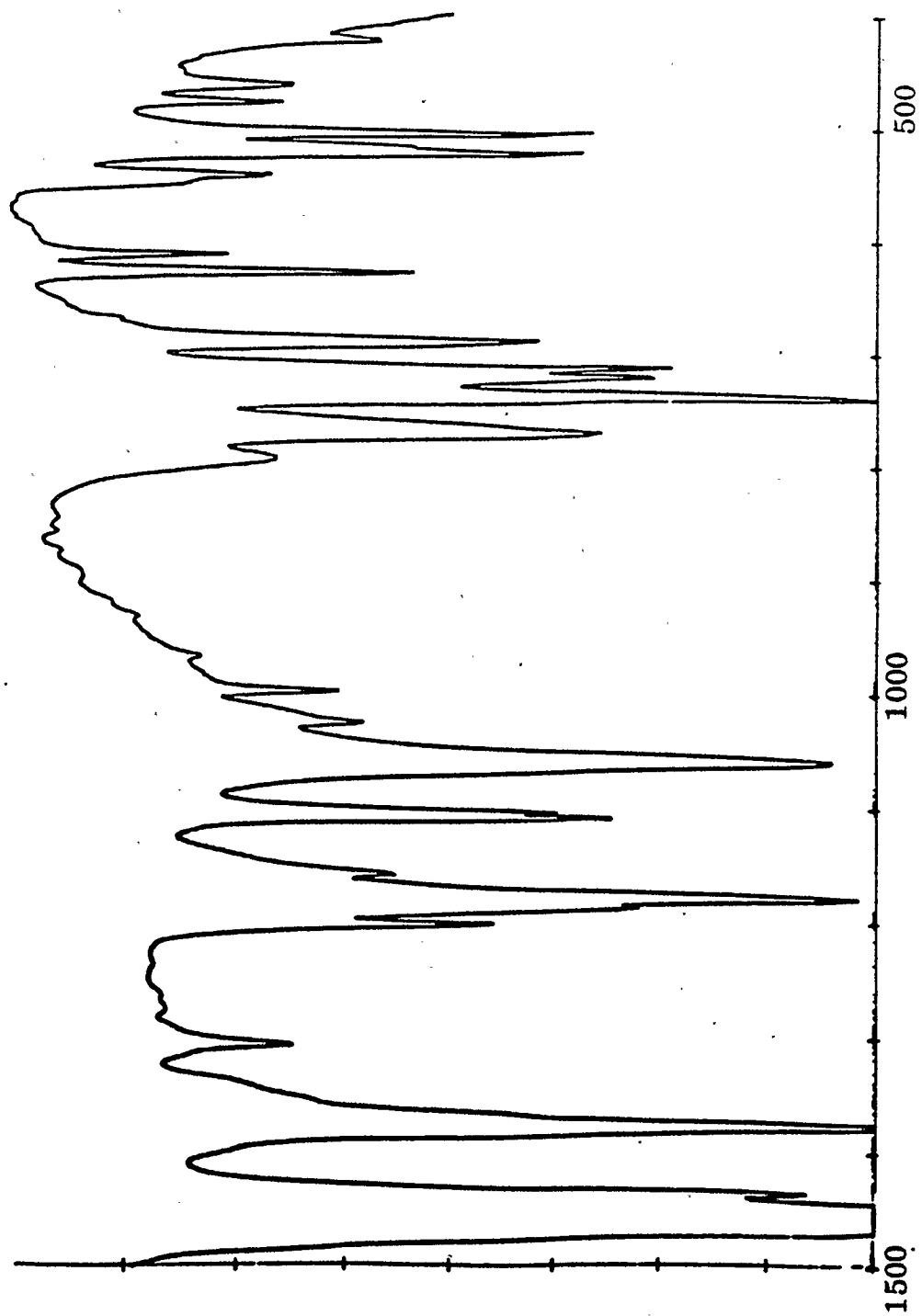


Figure 3.6 Infrared spectrum of $\text{Ph}_2\text{P}(\text{S})\text{NSnMe}_3$ (as Nujol mull)

Table 3.2 N=S=N Infrared Stretching Frequencies of Various Sulphur Diimides RNSNR'

R	R'	ν_{asym}	ν_{sym}	reference
Me ₃ Si	SiMe ₃	1260	1140	[110]
Me ₃ Sn	SnMe ₃	1160	1000	[110]
		1175	1060	[124]
Me ₃ Si	H	1265	1071	[133]
t-Bu	H	1238	1040	[133]
Bu ₂ ^t P	PBu ₂ ^t	1170	1070	[134]
Bu ₂ ^t (S)P	P(S)Bu ₂ ^t	1225	1088	[134]
Bu ₂ ^t (S)P	P(S)Bu ₂ ^t	1221	1081	[134]
Ph ₂ P(S)	SiMe ₃	1250	1107	
Ph ₂ P(S)	SnMe ₃	1179	1060	

3.6 Attempted Preparation of $\text{Ph}_2\text{PN}_2\text{S}_2^+$ from $\text{Ph}_2\text{P(S)NSNEMe}_3$
(E = Si, Sn)

Because of the moisture sensitivity of $\text{Ph}_2\text{P(S)NSNSiMe}_3$ the cyclization reactions to generate the five- and seven-membered rings (Figure 3.2) were attempted in situ.

The addition of 1/2 equivalent of sulphuryl chloride to an orange solution of $\text{Ph}_2\text{P(S)NSNSiMe}_3$ at room temperature resulted in an immediate change to a deep red colour and the generation of a species with a ^{31}P nmr resonance at -22.6 ppm with less than half of $\text{Ph}_2\text{P(S)NSNSiMe}_3$ being consumed (Figure 3.7b). After 24 hours, the addition of another 1/2 equivalent resulted in the reaction mixture becoming paler red and the generation of several signals at ca. 20 ppm (Figure 3.7c).

The reason for the generation of the many species with ^{31}P resonances in the region of 20 ppm may be due to the non-selective action of sulphuryl chloride as a chlorinating agent under these reaction conditions. In addition to effecting the cyclocondensation of the sulphur diimide, SO_2Cl_2 may also attack other centres on the molecule such as the P=S bond.

Preliminary attempts have been made to prepare the phosphadithiadiazolium cation by cyclizing in situ generated $\text{Ph}_2\text{P(S)NSNSnMe}_3$ in THF solution. The addition of a solution of SO_2Cl_2 to a $\text{Ph}_2\text{P(S)NSNSnMe}_3$ solution in THF resulted in an immediate colour change to red-brown and shortly thereafter red. The reaction mixture contains a number of phosphorus-containing species as shown by ^{31}P nmr spectroscopy (Figure 3.8), none of which are the same as those obtained in the reaction of the silicon derivative with SO_2Cl_2 . The differences are likely due to the higher concentration of the reaction mixture in the attempted cyclization of the tin derivative.

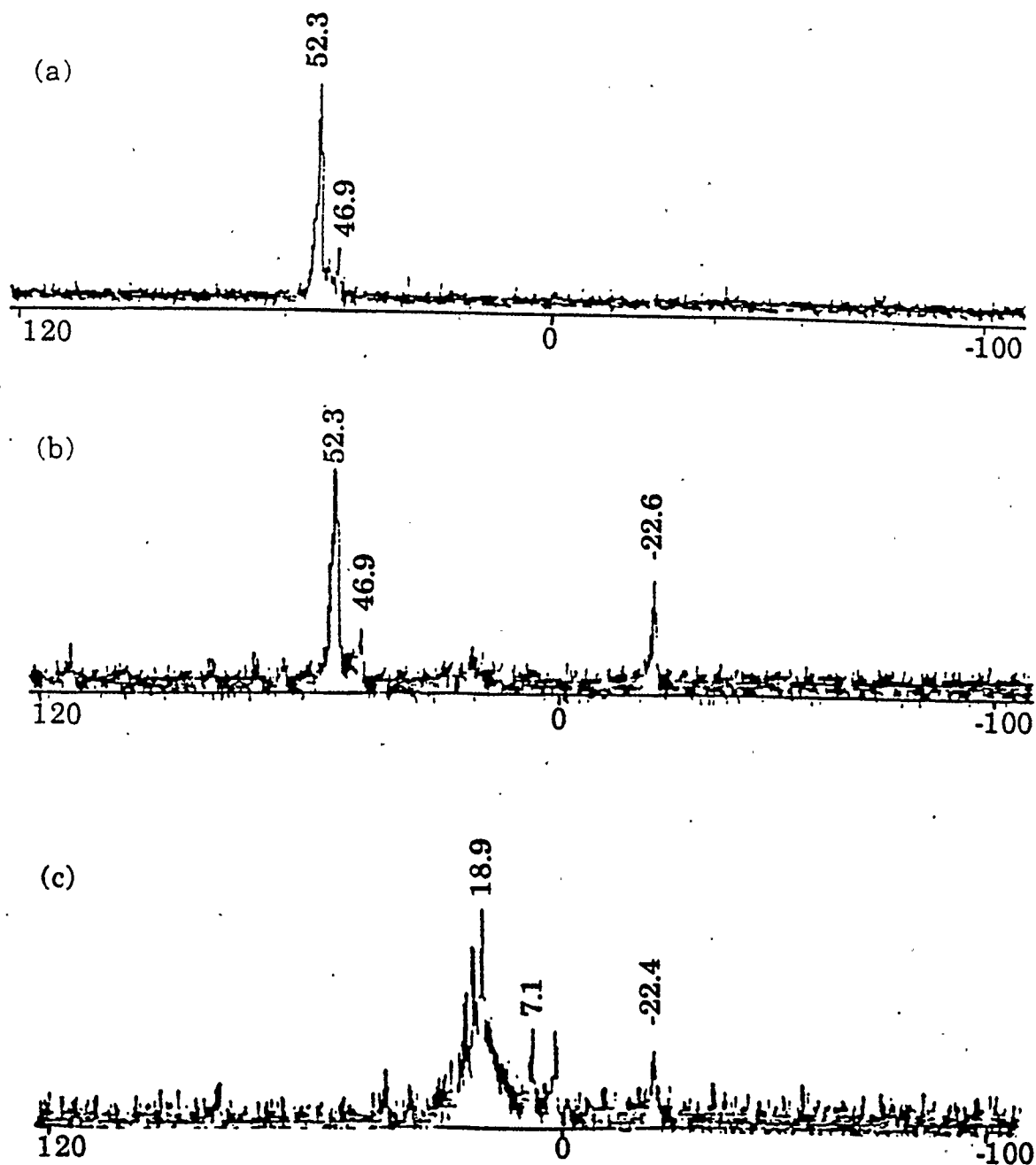


Figure 3.7 ^{31}P nmr spectra of the reaction of $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ with SO_2Cl_2 : a) Before the addition of SO_2Cl_2 b) After the addition of $1/2 \text{SO}_2\text{Cl}_2$ c) After the addition of $1 \text{SO}_2\text{Cl}_2$

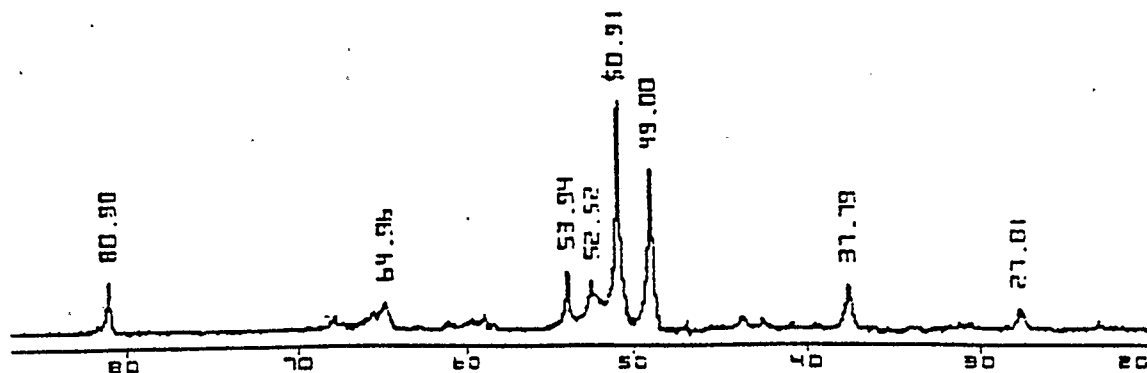


Figure 3.8 ^{31}P nmr spectrum of the reaction of $\text{Ph}_2\text{P}(\text{S})\text{NSNSnMe}_3$ with SO_2Cl_2

3.7 Attempted Preparation of $\text{Ph}_2\text{PN}_3\text{S}_3$ from $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$

An attempt to generate the seven-membered ring $\text{Ph}_2\text{PN}_3\text{S}_3$ (52) by the reaction $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ with NSCl (Figure 3.2) resulted in a considerably cleaner reaction than that which occurred with SO_2Cl_2 , according to preliminary ^{31}P nmr investigations. The addition of an excess (44%) of NSCl in THF solution to a solution of $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ generated a purple solution, which showed three signals in the ^{31}P nmr spectrum, at 53.7, 19.6 and -22.7 ppm (Figure 3.9). The signal at -22.7 ppm may be assigned to $\text{Ph}_2\text{PN}_3\text{S}_2$ (14) on the basis of its chemical shift and the fact that the solution displays a characteristic absorption at 550 nm^[64] for this six-membered ring in the visible spectrum. Since no absorption was found at 460 nm, the signal at 19.6 ppm is not due to 1,3- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ ^[65] and this major product remains unidentified.

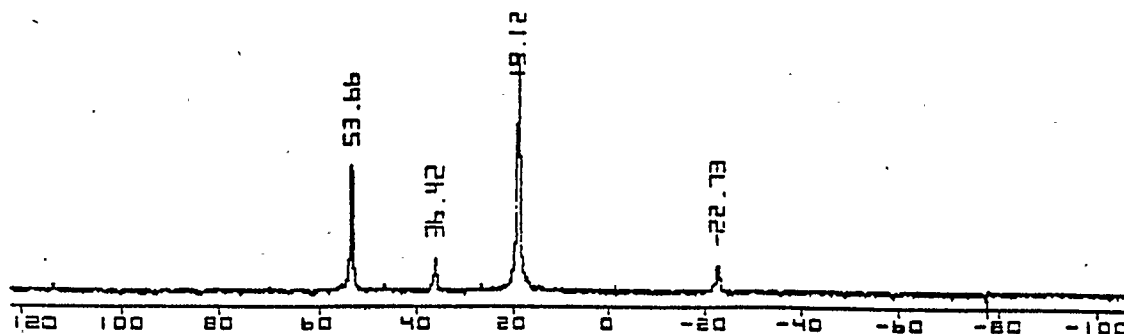


Figure 3.9 ^{31}P nmr spectrum of the reaction of $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ with NSCl

In the attempted generation of the seven-membered ring from $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ and 2 NSCl , the eight-membered ring $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (15) was observed as a major product in the reaction mixture (Figure 2.6). Its formation was proposed to be due to the dimerization of the seven-membered ring $\text{Ph}_2\text{PN}_3\text{S}_3$ followed by elimination of sulphur and nitrogen (Figure 2.7). In the present case, a solution approximately ten times as dilute in phosphorus was used and this may account for the lack of $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (15) among the products.

3.8 Conclusions

Various routes to the unsymmetrical sulphur diimides $\text{Ph}_2\text{P}(\text{S})\text{NSNEMe}_3$ ($\text{E} = \text{Si}, \text{Sn}$) have been investigated. The reaction of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ with $\text{Me}_3\text{SiNSNSiMe}_3$ occurs to only a small extent, even at reflux in toluene. The more reactive potassium salt, $\text{K}[\text{NSNSiMe}_3]$, reacts more readily with $\text{Ph}_2\text{P}(\text{S})\text{Cl}$, but the product, $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$, could not be obtained pure due to its moisture-sensitivity and contamination by oily by-products. The tin derivative $\text{Ph}_2\text{P}(\text{S})\text{NSNSnMe}_3$ was isolated as analytically pure yellow crystals from the reaction of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ with $\text{Me}_3\text{SnNSNSnMe}_3$ in THF at room temperature.

Preliminary attempts at the preparation of the five-membered ring $\text{Ph}_2\text{PN}_2\text{S}_2^+$ by the reaction of $\text{Ph}_2\text{P}(\text{S})\text{NSNEMe}_3$ with SO_2Cl_2 gave rise to a complex mixture of phosphorus-containing products. Future attempts at the synthesis of five- and seven-membered PNS rings should be carried out using the tin derivative (because it is more easily purifiable) at a lower temperature to minimize undesirable side reactions.

Initial attempts at the preparation of the seven-membered ring $\text{Ph}_2\text{PN}_3\text{S}_3$ from $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ (51) and NSCl also resulted in the production of several phosphorus-containing products, the identities of which are considerably different from those found in the reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with NSCl . In particular, the major product [δ (^{31}P) = 19.1 ppm] was not observed in the latter reaction while 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ is not formed from $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ and NSCl in dilute solution.

3.9 Experimental

3.9.1 General

The manipulation of solid materials as well as liquids and solutions was carried out as described in section 2.9.1

3.9.2 Solvents

All solvents were purified as described in Chapter 2. In addition, tetrahydrofuran was dried by refluxing over sodium wire and benzophenone prior to distillation. Ammonia (anhydrous) was obtained from Linde gas products and was used as received.

3.9.3 Reagents

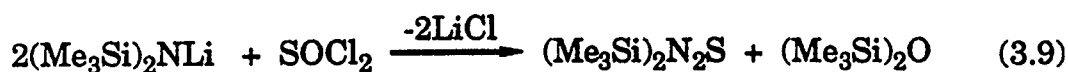
Chlorodiphenylphosphine, trimethyltin chloride, hexamethyldisilazane, thionyl chloride, sulphuryl chloride, and n-butyl lithium (2.5M solution in hexanes) were obtained from Aldrich and were used as received without further purification. Potassium amide was obtained from Ventron- Alfa Products and was also used as received .

Cyclo(trithiazyl trichloride), $(\text{NSCl})_3$, was prepared as described in section 2.8.4.

Chlorodiphenylphosphine sulphide, $\text{Ph}_2\text{P}(\text{S})\text{Cl}$, may be prepared by a number of routes, including fusion of the tertiary phosphine with elemental sulphur in the absence of solvent^[112], or oxidation by elemental sulphur in an inert solvent. In the present research, a suspension of elemental sulphur (1.67 g, 6.51 mmol) in 50 ml of anhydrous toluene was added rapidly via transfer needle to a solution of Ph_2PCl (11.31 g, 51.3 mmol) in 25 ml toluene

in a 100 ml side-arm flask. The reaction mixture was heated to 100°C overnight at which point a ^{31}P nmr spectrum showed only a singlet at 80 ppm (cf. lit $\delta^{31}\text{P} = 79.6 \text{ ppm}^{[135]}$). Evaporation of solvent left a yellow oil which was distilled (156 - 160°C at 0.3 torr) to give 9.8 g (76% yield) of product.

Bis(trimethylsilyl)sulphurdiimide was prepared according to the literature procedure^[132], except the sodium salt was replaced by the in situ generated lithium salt (Equation 3.9).



The potassium salt $\text{K}[\text{NSNSiMe}_3]^{[122]}$ and the tin derivative $\text{Me}_3\text{SnNSNSnMe}_3^{[132]}$ were also prepared according to the literature procedures. The potassium salt was recrystallized from warm tetrahydrofuran before use.

3.9.4 Instrumentation

Infrared, nmr and UV-visible spectra were obtained as described in Chapter 2.

3.9.5 Reaction of $\text{Ph}_2\text{P(S)Cl}$ with $\text{Me}_3\text{SiNSNSiMe}_3$

A three neck 100 ml round-bottom flask (fitted with a nitrogen inlet and a dropping funnel) was charged with a solution of $\text{Ph}_2\text{P(S)Cl}$ (1.12 g, 4.4 mmol) in 25 ml of carbon tetrachloride. A solution of $\text{Me}_3\text{SiNSNSiMe}_3$ (0.93 g, 4.45 mmol) in 10ml CCl_4 was added from the dropping funnel at 20°C over a period of 45 minutes to the stirring solution of $\text{Ph}_2\text{P(S)Cl}$ resulting in no

change in the colour of the reaction mixture. A ^{31}P nmr spectrum at this point showed no evidence of any species aside from the starting material so the flask was equipped with a condenser and heated to reflux for 24 hours, giving rise to two minor products at 52.3 and 21.1 ppm in the ^{31}P nmr spectrum making up less than 5% of the phosphorus-containing species in solution.

A similar reaction carried out in toluene at 90°C showed absolutely no consumption of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ after 24 hours.

3.9.6 Reaction of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ with $\text{K}[\text{NSNSiMe}_3]$

In a typical reaction, a solution of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ (0.54 g, 2.15 mmol) in THF (15 ml) was added from a dropping funnel over a period of 1.5 hours at 20°C to a stirred solution of $\text{K}[\text{NSNSiMe}_3]$ (0.34 g, 2.17 mmol) in 50 ml THF in a 100 ml round bottom flask, resulting in an immediate colour change from yellow to red to orange-red. After stirring for 4 hours, the resultant KCl was allowed to settle and the supernatant solution was removed by decanting it to another flask via transfer needle to provide 0.08 g of KCl. Attempts to crystallize the product by cooling the reaction mixture resulted in the precipitation of a dull yellow impure powder. Attempts at recrystallization of this solid from pentane, chloroform, THF, and combinations of these solvents resulted in the precipitation of a yellow oily powder from pentane/THF. Spectroscopic data (infrared and ^1H nmr) were consistent with the formation of $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ (see Section 3.4 and Figure 3.5) contaminated with the hydrolysis product $\text{Ph}_2\text{P}(\text{S})\text{NSNH}$, but the product could not be purified due to its moisture sensitivity.

3.9.7 Preparation of the Unsymmetrical Sulphurdiimide
 $\text{Ph}_2\text{P(S)NSNSnMe}_3$

In a typical reaction, a solution of $\text{Ph}_2\text{P(S)Cl}$ (1.01 g, 4.0 mmol) in 20 ml of anhydrous THF was added via transfer needle to a solution of $\text{Me}_3\text{SnNSNSnMe}_3$ (1.66 g, 4.28 mmol) in 50 ml THF over the course of one hour resulting in a slight darkening of the yellow solution. After stirring for three days, the solvent was removed in vacuo leaving a dark yellow solid residue. This was heated to 65-70°C under vacuum for about 1.5 hours to remove the byproduct Me_3SnCl . The residue was redissolved in THF and pentane was added before placing the solution into the refrigerator resulting in the growth of bright yellow plate-like crystals (0.56 g, 32% yield). Analytical data are reported in Table 3.3. Infrared spectroscopy confirmed the sulphurdiimido structure (Figure 3.6). ^1H and ^{31}P nmr data are presented in Table 3.1

Table 3.3. Analytical Data for $\text{Ph}_2\text{P(S)NSNSnMe}_3$

	<u>Calculated</u>	<u>Found</u>
C	40.84	40.78
H	4.34	4.34
N	6.35	6.27

3.9.8 Attempted Preparation of $\text{Ph}_2\text{PN}_2\text{S}_2^+$ from $\text{Ph}_2\text{P(S)NSNEMe}_3$
(E = Si, Sn)

A solution of $\text{Ph}_2\text{P(S)Cl}$ (0.54 g, 2.1 mmol) in 5 ml of anhydrous THF was added dropwise at 20°C to a stirred solution of $\text{K[NSNSiMe}_3]$ (0.38 g, 2.2 mmol) in 65 ml of THF via transfer needle. A ^{31}P nmr spectrum obtained 12 hours later showed consumption of $\text{Ph}_2\text{P(S)Cl}$ and generation of the sulphurdiimide at 52.2 ppm with two minor species at 47.0 and 49.5 ppm. Twenty-four hours after mixing the two solutions, sulphuryl chloride (0.1 ml, 1.24 mmol) was added dropwise to the stirred reaction mixture at room temperature, resulting in a rapid colour change to a deep red solution. This resulted in the appearance of a new signal in the ^{31}P nmr spectrum at -22.6 ppm (Figure 3.7b), which may be assigned to the six-membered ring $\text{Ph}_2\text{PN}_3\text{S}_2$, with no other change in the spectrum. Another aliquot of sulphuryl chloride (0.1ml, total 2.48 mmol) was added in a similar manner, resulting in a paler red colour and a significant change in the ^{31}P nmr spectrum with the generation of a number of species with resonances near near 20 ppm (Figure 3.7c).

A procedure similar to that described above was used to prepare $\text{Ph}_2\text{P(S)NSNSnMe}_3$ in situ. A solution of $\text{Ph}_2\text{P(S)Cl}$ (0.39 g, 1.5 mmol) in 5 ml THF was added dropwise for five minutes to a solution of $\text{Me}_3\text{SnNSNSnMe}_3$ (0.60 g, 1.5 mmol) in 5 ml of THF in a Schlenk tube resulting in a slight darkening of the solution overnight. Sulphuryl chloride (0.12 ml, 1.5 mmol) in 3 ml THF was added to the vigorously stirred reaction mixture, and the colour changed from yellow-orange to brown and then orange-red. The ^{31}P nmr spectrum (Figure 3.8) was very complicated so no attempt was made to separate the products.

3.9.9 Attempted generation of $\text{Ph}_2\text{PN}_3\text{S}_3$ by the reaction of $\text{Ph}_2\text{P(S)NSNSiMe}_3$ with NSCl

An in situ solution of $\text{Ph}_2\text{P(S)NSNSiMe}_3$ (1.04 mmol) in THF (55 ml) was prepared as described above. After stirring for 45 minutes at 20°C, a solution of NSCl (0.12 g, 1.5 mmol) in 25 ml THF was added dropwise via transfer needle to the reaction mixture to generate a purple solution, which was shown by ^{31}P nmr and visible spectroscopy to contain a small amount of $\text{Ph}_2\text{PN}_3\text{S}_2$ (14), some unreacted $\text{Ph}_2\text{P(S)NSNSiMe}_3$ (50) and a species with a ^{31}P nmr resonance at 19 ppm (Figure 3.9). The reaction was not worked up past this point.

Chapter 4
Conclusions and Future Research Directions

4.1 General

The reaction of $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{SiMe}_3)_2$ with NSCl produces a number of known cyclophosphathiazenes as well as a few unknown species as evidenced by ^{31}P nmr spectroscopy. The reaction in a 1:1 molar ratio proceeds very slowly to give a thermally unstable intermediate tentatively identified as the five-membered ring $\text{Ph}_2\text{PN}_2\text{S}_2\text{SiMe}_3$, which upon sublimation gives the expected product $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$, which has only been isolated in low yield. The reaction with two equivalents of NSCl , however, results in the production of a number of known cyclophosphathiazenes including $\text{Ph}_2\text{PN}_3\text{S}_2$, 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$, and $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$ as well as a number of minor unidentified species. The formation of $\text{Ph}_2\text{PN}_3\text{S}_2$ and 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ has been accounted for by means of an intermediate phosphatrithiatiazepine $\text{Ph}_2\text{PN}_3\text{S}_3$, which spontaneously decomposes to give the observed products.

The preparation of $\text{Ph}_2\text{P}(\text{S})\text{NSNEMe}_3$ ($\text{E} = \text{Si}, \text{Sn}$) has been achieved but attempts to cyclize these unsymmetrical sulphur diimides with SO_2Cl_2 to produce the phosphadithiazolium cation $\text{Ph}_2\text{PN}_2\text{S}_2^+$ have not provided any concrete evidence of its formation.

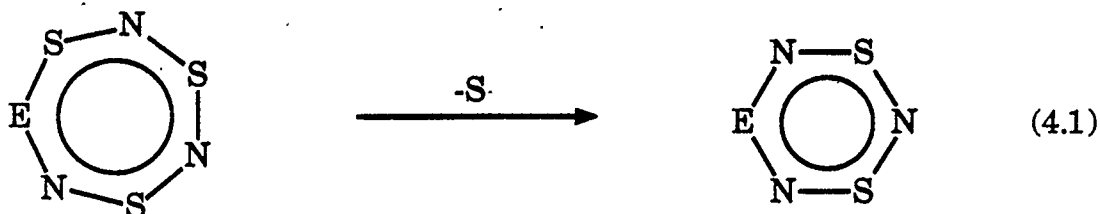
The reaction of $\text{Ph}_2\text{P}(\text{S})\text{NSNSiMe}_3$ with NSCl results in the formation small amounts of $\text{Ph}_2\text{PN}_3\text{S}_2$ and a major unknown species.

The results of the two approaches to the seven-membered ring differ remarkably. The former provides a number of known cyclophosphathiazenes whereas the latter results in small amounts of the six-membered ring

$\text{Ph}_2\text{PN}_3\text{S}_2$ and an unknown species with a resonance of 19.1 ppm in the ^{31}P nmr spectrum.

4.2 Conclusions

The apparent instability of the $\text{Ph}_2\text{PN}_3\text{S}_3$ ring is surprising because the carbon-containing and binary analogues RCN_3S_3 and S_4N_3^+ , respectively, are both stable species. The seven-membered ring RCN_3S_3 ($\text{R} = \text{CO}_2\text{Me}$) does not decompose even at 140°C in boiling xylene. In boiling decalin, it decomposes in 33 hours. However, no evidence for the production of the six-



($\text{E} = \text{S}^+, \text{R}_2\text{P}, \text{RC}$)

membered ring illustrated in Equation 4.1 was reported^[136]. The binary species S_4N_3^+ as the chloride salt shows a similar stability, decomposing on melting at $180\text{-}200^\circ\text{C}$, but not to give S_3N_3^+ .

Attempts to prepare the unknown cation S_3N_3^+ (an 8π -electron system, isoelectronic to $\text{R}_2\text{PN}_3\text{S}_2$) from the bicyclic cation S_4N_5^+ by loss of an N_2S fragment, have failed. Since S_3N_3^+ has a triplet ground state, its formation from S_4N_5^+ is symmetry forbidden^[137].

Substitution of S^+ by RC still results in a "pseudo-triplet" ground state so the conversion of the bicyclic to six-membered ring is almost symmetry

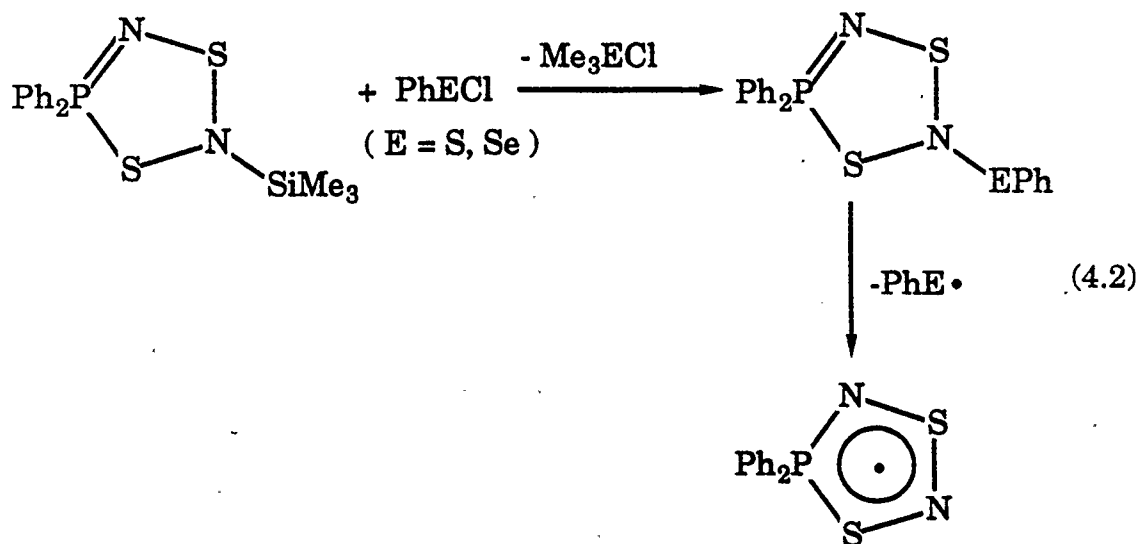
forbidden. Substitution by an R_2P fragment removes the degeneracy of the HOMO of $R_2PN_3S_2$ to give a stable singlet ground state^[137] so the reaction is symmetry allowed.

The instability of the phosphorus-containing seven-membered ring relative to the binary and carbon-containing analogues may be due to the fact that Equation 4.1 is symmetry allowed for $E = R_2P$ but not for $E = S$ or RC , because of the triplet ground states of $S_3N_3^+$ and RCN_3S_2 .

4.3 Directions for Future Research

The products of the reaction of $Ph_2P(S)N(SiMe_3)_2$ with $NSCl$ may possibly be separated by means of column chromatography under extremely careful conditions so as to eliminate any possibility of atmospheric hydrolysis. In addition the reaction must be carried out under milder conditions so that any intermediates may be isolated.

If the major product ($\delta^{31}P = 54.6$ ppm) is indeed $Ph_2PN_2S_2SiMe_3$, then a reaction in which the N-Si bond is homolytically cleaved would result in the production of the phosphadithiadiazole radical, $Ph_2PN_2S_2$, isoelectronic to $S_3N_2^+$ and RCN_2S_2 . A possible approach to the radical is illustrated in Equation 4.2.



Any future work regarding the cyclization of the unsymmetrical sulphur diimides should make use of $\text{Ph}_2\text{P}(\text{S})\text{NSNSnMe}_3$ as it can be purified more readily than the silicon derivative. In addition, these reactions must be carried out under much milder conditions to minimize side reactions.

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