CHEMISTRY OF COMPOUNDS CONTAINING SULFUR-NITROGEN BONDS

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By

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ABSTRACT

The sulfur-nitrogen bonds in N,N'-monothiobisdialkylamines (N,N,N',N'-tetraalkylsulfoxylic diamides) and N,N'-dithiobisdialkylamines have been shown to undergo new reactions. The reaction of the former compounds with heptasulfurimide, (S_7NH), has led to the formation of the new compounds N,N-dialkyl-N',N'-cycloheptathiosulfoxylic diamides (S_7NSNR_2, R = CH_3, C_2H_5, $CH(CH_3)_2$, C_6H_{11}) in good yields. These compounds have been shown by NMR spectroscopy to have slow N-S bond rotation at room temperature. Structural studies suggested that the slow bond rotation is caused by strong $p\pi$-$d\pi$ bonding in the single N-S bonds. The strength of the π - interaction appears to be a function of the substituents of the nitrogen and sulfur atoms. A synergic type of bonding is used to describe these saturated sulfur-nitrogen systems.

The S-N bonds in the N,N'-thiobisdialkylamines have also been found to be very reactive towards chlorine substituted phosphorus compounds. The reaction proceeds via an electrophilic attack of phosphorus on sulfur with subsequent loss of chloride ion from the intermediate. This species then rapidly rearranges to give a product in which the phosphorus atom has inserted into the sulfur-nitrogen bond. The stability of this species has been found to be dependent on the number of phenyl groups attached to phosphorus. With zero or one phenyl group the insertion product loses N,N- dialkyl-N-

sulfenyl chloride. Further reactions of these species are discussed. With two phenyl groups, the insertion product is quite stable. It, however, has been found to be susceptible to attack by another mole of $(C_6H_5)_2PCl$ to give further products. A discussion of the mechanisms of reactions in this system is given.

The sulfur-nitrogen bonds in the N,N'-dithiobisdialkylamines are considerably more stable towards these phosphorus compounds. The reactions that these compounds undergo suggest that the initial reaction involves fission of the sulfur-sulfur bond rather than N-S bond insertion. The reaction of $(C_6H_5)_3P$ with these compounds to produce $(C_6H_5)_3PS$ and the N,N'-thiobisamine offers a convenient method of purifying this latter compound from its major contaminant, the former compound. The reactions with $(C_6H_5)PCl_2$ and PCl_3 offer convenient methods of preparation of the compounds $(C_6H_5)P(S)(Cl)(N(CH_3)_2)$ and $((CH_3)_2N)P(S)Cl_2$ which have applications as insecticides. $(C_6H_5)_2PCl$ and $((CH_3)_2N)_2S_2$ have been shown to form a more complicated system in which reactions analogous to the two systems just discussed, occur. A discussion of the mechanisms of these reactions is presented. The chemical behaviour of these compounds suggests that the N-S bonds in the N,N'-dithiobisdialkylamines are considerably less reactive towards chlorine substituted phosphorus compounds than those in the monothio analogues.

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CHAPTER I

INTRODUCTION

I-1 INTRODUCTION TO SULFUR-NITROGEN CHEMISTRY

In the past few years much interest has been shown in the chemistry of sulfur compounds due to their importance in the fields of biochemistry, polymerchemistry, petrochemistry and pollution studies. Until recently, relatively few inorganic publications have been devoted to sulfur chemistry. This area, however, offers many chemical and structural problems to challenge the chemist. This is particularly true of compounds containing sulfur-nitrogen bonds and it is with some of these compounds that this work is primarily concerned.

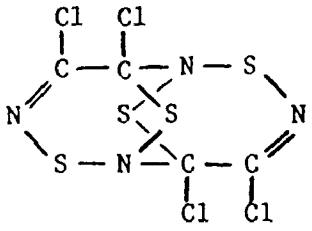
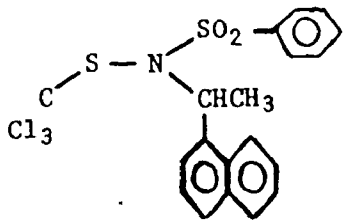
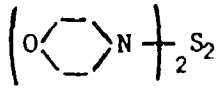
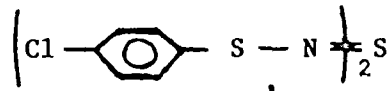
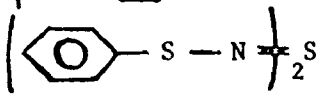
(a) The Sulfur-Nitrogen Bond

The nature of sulfur-nitrogen bonds has received considerable attention due to the large variation observed in their lengths. Table I-1 illustrates this fact in that it shows a distribution of bond lengths between 1.764 (20) Å and 1.25 Å. This distribution is quite continuous, especially in the region of lower bond order.

There has been some controversy over what constitutes a "single" sulfur-nitrogen bond and the corresponding single bond length. Chapman and Waddington[14] have considered that sulfamic acid ($H_3N^+SO_3^-$) contains a single sulfur-nitrogen bond (1.764 (20) Å) since here the

Table I-1

Sulfur-Nitrogen Bond Lengths

Compound	Bond Length (Å)	Reference
$H_3N - SO_3$	1.764 (20)	(1)
	1.740 (14) 1.705 (18) 1.644 (16)	(2)
	1.713 (9) 1.643 (9)	(3)
	1.686 (3)	(4)
S_7NH	1.676 (2)	(5)
$S_4N_4H_4$	1.674 (4)	(6)
$1,3\text{-}S_6N_2H_2$	1.660 (4) to 1.675 (4)	(7)
	1.657 (18), 1.662 (19) 1.539 (16), 1.561 (18)	(8)
	1.651 (5) 1.529 (5)	(9)
$SO_2(NH_2)_2$	1.600 (9)	(10)
$S_5N_5^+$	1.465 (9) to 1.590 (9)	(11)
SN	1.495	(12)
FSN	1.446	(13)
F_3SN	1.416	(13)
SN^+	1.25	(14)

possibility of a sulfur-nitrogen π-interaction is removed. This bond length agrees with the sum of Pauling's[15] covalent radii (1.74 Å)* but is slightly longer than the bond length predicted by the Schomaker-Stevenson[16] relationship (1.70 Å)*. Nyburg[19] has suggested that a true sulfur-nitrogen single bond is approximately 1.70 Å and that the bond order (N_{NS}) can be described by the empirical equation

$$N_{NS} = 0.429 + 6.850\ \ell_{NS} - 3.825\ \ell_{NS}^2$$

(ℓ_{NS} = sulfur-nitrogen bond length in angstroms).

Chapman and Waddington[14] have also presented a bond order-bond length correlation. Theirs differs from that of Nyburg's in that for the longer bond lengths it predicts a slightly higher bond order.

The shortening of an apparent single sulfur-nitrogen bond in a saturated system is often interpreted as being due to a π-interaction between the filled p-orbital on nitrogen and vacant d-orbitals on sulfur. This π-overlap is optimised when the p-character of the lone pair orbital is increased; the substituent bonding orbitals going from sp^3 to sp^2. A method of estimating this p-character from the angles between substituents at the nitrogen atom has been reported by Mislow[20]. Table I-2 contains a listing of structural data of compounds containing sulfur-nitrogen bonds, the corresponding bond lengths and sum of the angles between the substituents at the nitrogen atom. These data suggest that the apparent "single" bond length does

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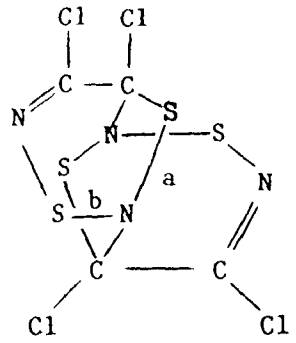
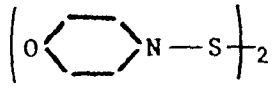
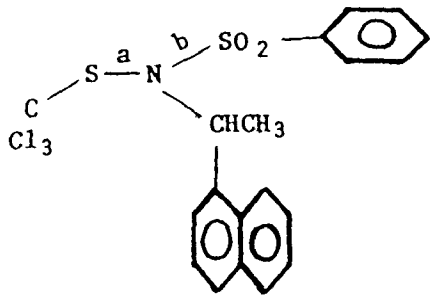
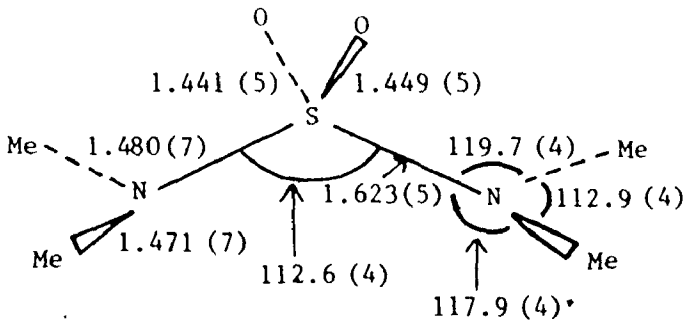
* Values for Pauling's electronegativities and covalent radii taken from reference (17).

Table I-2

Sulfur-Nitrogen Bond Lengths vs Sum of Substituent Angles at Nitrogen

Compound	Sum of Angles	Bond Lengths	Ref.
Sum of Pauling's covalent radii	328	1.74	(15)
Schomaker-Stevenson Relationship	328	1.70	(16)
$\overset{+}{N}H_3\bar{S}O_3$	323	1.764(20)	(1)
	335	(a) 1.705(18) (b) 1.740(14)	(2)
	344	1.686(3)	(4)
	357	(a) 1.643(9) (b) 1.713(9)	(3)

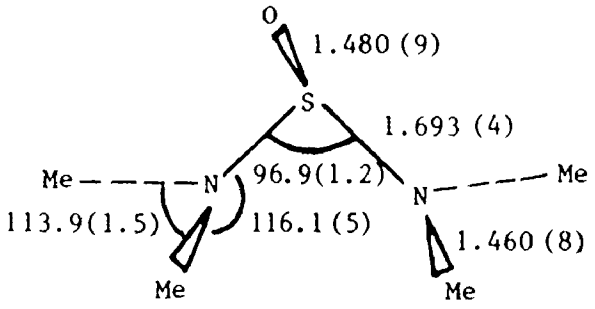
indeed become shorter as the sum of the angles about nitrogen approaches 360°. A similar "flattening" of the substituents around nitrogen has been observed in aminophosphines and aminosilanes[18,21]. It has been suggested that pπ-dπ bonding is involved in these systems as well. Although other possibilities have been suggested[22], the filled nitrogen p-orbitals are most likely donating electron density into empty d-orbitals on sulfur. A LCAO-MO analysis[23] of I



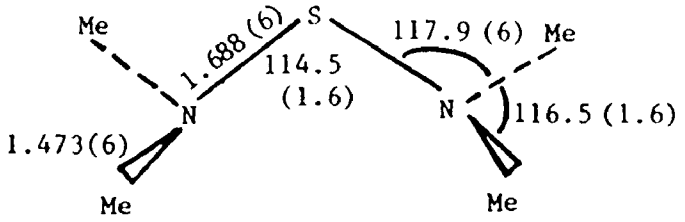
I

has suggested a pπ-dπ interaction of this type requires that the CNC planes are perpendicular to the NSN plane. This is in agreement with the structure as determined by X-ray diffraction[23]. Similar structures have been suggested with "short" single sulfur-nitrogen bonds on the basis of electron diffraction for the related compounds II[24] and III[21].

Although the sulfur 3d-orbitals are normally too high in energy to interact significantly with the nitrogen 2p-orbitals, it has been shown that electronegative groups attached to sulfur can contract the 3d-orbitals enough for effective π-overlap[3]. As will be described

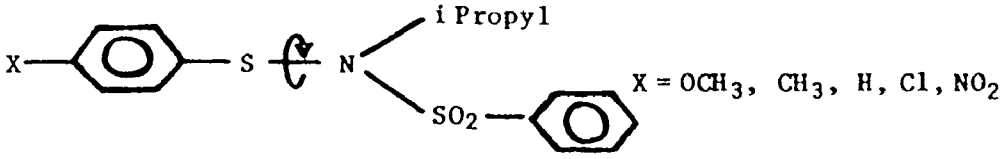


II



III

in a later section (II-7), this electronegativity effect has been observed in the hindered bond rotation of the sulfenamides IV[22].



IV

As the X-groups become more electron withdrawing, the barrier to bond rotation increases.

Many configurations have been described in which effective σ-

and π-overlap can be attained between d-orbitals and p-orbitals arranged in various symmetries[18]. The work presented here, however, is concerned only with pπ-dπ interactions found in single (Figure I-1) or nitrogen-branched (Figure I-2) sulfur-nitrogen chains. The use of the $d_{x^2-y^2}$ or dz^2 orbitals are important only for π-bonding in systems

Figure I-1 pπ-dπ Overlap in Single S-N Chains

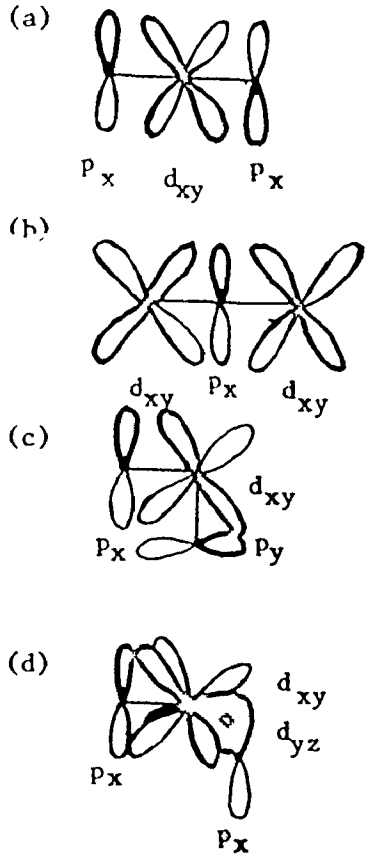
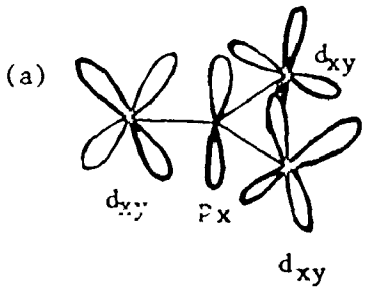


Figure I-2 pπ-dπ Overlap in Branched S-N Chains



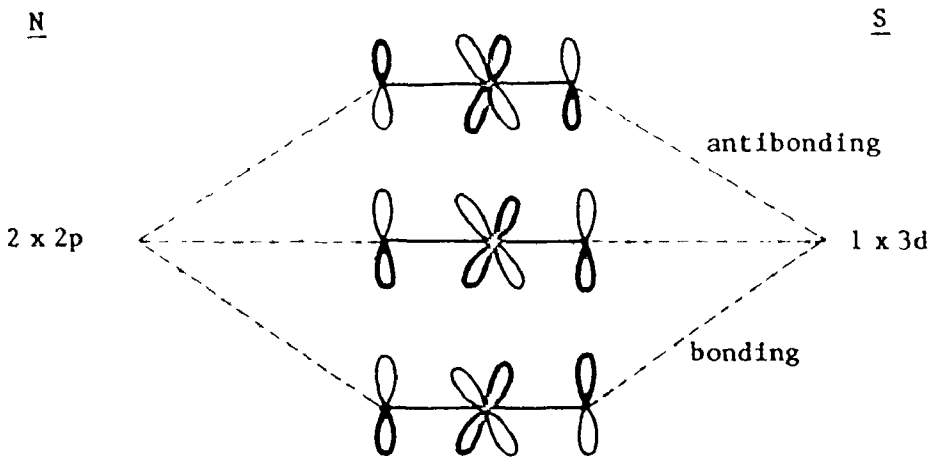
where the number of substituents about the d-orbital atom makes it 4, 5 or 6 co-ordinate.

Craig[25] has found it useful to qualitatively describe the

π-bonding situation in phosphonitrilic halides using LCAO-MO theory. It has also been used to investigate some sulfur-nitrogen bonded systems ($S_4N_3^+$[26], S_4N_4[27], SN[28], SN^+[29]). Chapman et al[14] have also described a molecular orbital picture for S_4N_4, not using p- and d-orbitals, but by deriving molecular orbitals entirely from a model of free electrons on a sphere.

Although the above examples contain formal double bond character, this treatment can be extrapolated to the π-bonding situations described in Figure I-1 and I-2 for formally saturated systems. For a simple qualitative example, the two p-orbitals of nitrogen and the d-orbital of sulfur in Figure I-1 (a) are considered. Figure I-3 shows that three molecular orbitals are generated. Upon inserting

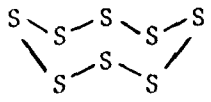
Figure I-3 MO Theory Applied to N-S π-Bonding



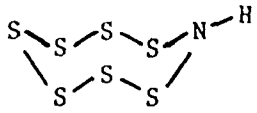
four electrons from the two nitrogen atoms, two are found in a bonding orbital and two in a non-bonding orbital to give a total bonding interaction.

(b) Cyclothiazocine (Heptasulfurimide)

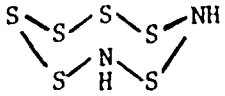
One class of compounds containing the sulfur-nitrogen bond is the sulfur imides. The structures of these compounds can be derived by replacing sulfur atoms by >N-H groups in octasulfur. All isomers which do not contain an N-N bond have been isolated and characterized. These include one isomer of heptasulfurimide V, three isomers of hexasulfurdiimide VI, VII, VIII, two isomers of pentasulfur-



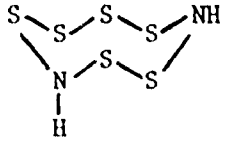
Octasulfur



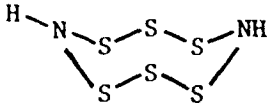
Heptasulfurimide
V



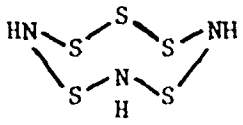
1,3-Hexasulfurdiimide
VI



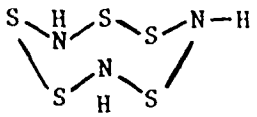
1,4-Hexasulfurdiimide
VII



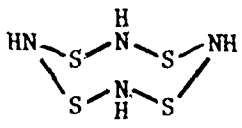
1,5-Hexasulfurdiimide
VIII



1,3,5-Pentasulfurtriimide
IX



1,3,6-Pentasulfurtriimide
X



Tetrasulfurtetraimide
XI

triimide IX, X, and tetrasulfur-tetraimide XI.[9] The crystal structures of most of the sulfur imides have been determined and the sulfur-nitrogen bond distances are presented in Table I-3.

Table I-3

Sulfur-Nitrogen Bond Lengths in the Sulfur Imides

Compound	SN Bond Length (Å)	Ref.
S_7NH	1.676 (2)	(5)
1,3-$S_6N_2H_2$	1.660(4) to 1.675(4)	(7)
1,4-$S_6N_2H_2$	1.68*	(31)
1,5-$S_6N_2H_2$	1.62* 1.68*	(31)
1,3,5-$S_5N_3H_3$	1.676*	(30)
1,3,6-$S_5N_3H_3$	--	
$S_4N_4H_4$	1.674 (4)	(6)

* Errors not quoted on bond lengths, only on unit cell dimensions.

Although some of this work should be repeated, the errors being rather large, one can notice that the sulfur-nitrogen bonds in these compounds are considerably shorter than a typical single bond (1.70 to 1.74 Å).

Heptasulfurimide itself was reported as early as 1923[32] but was correctly identified only in 1951 by Goehring[33]. A crystal structure determination[34] in 1960 confirmed the ring structure. This compound has

been isolated from the products of the following reactions [1], [2] and [3].

$$[1]^{(35)} \quad S_2Cl_2 + NH_3 \xrightarrow[-10^{\circ}C]{DMF} S_7NH$$

$$[2]^{(36)} \quad NaN_3 + S_8 \xrightarrow{HMPA} S_7NH$$

$$[3]^{(37)} \quad S_2Cl_2 + NH_3(aq) \longrightarrow S_7NH$$

All three reactions yield elemental sulfur and heptasulfurimide as the major products with minor amounts of the di- and tri-imides being produced. All three reactions probably proceed via the intermediate perthionitrate anion (NS_4^-) which has been shown to be in equilibrium with S_7NH in basic solution[38]. This is consistent with the fact that substitution of S_7Cl_2 for S_2Cl_2 in reaction [1] does not increase the yield significantly[39]. Also it has been shown[38] that hydrolysis of the tetrabutylammonium salt of the perthionitrate anion results in production of elemental sulfur and the imides in similar proportions to those obtained according to reaction [1].

Most of the chemistry involving preparation of derivatives of the sulfur imides has been carried out with heptasulfurimide. The chemistry of heptasulfurimide is dominated by the low basicity of the nitrogen lone pair and the acidity of the imido hydrogen. One of the reasons given[40] to explain this behaviour is the possibility of the lone pair on nitrogen being involved in $p\pi$-$d\pi$ bonding with the adjacent sulfur atom. As has been mentioned earlier, this results in a flattening of the three substitutents on nitrogen. This is found in the recent structural data for S_7NH and the related compounds $S_4N_4H_4$ and $S_4N_4(CH_3)_4$. In S_7NH, the hydrogen atom has

been found crystallographically averaged over two positions approximately 14° out of the SNS plane[5]. The hydrogen atoms in tetrasulfur-tetraimide have been shown by neutron diffraction[41] to be in the SNS plane. Similar results were found for the carbon atoms in tetramethyl-tetrasulfur-tetraimide[42].

The aqueous pKa of the imido hydrogen has been estimated by Chivers and Drummond[38] to be approximately 4.6 ± 0.2 (H_2O, 25°C) which is about 10^{34} times more acidic than ammonia (Ka = 10^{-39}). This fact suggests that electron density is being withdrawn from the nitrogen into the ring.

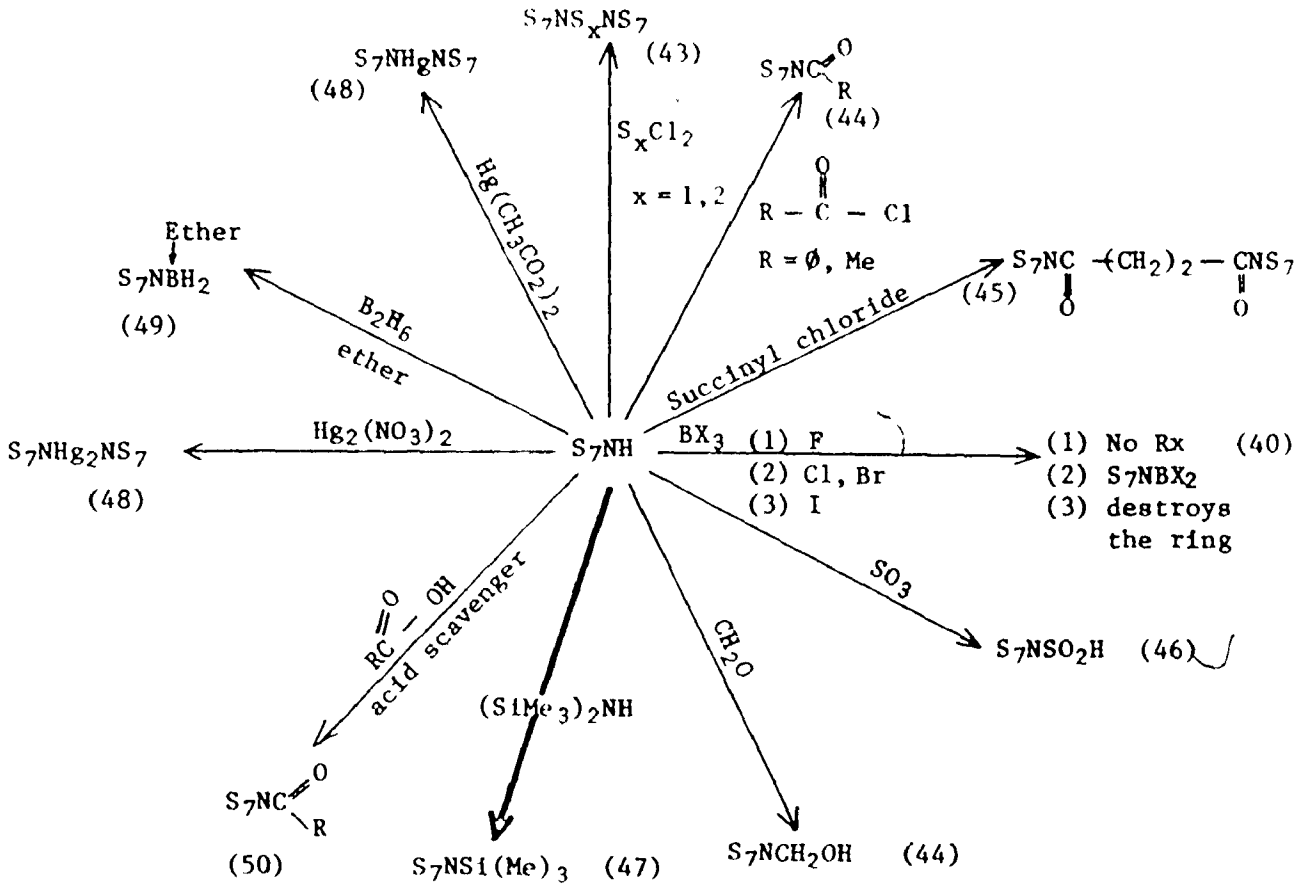
The factors mentioned above dominate the chemistry of S_7NH. Over the past few years many derivatives of S_7NH have been prepared. These preparations can be divided into two types of reaction. In the first type, heptasulfurimide reacts with a reagent which alone will remove the imido hydrogen. Such reactions are shown in Figure I-4.

Most of the reactions (Figure I-4) result in the loss of HCl or a hydroxy species. The reaction which bears most relevance to the present work, however, is that involving bistrimethylsilylamine. In this reaction the imido hydrogen is abstracted by the amine nitrogen which, after loss of the trimethylsilyl group to the ring, produces ammonia. The reaction with the boron trihalides illustrates the limited basicity of the imido nitrogen. The chloride and bromide both react whereas the fluoride with its lower Lewis acidity does not.

Other derivatives of S_7NH have been prepared by removal of the imido hydrogen using a strong base and subsequent reaction of the resulting

Figure I-4

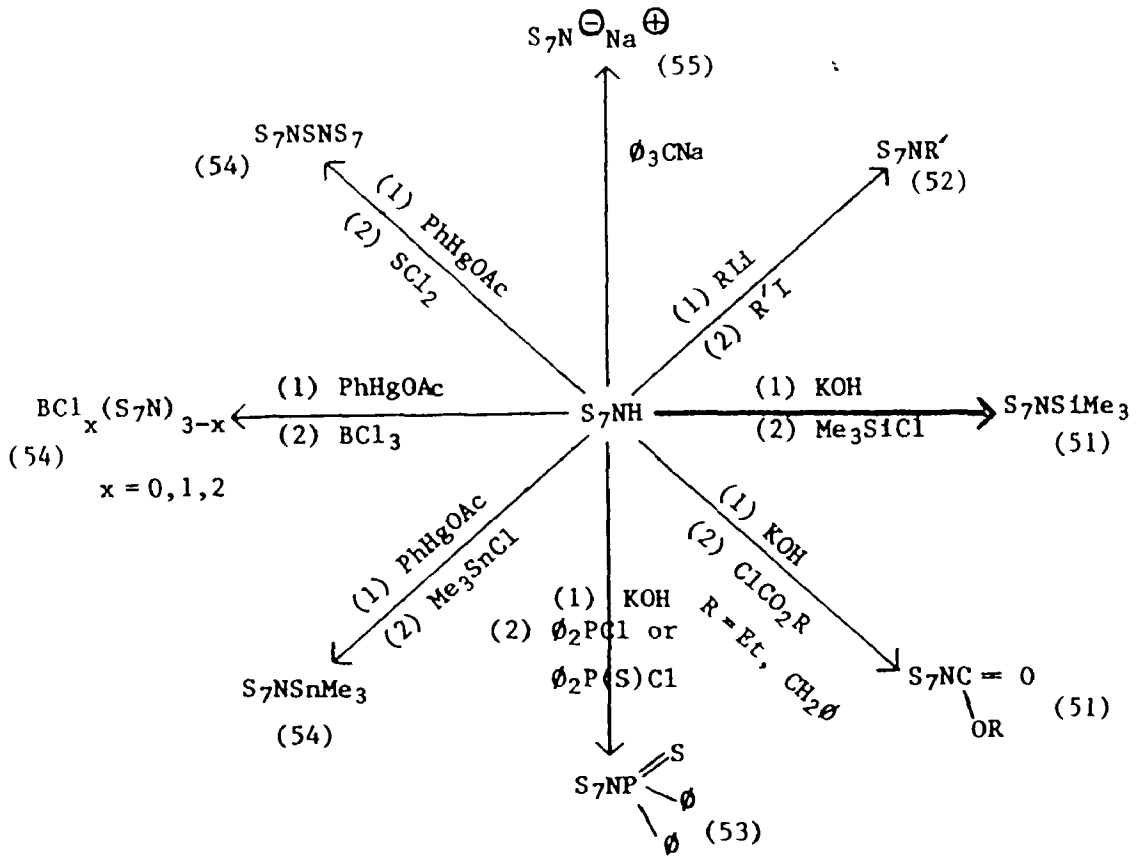
Derivatives of S_7NH From Direct Reaction



anion. The anion S_7N^- has been reported to be stable below -63°C[51] but above this temperature reacts to give the perthionitrate anion. A summary of the derivatives of S_7NH prepared by this route is given in Figure I-5.

Figure I-5

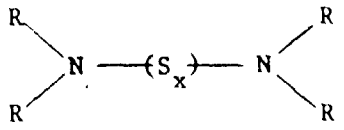
Derivatives of S_7NH Using Base Then Reagent



The condensation reaction of heptasulfurdichloride with $H_2NN(COOEt)$ has also resulted in a derivative of S_7NH[56] but this compound, $(S_7NN(COOEt)_2)$, has not been formed from S_7NH itself.

(c) The N-S-N and N-S-S-N Linkage

In light of the unusual bonding described above, it might be expected that the chemistry of some of these sulfur-nitrogen bonded species would be of interest. The N,N'-polythiobisamines XII for example have



$x = 1,2,3,4 \ldots$

XII

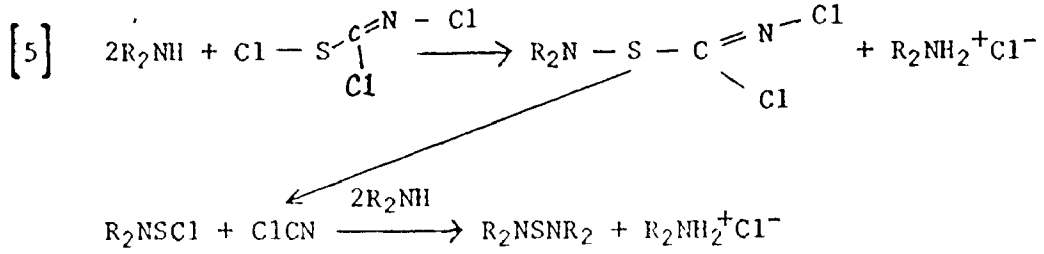
received considerable attention in the recent literature, perhaps due to their utility in the vulcanization of rubber[57] or polymerization of α-olefins[58]. Thompson[77] has reviewed the chemistry of these compounds, the largest amount of work being concentrated on the N,N'-thiobisamines (X=1 in XII above) or sulfoxylic diamides as these compounds are called in Chemical Abstracts.

(i) N,N'-Thiobisamines - Preparation, Physical Properties and Chemistry

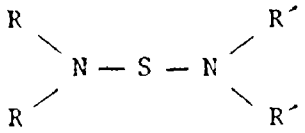
The N,N'-thiobisamines are most conveniently prepared from sulfur dichloride and a secondary amine[59].

$$[4] \quad SCl_2 + 4R_2NH \xrightarrow[\text{solvent (ether)}]{\text{cold inert}} R_2NSNR_2 + R_2NH_2^+Cl^- \downarrow$$

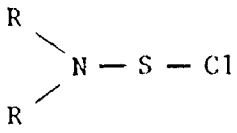
A related though less practical preparation of these compounds involves the use of thiocyanogen trichloride as in reaction [5] (60).



The preparation of the unsymmetrical thiobisamines, XIII

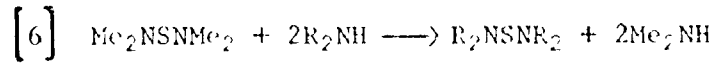


XIII

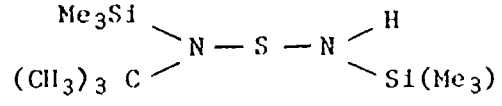


XIV

using N-sulfenyl chlorides XIV and amine has been shown to be generally unsatisfactory due to rearrangement of the product to give the symmetrical compounds. A trans-amination reaction [6] of these compounds



has been studied (61) and it is likely that this type of reaction hinders formation of the pure unsymmetrical N,N'-thiobisamines. There has been some success in preparing these compounds, however, and many are reported in the German patent literature (62). The compound XV has



XV

been prepared from N-(trimethylsilyl)-N-(t-butyl) - N - sulfenyl chloride[63] but here trans-amination is most likely sterically hindered. An unsymmetrical N,N'-thiobisamine XVI has been prepared by a different route involving the amide, rather than the amine, reacting with the sulfenyl chloride (reaction [7])[64]

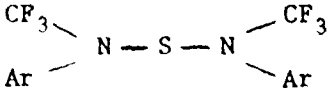
[7] $R_2NSCl + NaN(SiMe_3)_2 \longrightarrow R_2NSN(SiMe_3)_2 + NaCl$

R = Me, Et

XVI

The formation of N,N'-thiobisamines is actually quite a common reaction in that secondary amines will attack many sulfur compounds (e.g. S_4N_4, $ROSO_2SSSO_2OR$) to produce N,N'-thiobisamines as one constituent of a complex product mixture[59].

Stevens[65] has reported an interesting reaction [8] to produce N,N'-thiobisaryltrifluoromethylamines XVII in good yields.

[8] $Ar - N = C = S + IF_5 \longrightarrow$ 

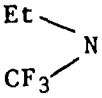
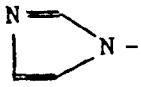
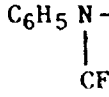
XVII

In general these compounds are colourless liquids or low melting solids with strong odours which are especially noticeable for the lower molecular weight derivatives. These compounds darken in air and must be distilled under reduced pressure to avoid decomposition at higher temperatures. They are, however, quite stable for weeks at -20°C. The Raman and infra-red spectra have been investigated in many

laboratories[66,67,68] with some variation in interpretation. A list of the physical properties of some of these compounds is given in Table I-4.

Table I-4

Physical Properties of Some N,N'-Thiobisdialkylamines (R_2NSNR) (reproduced from reference (77))

R_2N	mp (°C)	bp (°C at mm Hg)
Me_2N	20	36(14)
Et_2N	--	85(19)
Pr_2N	--	$41(10^{-4})$
	--	44(30)
Morpholino	125	--
	74	--
	111	--
$(cyclo\text{-}C_6H_{11})_2N-$	150	--
C_6H_5NH-	--	oil
$4ClC_6H_4NH-$	102	--
$4BrC_6H_4NH-$	106	--
$4NO_2C_6H_4NH-$	208	--
	54	--

A structure determination by electron diffraction has been carried out on the dimethylamine derivative, the results of which have already been discussed in the section concerning the sulfur-nitrogen bond. Analysis by X-ray diffraction has not been carried out for any of the molecules listed in Table I-4.

Alkyl derivatives of the N,N'-thiobisamines readily react with carbon disulfide and other reagents of the type X = C = Y to give insertion products. Some of these are described in reaction [9].

[9a] $R_2NSNR_2 + CS_2 \longrightarrow R_2NC(=S)-(S)_n-C(=S)-NR_2$

R_2N = morpholine $n = 3$ (70)

R_2N = piperidine $n = 2,6$ (69)

[9b] $R_2NSNR_2 + EtN=C=O \longrightarrow R_2NSN(Et)-C(=O)-NR_2$ (71)

[9c] $R_2NSNR_2 + MeN=C=S \longrightarrow R_2N-S-N(Me)-C(=S)-NR_2$ (71)

N,N'-Thiobisdimethylamine has been found to be sufficiently reactive to act as a sulfurizing agent (reaction [10]) (72).

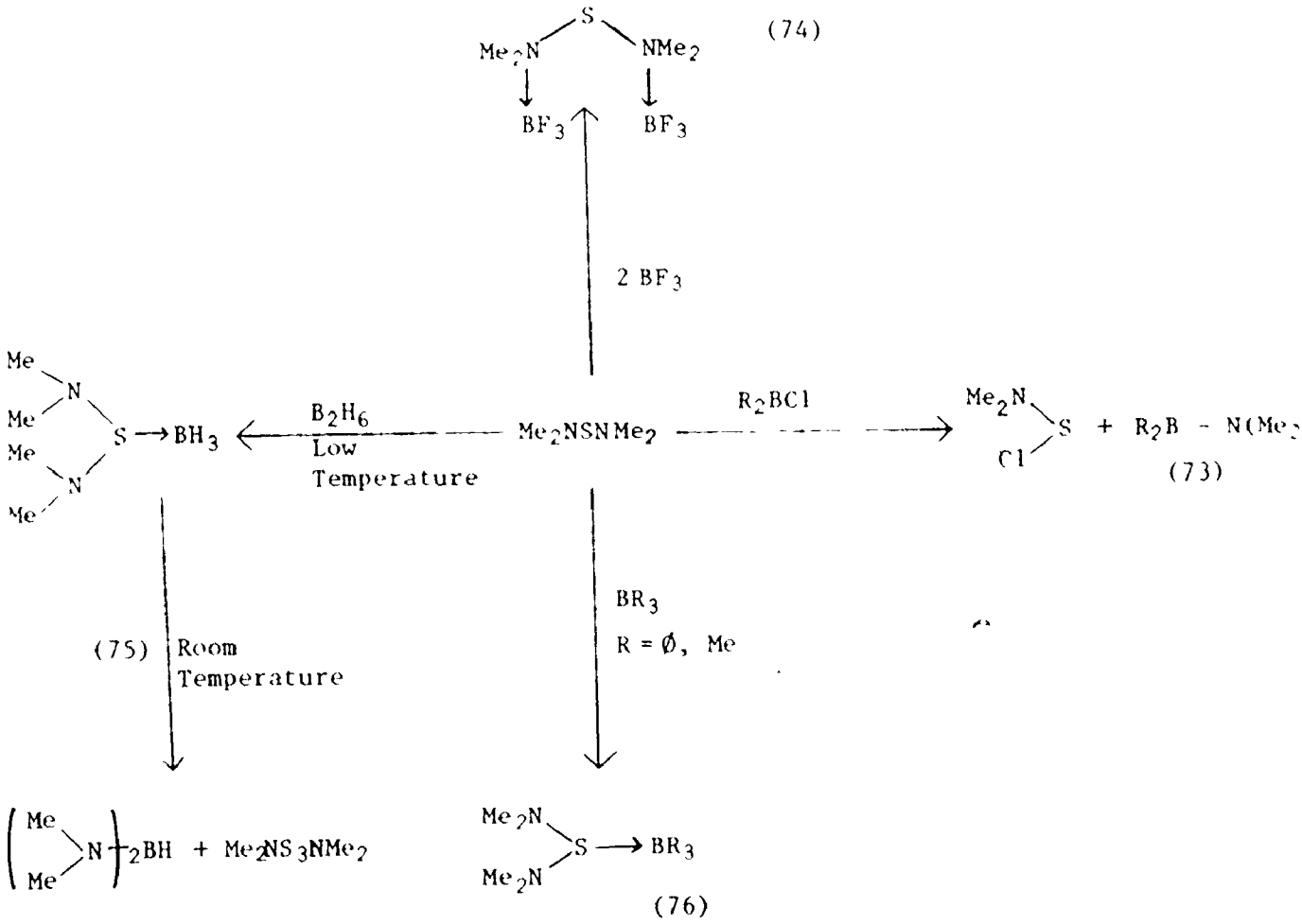
[10a] $2R_2NCH=C(H)-C(=O)H + Me_2NSNMe_2 \longrightarrow R_2NCH=C(H)-CHO$ (S) $R_2NCH=C(H)-CHO + 2Me_2NH$

[10b] $2CH_3C(O)CH(H)C(=O)OEt + Me_2NSNMe_2 \longrightarrow CH_3C(O)CH(C(=O)OEt)-S-CH(C(=O)OEt)C(O)CH_3 + 2Me_2NH$

The N,N'-thiobisamines have also been found to react with various inorganic reagents. N,N'-thiobisdimethylamine has been reported to react with a number of boron compounds, the reactions being shown in Figure I-6.

Figure I-6

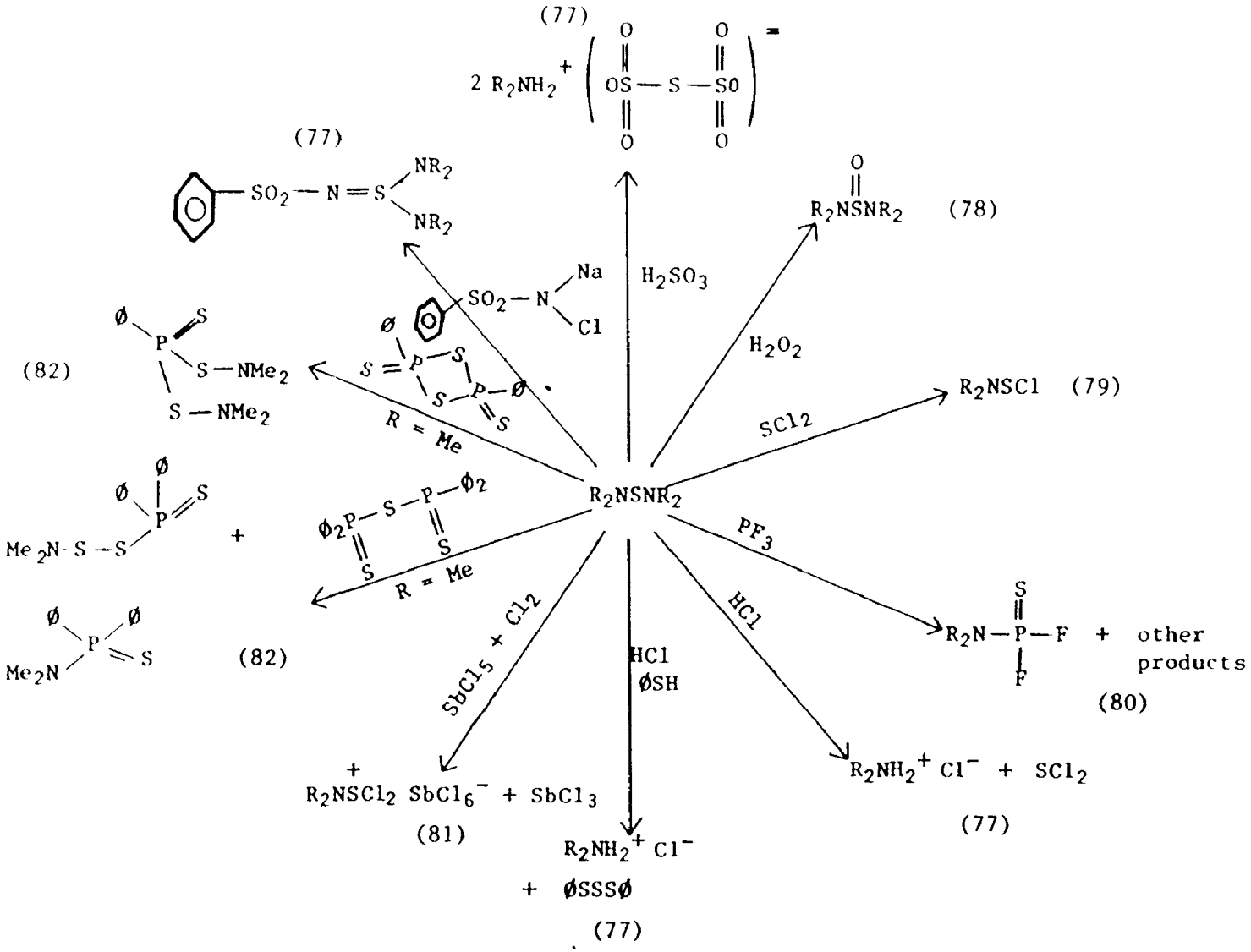
Reactions of N,N'-Thiobisdimethylamine with Boron Compounds



Many other reactions have been investigated and some of these are shown in Figure I-7. Some of these were taken from the review by Thompson[77] but other more recent reactions are also shown.

Figure I-7

Other Reactions of N,N'-Thiobisdialkylamines



Recent work[83] on the NMR spectra of the isopropyl and ethyl derivatives has shown that there is a barrier to sulfur-nitrogen bond rotation (10.3 to 11.4 kcal/mole) similar to that found in the sulfenamides IV mentioned earlier. The structure of the low energy rotomer is in agreement with the electron diffraction data[21] for the N,N'-thiobisdimethylamine in that the CNC planes are perpendicular to the NSN plane.

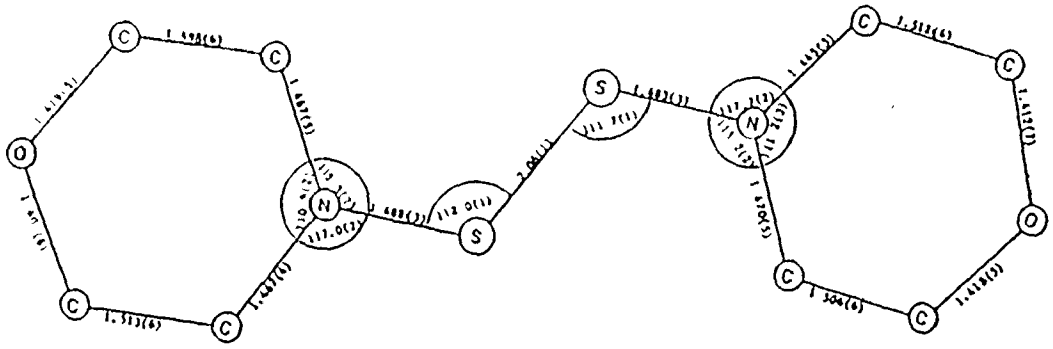
(ii) N,N'-Dithiobisamines - Preparation, Physical Properties and Chemistry

Many derivatives of the N,N'-dithiobisamines have been reported in the literature. Most frequently they have been prepared from the amine and sulfur monochloride in an inert solvent[84]. Other more economical synthetic procedures employing aqueous alkali[86,87] or water[85] as acid scavenger have been described. The reaction often produces the N,N'-thiobisamines or N,N'-polythiobisamines (I, X > 2) due to the rearrangement of the disulfide either during reaction or upon distillation. It has been suggested that minor amounts of $R_2N(S_x)Cl$ impurities catalyse this reorganization[69].

Like the N,N'-thiobisamines, the N,N'-dithiobisamines are clear liquids or low melting solids with a strong odour. The Raman and infra-red spectra of some have been studied[84,88]. An X-ray structure determination has been done on the morpholine derivative[4] and is presented in Figure I-8. Notice that the sum of the angles about nitrogen (343°) is intermediate between pyramidal and planar and that the sulfur-nitrogen bond lengths

Figure I-8

Crystal Structure of N,N'-Dithiobismorpholine[4]



(1.69 Å) suggest some double bond character. Dynamic NMR measurements have shown that there is a barrier to NS bond rotation as well as S-S bond rotation[83]. It was postulated that the kinetic effect observed at low temperature (-70 to -118°C) was due to hindered N-S bond rotation and that the S-S bond rotation was already slow on an NMR time scale at room temperature.

The physical properties of some simple N,N'-dithiobisamines are listed in Table I-5.

These compounds, like their monosulfur analogues, react with compounds of the type X = C = Y. Some examples which illustrate the complexity of the reaction are given in reaction [11].

[11a] $R_2NSSNR_2 + CS_2 \longrightarrow R_2NC(=S)(S)_xC(=S) - NR_2 + yS^o$

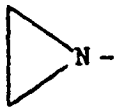
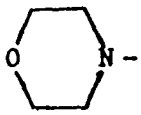
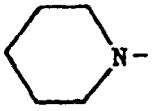
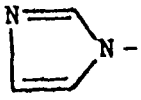
R_2N = morpholine x = 3 y = 1 (69)

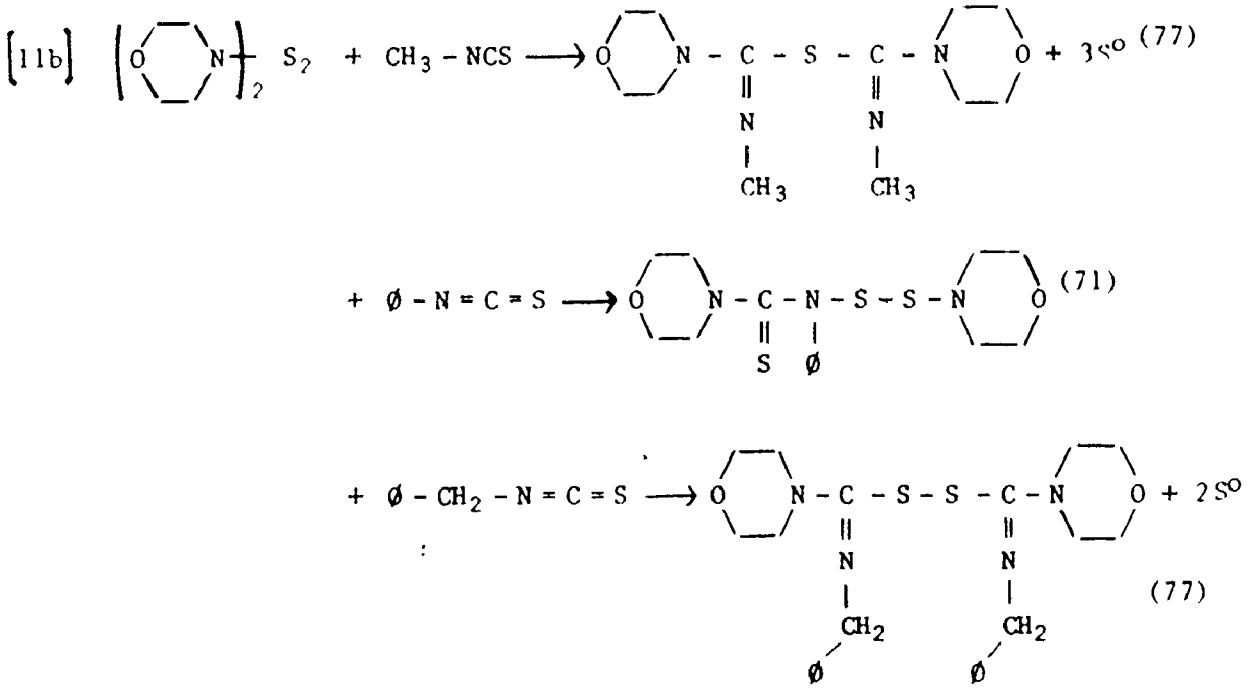
R_2N = piperidine x = 2,6 y = 0 (69,70)

Table I-5

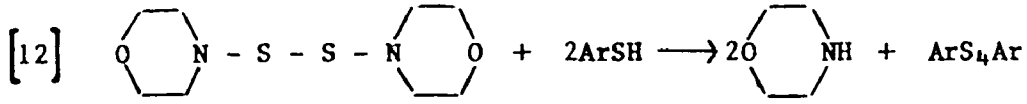
Physical Properties of Some

N,N'-Dithiobisamines[77]

R_2N -	mp (°C)	bp	(mm Hg)
$(CH_3)_2N$ -	--	82	22
$(C_2H_5)_2N$ -	--	137	29
$(n\text{-}C_3H_7)_2N$ -	--	oil	
$(iso\text{-}C_4H_9)_2N$ -	31	--	--
$(PhCH_2)_2N$ -	79	--	--
	--	46	0.03
	124	--	--
	64	--	--
	92		



Reactions related to rubber vulcanization and α-olefin polymerization have also been studied[77] for these compounds. Reaction [12] for example, has been implicated in rubber vulcanization processes which use accelerators containing N-S bonds. Thiols are found to catalyse vulcanization in these systems.



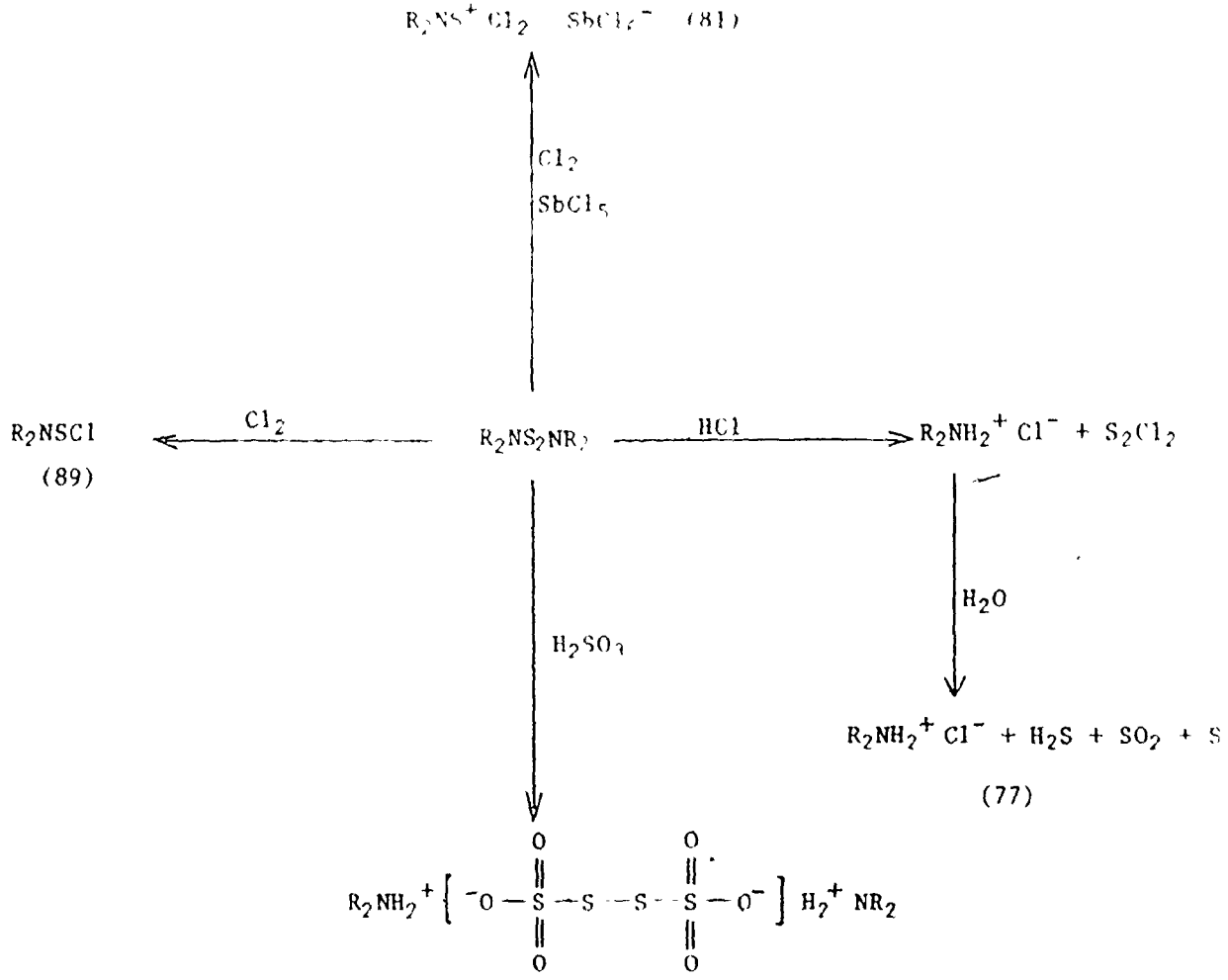
The N,N'-dithiobisamines are also found to react with many inorganic reagents and the products of these reactions are shown in Figure I-9.

I-2 INSERTION REACTIONS

The insertion reactions which are most commonly studied are those involved in metal co-ordination chemistry. The molecules CO, SO_2, CO_2, CS_2, $SnCl_2$, C_2H_4, C_2F_4 etc. have all been inserted into M-X (M=metal, X=metal, H,

Figure I-9

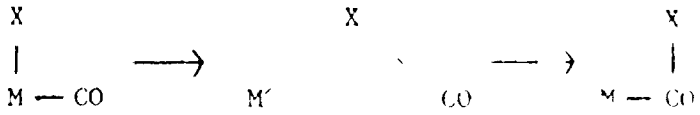
Inorganic Reactions of N,N'-Dithiobisamines



C, OH...) bonds[90]. These reactions are usually considered group transfer reactions in which the X substituent migrates from the metal to the inserted molecule via a three-centre transition state (example (I) in Figure I-10).

Figure I-10

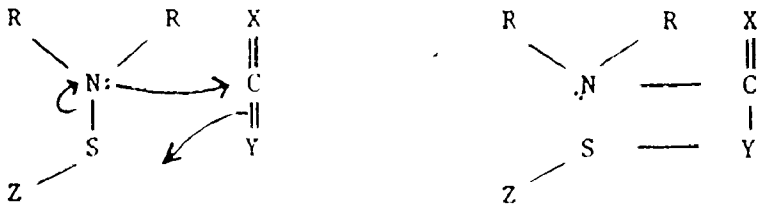
Group Migration in Insertion Reactions



It has already been pointed out, however, that molecules of the type X = C = Y can be inserted into sulfur-nitrogen bonds of N,N'-thio- and N,N'-dithiobisamines. The mechanism proposed[77] for this reaction is presented in Figure I-11.

Figure I-11

Insertion of X = C = Y into N - S Bonds



if R_2N = morpholine then Y = S and X = CH_3 - N

if R_2N = Et_2N then Y = CH_3 - N and X = S

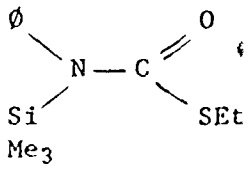
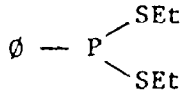
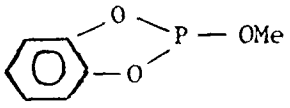
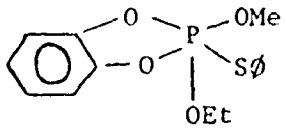
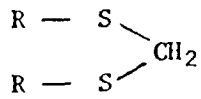
for Z = -S — NR_2

Other insertion reactions have been reported in which molecules have

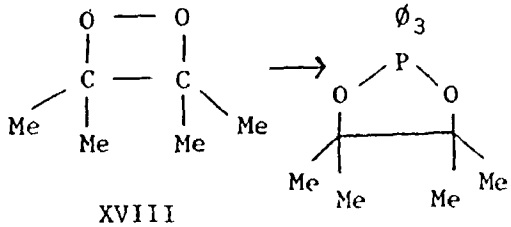
inserted themselves into S-X bonds. A few of these are shown in Table I-6.

Table I-6

Insertion Reactions into S - X Bonds

Inserted Molecule	Substrate	Product	Ref.
Ø - N = C = O	Me_3Si — SEt		(91)
[Ø - P:]	EtS — SEt		(92)
	EtO — SØ		(93)
CH_2I_2 + Zn/Cu	RS — SR		(94)

Phosphines and phosphites have been found to insert into the oxygen-oxygen bond of XVIII, (Reaction [13]) and it is conceivable that a similar

[13] (95) $Ø_3P$ + 

XVIII

reaction is the first step[96] in the desulfurization of organic disulfides by triphenylphosphine (reaction [14]). A similar reaction

$$[14] \quad \emptyset_3P + R - S - S - R \longrightarrow \emptyset_3PS + R - S - R$$

is used as an analytical method of determining aromatic disulfides in the presence of alkyl disulfides because of their large difference in reactivities (reaction [15])[97].

$$[15] \quad \emptyset_3P + RSSR + ArSSAr + H_2O \longrightarrow \emptyset_3PO + 2ArSH + RSSR$$

I-3 FOURIER TRANSFORM NMR AS APPLIED TO THE PHOSPHORUS NUCLEUS

(a) Fourier Transform NMR

As early as 1946, Block[98] suggested that there were many different ways in which to observe nuclear magnetic resonance. Three methods suggested were (a) "slow passage", (b)"adiabatic rapid passage", and (c) "pulse" techniques. The "slow passage" experiment is the method used normally to record routine spectra. "Adiabatic rapid passage" is used relatively infrequently, it being applied to weak samples. "Pulse" techniques have become more popular recently with the advent of reasonably priced commercially built spectrometers. The theory behind "pulse" techniques has been described by many authors[99] and will not be discussed here. Applications of pulse techniques include the study of relaxation times and the recording of spectra of weakly magnetic samples. These weakly magnetic samples can occur either because the isotope being observed is

present only in small abundance (eg. ^{13}C) or because the sensitivity of the nuclei is considerably lower (eg. ^{13}C, ^{31}P) than for nuclei studied normally by slow-passage techniques (eg. ^{1}H, ^{19}F).

In general, "pulse" NMR spectra are observed in the following manner. Rather than slowly sweeping the sample with a radio frequency in a fixed magnetic field (frequency sweep spectra), a strong square wave pulse of radio frequency is applied to the sample. This pulse can be broken down into its Fourier components and be represented as a range of frequencies depending on the duration of the pulse. The frequencies found in the pulse fall into the range $\nu \pm \frac{1}{tp}$ where ν is the monochromatic frequency and tp is the duration of the pulse. After excitation, a detector shows that the magnetic nuclei exponentially decay back to equilibrium. If the radio frequency ν is not precisely at the resonance frequency of the nuclei and is also applied to the detector, the output signal observed will be an interference pattern made up of the applied and resonance frequencies. This signal is then Fourier analysed by computer, to produce the normal output signal versus frequency spectrum.

Since the whole NMR spectrum is recorded after each pulse and the results computer analysed, the time required to obtain a single scan is much shorter. Many scans can be recorded and stored in order to increase the signal to noise ratio of the NMR spectrum. While a continuous wave spectrum may take hundreds of seconds to run each scan, the pulse NMR spectrum is about two orders of magnitude faster. This makes it very useful in the recording of spectra of weakly magnetic samples.

(b) Application of the ^{31}P Nucleus

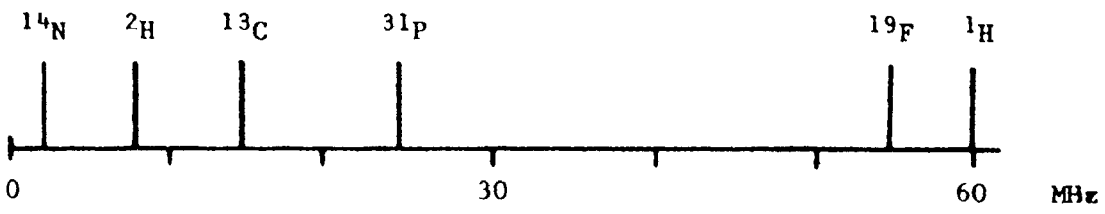
The only stable isotope of phosphorus (^{31}P) has a spin of ½ and sensitivity of approximately 0.405 times[100] that of protons. When atomic weights are taken into consideration, however, an approximately 75-fold increase in weight of magnetic sample (^{31}P nuclei) is necessary for spectra equivalent to proton spectra. Often the NMR samples cannot accommodate this experimental difficulty for reason of solubility, sample tube size, etc. By using the "accumulation of several spectra" aspect of Fourier transform pulse NMR, the quality of the ^{31}P NMR spectra is greatly increased when compared to continuous wave spectra.

(c) Characteristics of ^{31}P NMR Spectra

Although the ^{31}P nucleus suffers somewhat in sensitivity, the usefulness of this nucleus is enhanced by the characteristic of phosphorus in its compounds of forming the "backbone" of the molecule. In this respect possibly the ^{13}C and ^{31}P NMR spectra supply more information than a ^{1}H or ^{19}F spectrum. The magnetogyric ratio of 1.082×10^{4} gauss^{-1} sec^{-1} places the resonance frequency of the ^{31}P nucleus (in a field of 14,092 g) at 24.288 Mhz. This is compared to some other magnetic nuclei in Figure I-12.

Figure I-12

Resonance Frequencies of Magnetic Nuclei (H_o = 14,092 g)[101]

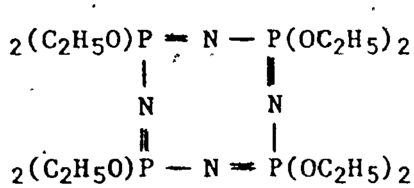
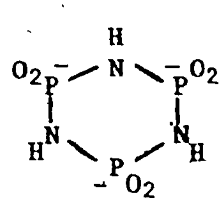


The best discussion of ^{31}P NMR spectra is that given by Crutchfield et al [102]. This reference also contains an extensive collection of experimental data.

The range of chemical shifts of the ^{31}P nucleus is quite large, from -229 ppm for PBr_3 to + 450 ppm for P_4 with reference to 85% phosphoric acid (negative chemical shifts at low field). To a first approximation, ^{31}P chemical shifts are determined by the number and kinds of atoms immediately adjacent to phosphorus in the molecule and are unaffected by the charge. Examples to support this are given in Table I-7 for 4 co-ordinated phosphorus. It should be noticed that the compounds (a) to

Table I-7

^{31}P NMR Chemical Shifts of Some Phosphorus Compounds [102]

(a)	$(H_2N)_2PO_2^-$	+ 4 ppm
(b)	$((C_6H_5)_2N)_2PO_2^-$	+ 4 ppm
(c)	$((CH_3)_2N)_2(O)P-O-P(O)[N(CH_3)_2]_2$	- 11 ppm
(d)		+ 1 ppm
(e)		+ 4 ppm
(f)	$SP(OC_2H_5)_2O^-\ Na^+$	- 57 ppm
(g)	$SP(OC_2H_5)_3$	- 68 ppm
(h)	$OP(OCH_3)_3$	- 2 ppm
(i)	PO_4^{3-}	- 6 ppm

(c) (Table I-7) all have similar chemical shifts. Even replacement of an imido group (e) by a nitrilo group (d) does not affect the chemical shift. If, however, a highly polarizable group like sulfur (f,g) is introduced, there is a large change in chemical shift as well as an increase in the range over which the chemical shifts of these compounds are found. The lack of a charge effect on the chemical shift is illustrated by the fact that the ^{31}P chemical shift hardly changes between the triply-charged phosphate anion (i) and the neutral trimethyl-phosphate (h)[102].

Phosphorus shows coupling to many kinds of magnetic ligands. Table I-8 contains some compounds with some typical coupling constants.

Table I-8

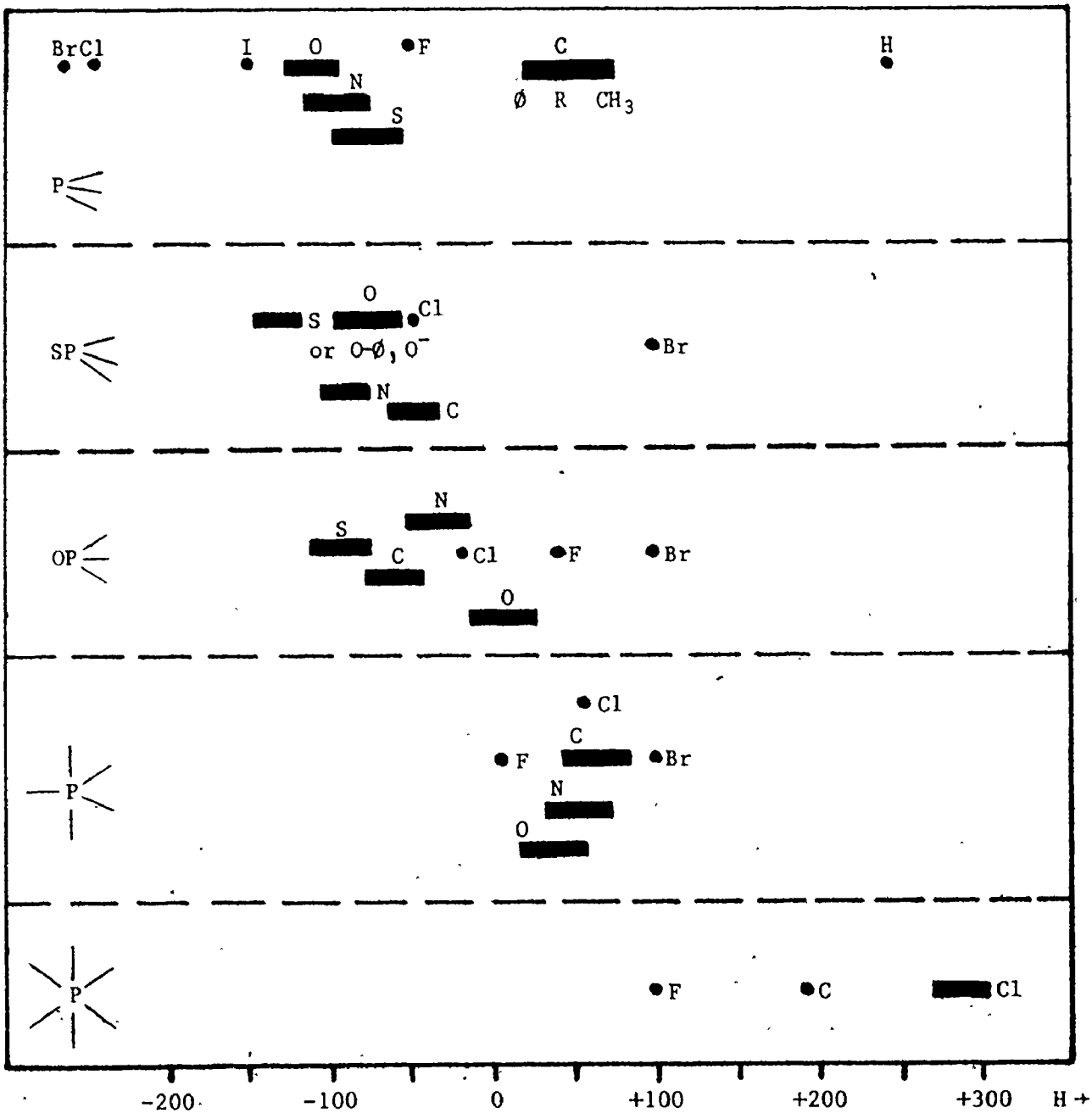
Coupling Constants to Phosphorus

Substituent	Compound	Coupling Constant (Hz)[102]
P — H	PH_3	$J_{P-H} = 180.4$
	CH_3PH_2	$J_{P-H} = 186$
P — CH	$P(CH_3)Br_3$	$J_{PH} = 19.3$
	$P(CH_3)_3$	$J_{PH} = 2.66$
P — N(CH$_3$)(CH$_3$)	$P(N(Me)_2)_3$	$J_{PH} = 8.9$
	$SPCl_2(NMe_2)$	$J_{PH} = 17.2$[105]
P — F	PF_3	$J_{PH} = 1400$
	$H^+ PF_6^-$	$J_{PH} = 710 - 855$
P — CF	$P(CF_3)$	$J_{PH} = 85.5$
	$P(CF_3)_2F$	$J_{PH} = 89.6$

Figure I-13 shows the range of chemical shifts for different types of phosphorus molecules. Notice that in general there is a shift to high

Figure I-13

Chemical Shifts of Phosphorus Containing Molecules[102]



field as the number of substituents increases. Also for any particular type of molecule, the polarizable ligands (or π-bonding ligands) shift the ^{31}P resonance to lower field. Van Wazer et al[103] have shown that while the substituent effect is not quite additive, it is often quite predictable. They have broken down the chemical shifts of various types of phosphorus compounds into σ- and π-bonding components. The π-bonding components they have suggested arise from electron occupation of d-orbitals on phosphorus. The chemical shifts have been related to electronegativities of substituents, π-bonding abilities of substituents and the angles between substituents.

I-4 CHROMATOGRAPHY

Reactions of sulfur compounds often produce many products even when simple reactions are expected. For this reason, chromatography has often been used in this field. The sulfur imides, for example, are prepared as a product mixture and then separated using adsorption chromatography. Thin layer adsorption chromatography is also often used in sulfur chemistry as a method of checking purity (S_8 in S_7NH).

Often sulfur compounds have very little interaction with the typical adsorption column materials (alumina, silica). As a result long columns of very active packings are used in conjunction with very poor eluting solvents (hexane, CS_2, benzene). This problem may be solved with the utilization of preparative scale molecular exclusion chromatography[104]. These columns elute in order of increasing molecular weight and therefore give much better separation than typical absorption columns for non-polar

compounds. Also the packing material (typically polystyrene) is more inert to sulfur compounds and therefore does not catalyse decomposition (for example, alumina decomposes $S_7NS_xNS_7$)[104].

I-5 AIMS OF PRESENT WORK

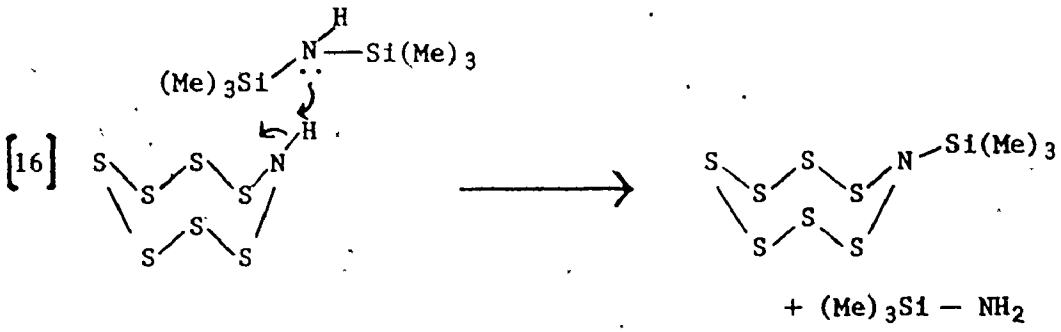
The above discussion has shown that sulfur-nitrogen chemistry has received some attention over the past few years but that there is still much to be learned. Preliminary work on the general chemistry of the N,N'-thiobisdialklyamines (N,N,N',N'-tetralkylsulfoxylicdiamides) and N,N'-dithiobisdialkylamines showed that these molecules underwent many types of reactions which were as yet unreported in the literature. The reactions of these molecules with heptasulfurimide and chlorophosphines were chosen for further study since these reactions could be conveniently followed using many spectroscopic techniques.

CHAPTER II

PREPARATION AND CHARACTERIZATION OF THE N,N-DIALKYL-N',N'-CYCLOHEPTATHIOSULFOXYLIC DIAMIDES (XIX)

II-1 PREPARATION, STABILITY AND PHYSICAL PROPERTIES

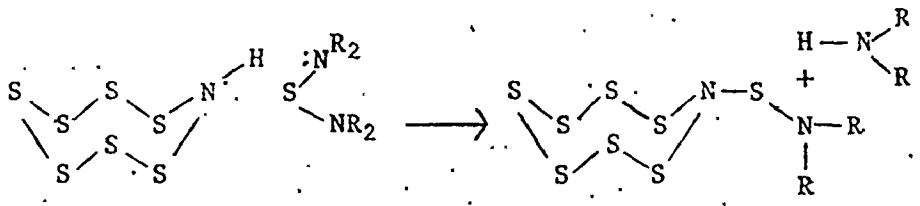
In the introduction, it was mentioned that a derivative of S_7NH can be prepared using bis-trimethylsilylamine[47]. This reaction involves donation of a proton from the protic acid heptasulfurimide to the basic amine [16]. The fact that an amine is strong enough



to abstract this proton is proven by the fact that S_7NH in hexamethylphosphoramide, ammonia or pyridine gives solutions containing the blue S_4N^- ion, the decomposition product of the S_7N^- anion.

A similar reaction to [16] above occurs when N,N'-thiobisdialkylamines are allowed to come into contact with the imide. The N — S — N linkage formally contains four lone pairs which may be basic enough to abstract the acidic proton from S_7NH. In the introduction, it was suggested that the nitrogen lone pairs of the sulfoxylic diamides

(N,N'-thiobisamines) may be involved in pπ-dπ bonding to the sulfur. This does not decrease the basicity of the molecule, however, since it reacts quickly with weak acids such as acetylacetone or thiourea. Heptasulfurimide is also quite reactive, the products being shown in [17].

[17] 

XIX

The methyl, ethyl, isopropyl and cyclohexyl derivatives of XIX have been prepared. The melting points and analytical data are given in Table II-1. Elemental analysis was obtained only for three of the derivatives, the fourth (R = ethyl) not being sufficiently stable at room temperature. All four compounds are pale yellow solids which are best recrystallized from pentane. They are extremely soluble in other typical organic solvents (benzene, chloroform, methylene chloride, carbon disulfide).

The ease with which these compounds could be prepared was a function of the size of the alkyl groups attached to the nitrogens of the N,N'-thiobisdialkylamine. Reaction occurred at room temperature when there was only methyl groups attached whereas the di-isopropyl and di-cyclohexyl analogues required warming to 40°C to get the reaction to proceed at a reasonable rate.

The yields of the derivatives became smaller as the alkyl

Table II-1

Melting Points and Analytical Data for S_7NSNR_2

	Melting Point		Analysis
$S_7NSN\,Me_2$	55°C	calculated	S(81.70%),N(8.88%),C(7.76%),H(1.87%) S(81.54%),N(8.91%),C(7.63%),H(1.92%)
$S_7NSN\,Et_2$	30°C		
$S_7NSN\,iPr_2$	66°C	calculated	S(66.35%),N(7.65%),C(19.49%),H(3.80%) S(69.21%),N(7.56%),C(19.42%),H(3.81%)
$S_7NSN\,cHexyl_2$	some decomposition at 89°C, melts at 97 - 98°C.	calculated	S(56.77%),N(5.86%),C(32.08%),H(4.78%) S(56.91%),N(6.22%),C(31.95%),H(4.92%)

groups became larger since reaction at the higher temperatures necessary for these bulky groups caused decomposition of the products. Heating above 60°C caused much red colouration in the reaction mixture and poorer yields after chromatography.

Even though the compounds were not very active towards silica gel, they were easily separated from decomposition products and reactants since they were the very first compounds off the column. The first faint yellow colouration of the eluent solvent signalled the presence of compound XIX. Hexane was used as eluent due to its very low polarity but even then long columns were necessary to separate XIX from its major contaminants, the N,N'-polythiobisdialkylamines. Final purification was effected by recrystallization from pentane at -20°C. Recrystallization of the ethyl compound was more difficult than the others due to its low melting point (30°C). Typical yields were over

80% for the methyl derivative and about 60% for the cyclohexyl, isopropyl or ethyl derivatives.

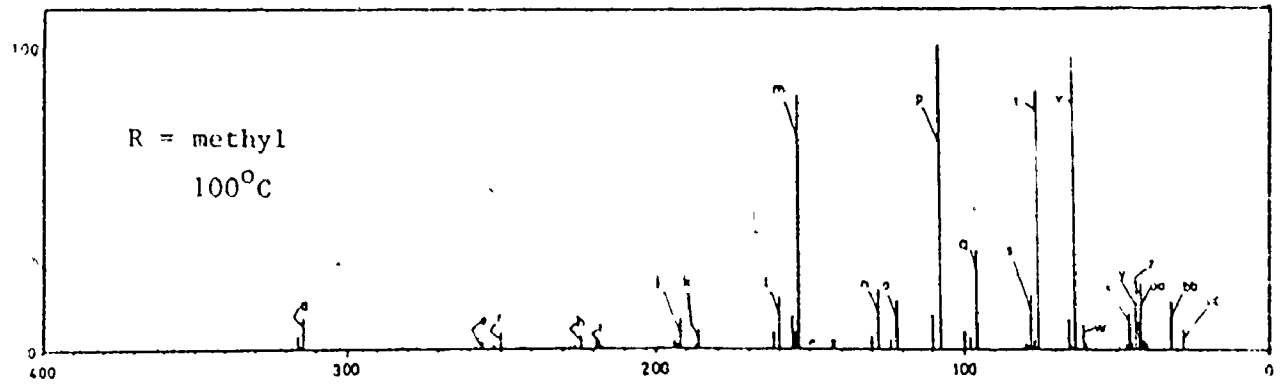
The compounds were all stable at -20°C after purification by recrystallization but rather unstable at higher temperatures. The methyl compound was most stable, approximately two months at room temperature with little decomposition. The cyclohexyl and isopropyl derivatives were reasonably stable, lasting two to three weeks at room temperature. The ethyl compound was quite unstable, decomposing in less than a week if special care was not taken. The ethyl compound decomposed more rapidly when molten than when crystalline. As would be expected, these compounds were unstable towards acidic protons (water, acid, etc.). They were also unstable towards light. Even the methyl derivative decomposed in a few days when exposed to direct sunlight.

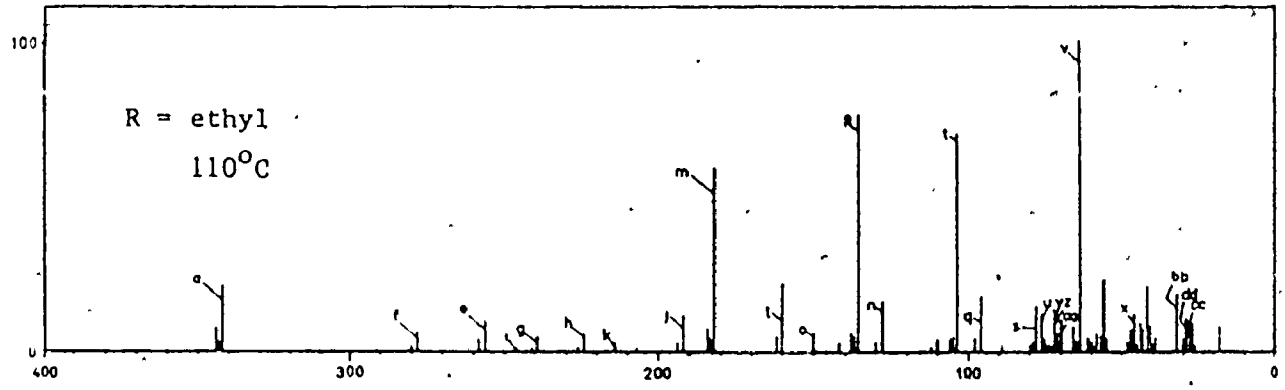
II-2 MASS SPECTRA

Mass spectrometry was used to study the N,N -dialkyl - N',N'-cycloheptathiosulfoxylic diamides. At temperatures necessary for vaporization of the cyclohexyl derivative, decomposition occurred and the spectrum showed only elemental sulfur and N,N'-polythiobisdicyclohexyl amines. Typical mass spectra for the other three derivatives (methyl, ethyl, isopropyl) are given in Figure II-1. Table II-2 contains the key to peak assignments made in Figure II-1 and shows that the parent peaks of these compounds are readily observed. The large P+2 isotope peaks due to ^{34}S (4.76% nat. abundance)[105] are not

Figure II-1

Mass Spectra of S_7NSNR_2





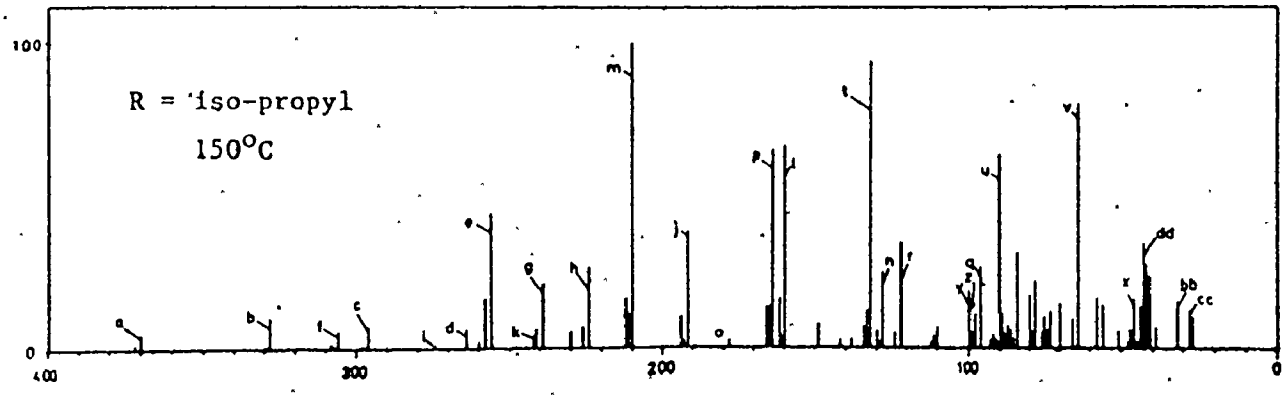


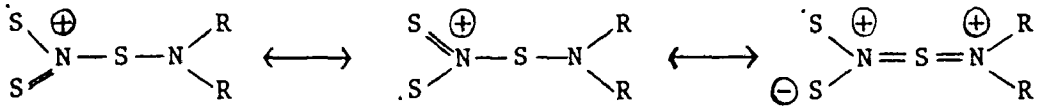
Table II-2

Mass Spectra Assignments - S_7NSNR_2 (R = methyl, ethyl, isopropyl)

	Fragment	R = Methyl		R = Ethyl		R = iPropyl	
		Intensity	Molecular Weight	Intensity	Molecular Weight	Intensity	Molecular Weight
a	S_7NSNR_2	10	314	21	342	5	370
b	$R_2NS_4NR_2$					10	328
c	$R_2NS_3NR_2$					7	296
d	$R_2NS_2NR_2$					6	264
e	S_8	2	256	10	256	44	256
f	S_5NSNR_2	6	250	6	278	5	306
g	S_7NH			5	239	21	239
h	S_7	4	224	7	224	23	224
i	S_4NSNR_2	3	218	2	246	2	274
j	S_6	10	192	12	192	38	192
k	S_3NSNR_2	6	186	5	214	4	242
l	S_5	17	160	22	160	66	160
m	S_2NSNR_2	83	154	59	182	100	210
n	S_4	19	128	16	128	23	128
o	$SNSNR_2$	16	122	6	150	3	178
p	S_2NR_2	100	108	76	136	65	164
q	S_3	32	96	18	96	26	96
r	S_2NRH					34	122
s	NS_2	18	78	15	78		
t	SNR_2	86	76	70	104	94	132
u	SNRH			16	76	63	90
v	S_2	97	64	100	64	80	64
w	SNR	8	61				
x	SN	12	46	12	46	14	46
y	NR_2	15	44	14	72	18	100
z	NR_2 - 1H	9	43	6	71	5	99
aa	NR_2 - 2H	22	42	10	70		
bb	S	16	32	18	32	15	32
cc	N_2	6	28	10	28	12	28
dd	R			10	29	34	43

given in Table II-2 but are shown in Figure II-1. The fact that many of the peaks in the three mass spectra can be assigned to a common fragment (Table II-2) shows that their fragmentation patterns are quite similar. This pattern indicates that ionization is often accompanied by loss of a Sy fragment where y = 2,3,4,5 or 6. Loss of only one sulfur atom never occurs upon ionization. Although these sulfur molecules are all observed in the mass spectra, they may be derived from elemental sulfur (S_8) which is also observed. As the alkyl groups become larger, the peaks corresponding to elemental sulfur become stronger in comparison to the peaks derived from the parent ion.

When Sy (y = 2,3,4,5 or 6) is lost from the parent ion, the fragment left is $S_{7-y}NSNR_2$. The most intense peak corresponds to y = 5 (peak m, Table II-2, Figure II-1). The enhanced stability of this ion can be attributed to the resonance structures shown below.

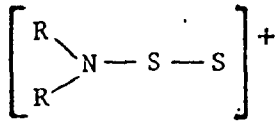


The other peaks corresponding to $S_{7-y}NSNR_2$ (y = 2,3,4 and 5) are also quite strong suggesting that these ions may be stabilized in a similar fashion.

Another very strong peak in the mass spectra corresponds to loss of the entire S_7N ring leaving the R_2NS cation (peak t, Figure II-1, Table II-2). It is expected that this would be a common

fragment since the cation should be quite stable. Structural evidence to be presented later in this chapter (section II-5) suggests that the NS bond between the SNR_2 fragment and the ring is much weaker than other NS bonds in the molecule. Breaking at this bond upon ionization is therefore expected.

The peak corresponding to S_2NR_2 (peak p, Table II-2 Figure II-1) is also found to be very strong in the mass spectrum of all three derivatives. This is somewhat unusual since this fragment, XX, is not found in



XX

the framework of the original molecule. This fragment could arise from decomposition products (the N,N'-polythiobisdialkylamines) or by rearrangement of the parent molecule. The former is unlikely for the methyl and ethyl derivatives since molecular ions are not observed for the N,N'-polythiobisdialkylamines (alkyl = methyl, ethyl) although these compounds are quite volatile. Therefore, a rearrangement is indicated here although it is not obvious how it could occur or why it is so prevalent.

The isopropyl derivative had to be heated to 150°C to obtain a reasonable mass spectrum. The peaks corresponding to the N,N'-polythiobisdiisoproplyamines (peaks b,c,d; Figure II-1, Table II-2) were observed in this case. This suggests that some decomposition had

occurred. For this derivative (R = i-Propyl), the mass spectral peak corresponding to R_2NS_2 (peak p, Table II-2, Figure II-1) could be derived from the N,N'-polythiobisdiisopropylamines. The masses 264, 296 and 328 were assigned to the N,N'-polythiobisdialkylamines rather than to $S_{7-y}NSN\langle^{R}_{H}$ (which has an identical molecular weight) on the basis of the P + 2 isotope peak heights. The observed P + 2 heights were much smaller than those in $S_{7-y}NSN\langle^{R}_{R}$ although it would be expected that they be almost exactly the same. These smaller P + 2 peak heights, however, would be expected for the N,N'-polythiobis-dialkylamines since they contain fewer sulfur atoms.

Infra-red Spectra

Infra-red spectroscopy was quite useful in studying these compounds. Table II-3 contains the infra-red data for the N,N'-dialkyl-N',N'-cycloheptathio-sulfoxylic diamides XIX as well as that of N,N'-thiobisdimethylamine (N,N,N',N'-tetramethylsulfoxylic diamide). Comparison of the infra-red spectra of compounds XIX with the IR spectra of the N,N'-thiobisdialkylamine from which it was derived showed that the spectra were very similar. The only major difference was the presence of a very strong band around 700 cm^{-1} in the spectra of compounds XIX. This somewhat broadened band most likely corresponds to the two unresolved SN stretching modes associated with the ring. A similar strong band is observed in other hepta-sulfurimide derivatives (e.g. S_7N Methyl, $\nu_{SN} = 760\ cm^{-1}$)[106] or in the imide itself ($\nu_{SN} = 815\ cm^{-1}$)[40].

Table II-3

Infra-red Spectra of S_7NSNR_2 and $((Me)_2N)_2S$, (R = Me, Et, iPr, cHex)

Me_2NSNMe_2 Oil	S_7NSNMe_2 Solution(CS_2)	S_7NSNMe_2 Solution(CCl_4)	S_7NSNEt_2	$S_7NSNiPr_2$ Solution(CS_2)	$S_7NSNiPr_2$ Solution(CCl_4)	$S_7NSN(cHex)_2$ Oil	Assignment
2980 (4)	3000 (2)	3000 (1)	2980 (10)	2980 (10)	2975 (10)		
2920 (7)	2940 (7)	2940 (6)	2940 (8)	2940 (7)	2930 (6)	2930 (10)	
2860 (7)	2905 (4)	2910 (3)	2860 (7)	2880 (4)	2880 (3sh)		
	2890 (4)	2892 (3)					ν_{C-H}
2810 (5)		2865 (3)				2845 (8)	
	2820 (3)	2838 (2)		↑			
2780 (5)	2790 (2)	2789 (2)					
	↑ S ↓			S			
1442 (5b)		1464 (2)	1460 (5b)	↓			
	1440 (10)	1442 (6)	1445 (6)	1438 (5)	1452 (4)	1438 (4)	
			1375 (8)	1376 (6)	1380 (5)		δ_{CH}
			1343 (4)	1360 (8)	1363 (6)	1360 (2)	
			1295 (5)	1350 (5)	1352 (4)	1340 (2b)	
				1324 (2)			
1230 (3)	1250 (1)					1248 (1)	
1190 (6)	1194 (4)	1193 (3)	1185 (7)	1188 (7)	1188 (6)		
			1170 (8)	1170 (8)	1165 (7)	1153 (3)	
1125 (2)				1153 (7sh)	1150 (6sh)		
				1113 (7)	1110 (7b)		
			1060 (8)	1088 (3sh)	1090 (6b)	1052 (6)	
1030 (4)	1028 (2)	1026 (2)	1040 (7)	1003 (5)	1001 (3)	1020 (2)	
960 (6)	978 (9)	975 (9)		976 (8)	975 (8)	975 (5)	
938 (10)			930 (6)	930 (1)			
				874 (1)			
		↑				883 (3)	
		S			↑	847 (1)	
	765 (4)		775 (9)	770 (5)	S		
		↓				770 (3)	
	*716 (10)	*716 (10)	*710 (10)	*695 (9)	*700 (9)	*690 (6)	
632 (7)	672 (5)	670 (10)	650 (8)				ν_{S-N} of ring
			635 (6)	626 (3)	620 (2)		

(frequencies in wavenumbers(cm^{-1}))

* Indicates NS stretching modes of the sulfur-nitrogen ring.

Me = methyl, Et = ethyl, iPr = isopropyl, cHex = cyclohexyl, b = broad, sh = shoulder

Relative intensities given in brackets. Oils run in KBr, solution in NaCl. ν = stretch, δ = bend.

The experimental chapter contains reproductions of the spectra of the compounds for "fingerprinting" purposes. Assignment of the peaks in Table II-3 was not attempted other than for the most obvious peaks. There are four sulfur-nitrogen bonds which would be expected to give vibrational modes coupled to one another as well as to other vibrations in the molecule. There is even some disagreement as to the assignment of the bands at 630 - 660 cm^{-1} and 940 - 1000 cm^{-1} in the spectra of the N,N'-thiobisdialkylamines. One author[67] believes the low frequency band arises from the SN stretches and the high energy band belongs to the $N\begin{smallmatrix}C\\C\end{smallmatrix}$ stretching modes. The other author[68] has reversed these assignments. Therefore, these molecules cannot be used for comparison to assign the IR spectra of compounds XIX. Later in this chapter structural analyses will be discussed of compounds belonging to both of these classes. From this it can be shown that one of these assignments (the latter) is more reasonable than the other.

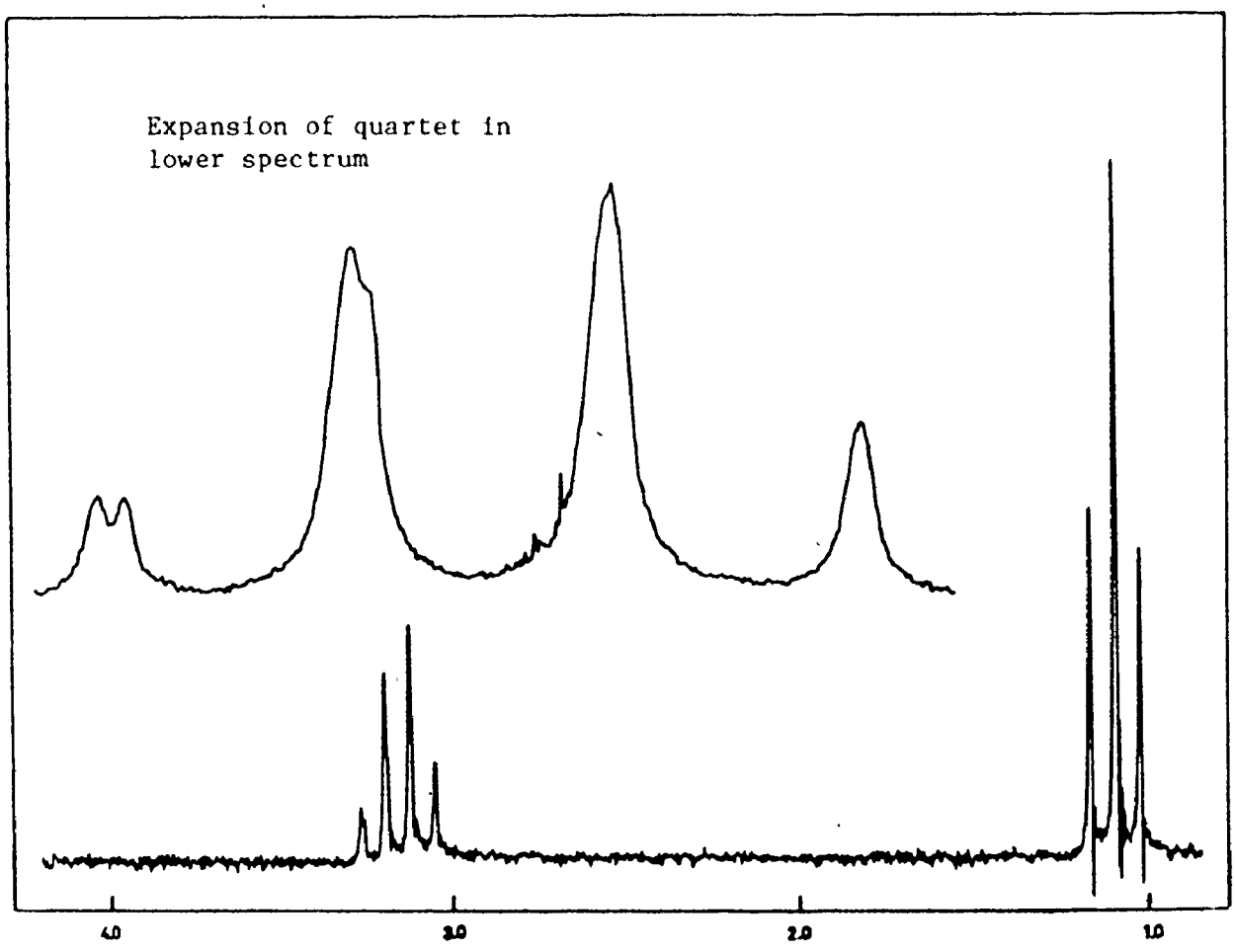
II-4. NUCLEAR MAGNETIC RESONANCE MEASUREMENTS

The most interesting of all the physical measurements performed on these compounds involved the use of NMR spectroscopy. While the NMR spectrum of the methyl derivative showed no unusual features, it consisting of a singlet at +3.08 ppm, the other derivatives gave more complex spectra. The ethyl derivative gave a room temperature NMR spectrum at 100 MHz which could be resolved into two closely overlapping quartets (δ = +3.16 ppm, J = 7.4 Hz,

δ = +3.15 ppm, J = 7.1 Hz) and one triplet (δ = +1.09 ppm. J = 7.2 Hz) (Figure II-2). The NMR spectrum of the isopropyl compound was easily

Figure II-2

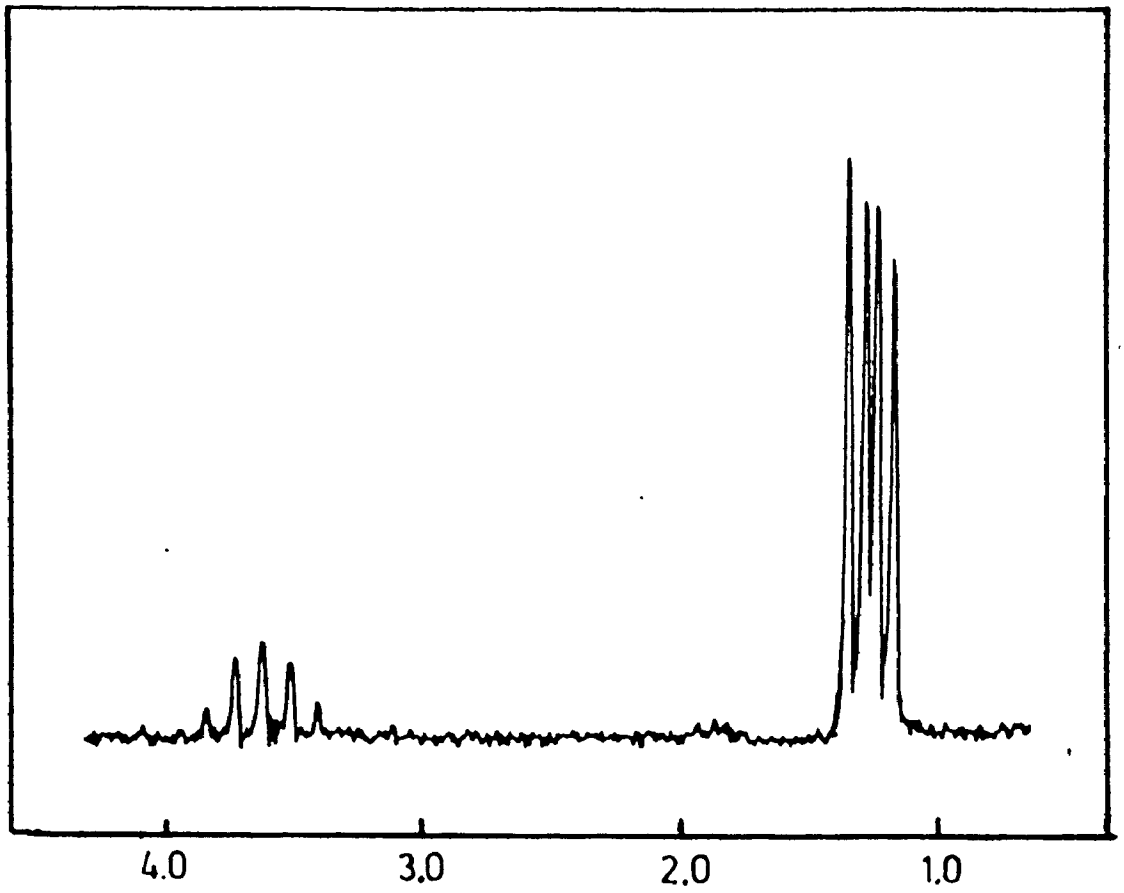
^{1}H NMR Spectrum of S_7NSNEt_2 at 100 MHz



resolved at 60 MHz into two doublets (δ = +1.14 ppm, J = 6.5 Hz, δ = +1.31 ppm, J = 6.5 Hz) and a septet (δ = +3.64 ppm, J = 6.5 Hz) (Figure II-3). At 80°C the two doublets begin to coalesce but sample decomposition at this temperature prevented collection of useful

Figure II-3

^{1}H NMR Spectrum of $S_7NSN(iPr)_2$ (60 MHz)

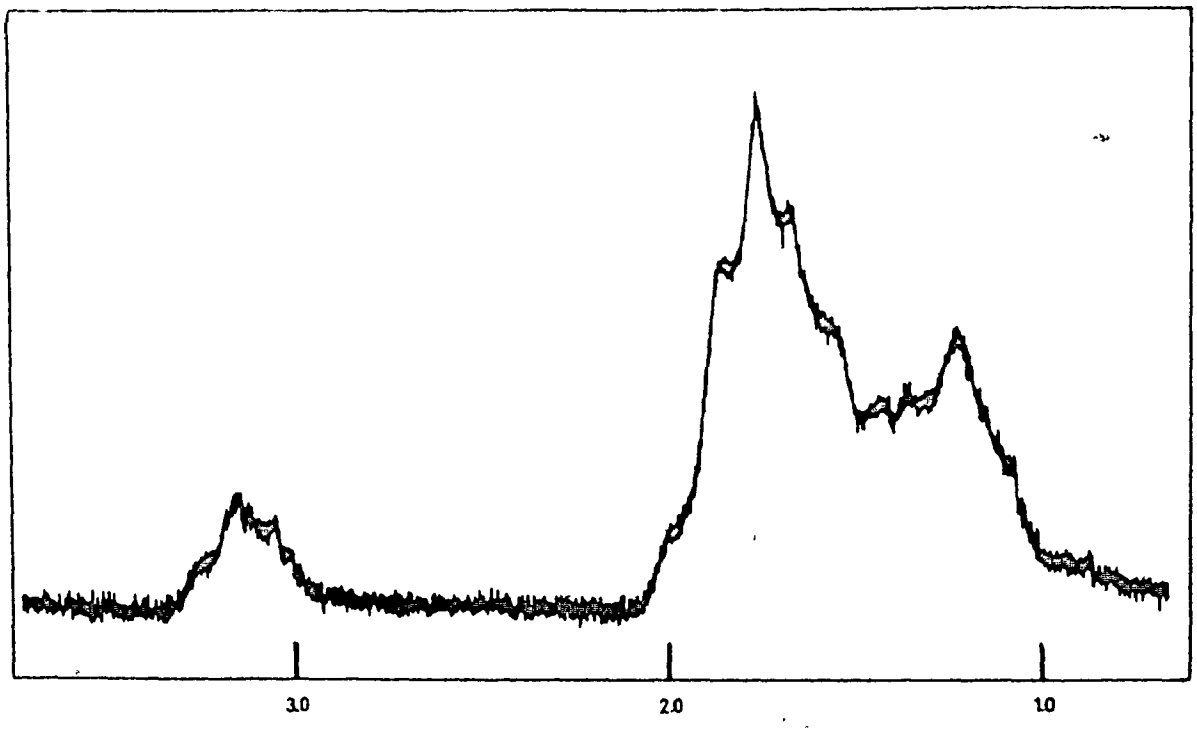


dynamic NMR coalescence spectra.

The ^{1}H NMR spectrum of the cyclohexyl derivative was a very complex proton-coupled multiplet as shown in Figure II-4 and was not very useful in characterizing the compound. The proton decoupled ^{13}C NMR spectrum, however, showed six peaks of equal intensity (δ = +66.9, +34.8, +33.3, +26.2, +26.0, +25.5 ppm relative to TMS) rather than the expected four peaks of relative intensity 1:2:2:1. The ethyl, isopropyl

Figure II-4

^{1}H NMR Spectrum of $S_7NSN(cHexyl)_2$ (100 MHz)

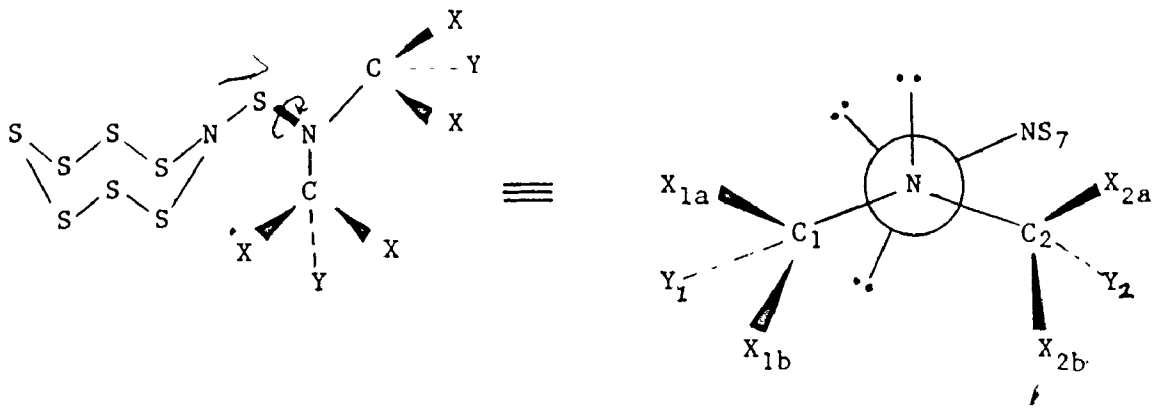


and cyclohexyl derivities therefore all show peculiarities in what at first glance should be very simple NMR spectra. These peculiarities could arise in a number of different ways.

The first possibility which should be investigated is that the two groups attached to nitrogen may be held in chemically different positions. This could happen if there was a $p\pi$-$p\pi$ interaction or lone pair - lone pair repulsions giving restricted N — S bond rotation. Using the model in Figure II-5, this would mean that C_1, X_1 and Y_1 were all different from C_2, X_2 and Y_2. This would be consistent with the ^{1}H NMR data of the ethyl and isopropyl compounds only if there are

Figure II-5

Chemical Non-Equivalence of Alkyl Groups in S_7NSNR_2



S_7NSNMe_2	X = Y = H
S_7NSNEt_2	X = H, Y = CH_3
$S_7NSNiPr_2$	X = CH_3, Y = H
$S_7NSNcHex_2$	X = CH_2, Y = H

accidental chemical shift equivalences of groups labelled Y_1 and Y_2 for each compound. It is unlikely that the X groups would always be different (i.e. X_1 from X_2) when the Y groups all have the same chemical shift. The ^{13}C NMR spectrum of the cyclohexyl derivative is inconsistent with chemical non-equivalence since it would require that the two carbon atoms attached to the nitrogen also have accidentally equivalent chemical shifts. This is highly unlikely considering the large range over which ^{13}C chemical shifts are found. Neither does this interpretation explain the other five peaks in this

^{13}C NMR spectrum.

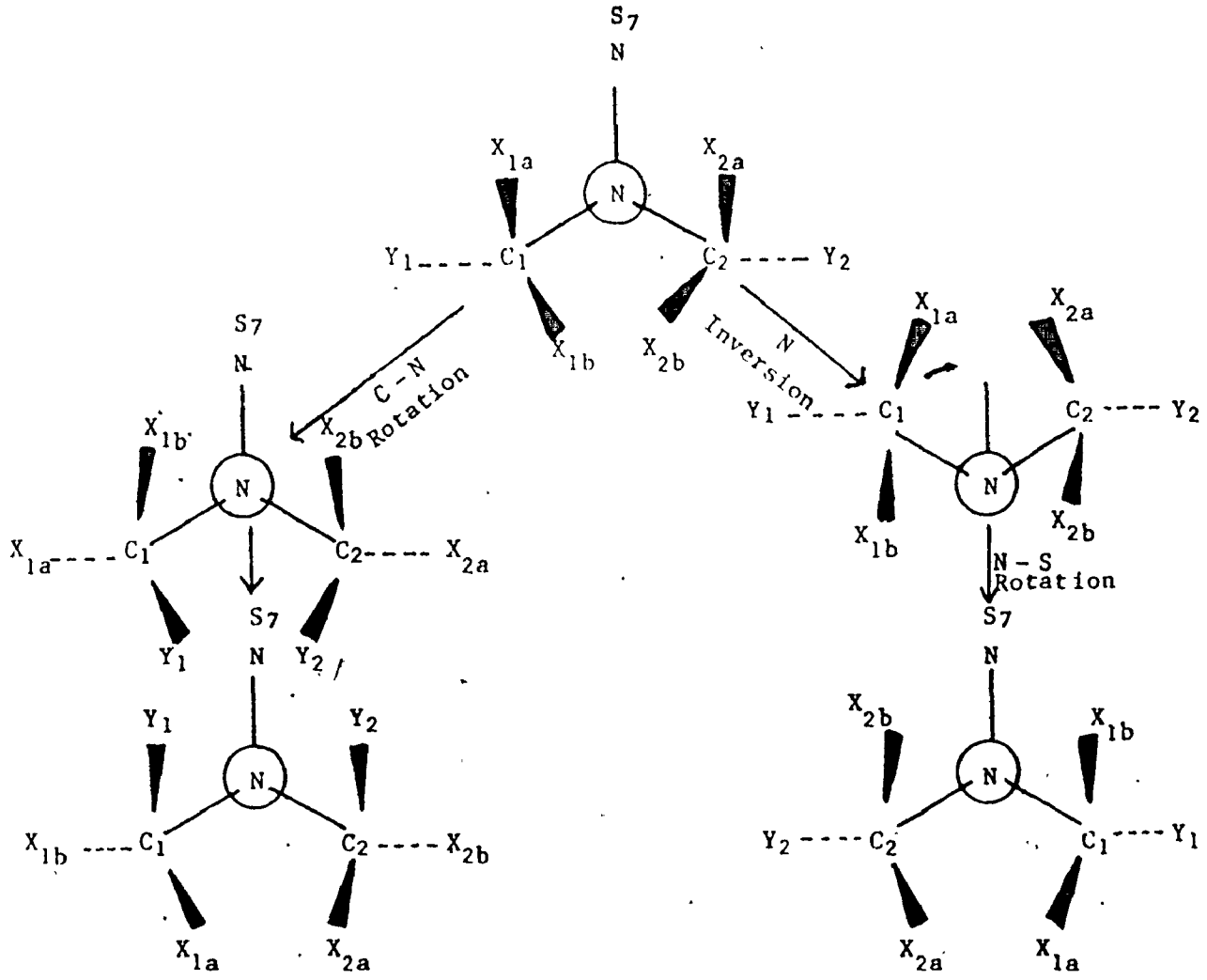
Another problem with the conformer suggested in Figure II-5 is that it also predicts that the group X_{1a} (or X_{2a}) would be unequivalent to X_{1b} (or X_{2b}). This would make 4 different resonances resulting only from the X groups. It is unlikely that accidental chemical shift equivalences will also explain away these predictions.

A second explanation for the peculiarities associated with these NMR spectra is that the two alkyl groups attached to the nitrogen are chemically equivalent but that for some reason the two X substituents (X_a and X_b, Figure II-5) are not equivalent to one another. Normally some process (bond rotation, atomic inversion) interchanges X_a and X_b so that it is usually thought that they are equivalent. The same NMR effect was observed in the spectra of the N,N'-thiobisamines (R = ethyl, isopropyl) as mentioned in section (I-1c). While this NMR effect was attributed to slow N — S bond rotation in the N,N'-thiobisamines, another possibility could give the same effect. Instead of there being slow N — S bond rotation (or the equivalent S - inversion at the sulfoxylic sulfur atom), slow nitrogen inversion could produce this effect.

Considering slow nitrogen inversion, Figure II-6 shows that two X-groups cannot interconvert. It can be seen from this diagram that conversion of X_a to X_b occurs only after nitrogen inversion and then reorientation of the molecule via N — S bond rotation. X_{1a} is converted to the environment of X_{2b} and X_{2a} is converted to X_{1b} making the NMR spectra of groups in these positions equivalent. Rotation

Figure II-6

Slow Nitrogen Inversion in S_7NSNR_2

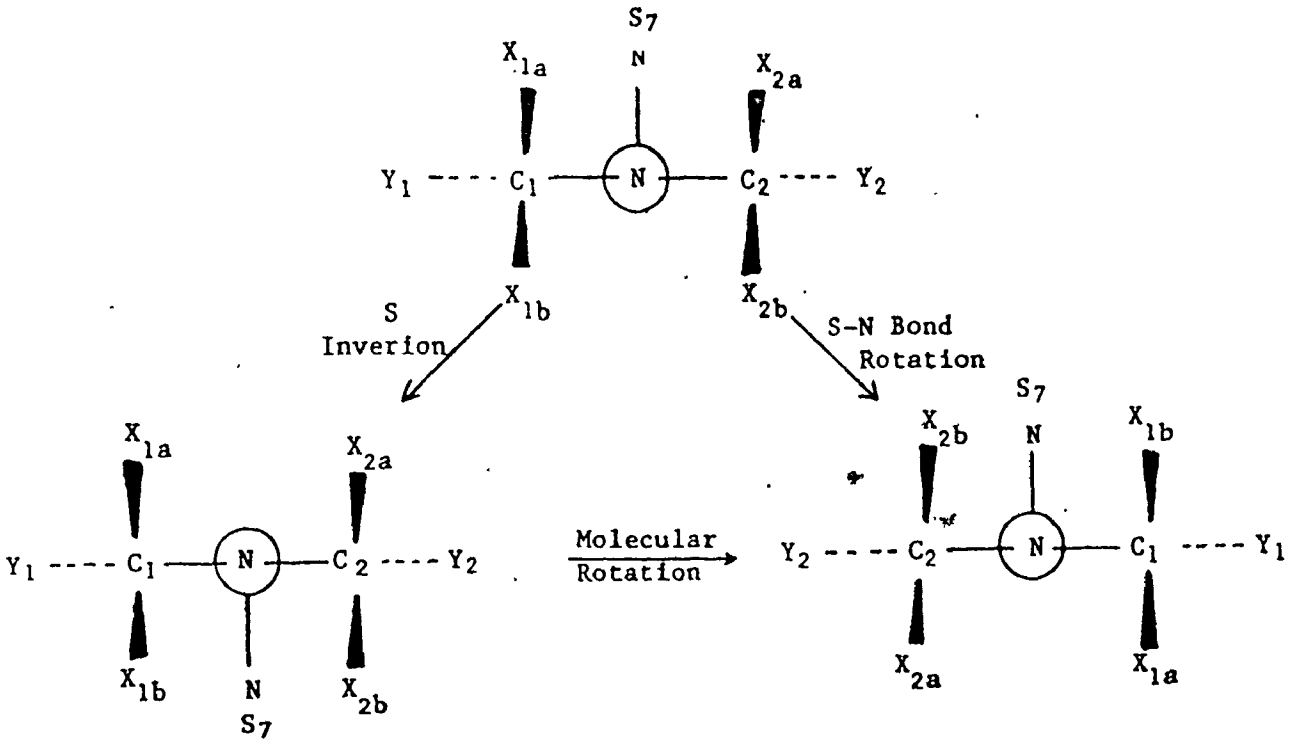


about the carbon-nitrogen bond (as is also shown in Figure II-6) never gives identical environments for X_a and X_b since no conformation results in equivalence.

If nitrogen inversion is very fast, the nitrogen atom can be considered to have its three substituents in a plane containing the nitrogen atom. Diastereotopic X-groups are still possible. One side of the $N\begin{smallmatrix}C\\C\end{smallmatrix}$ plane is different from the other making the environment of X_a different from X_b. These can be exchanged, however, either by inversion at sulfur or rotation about the N — S bond. Figure II-7 shows how X_a is different from X_b if these processes are both slow. Again rotation about the carbon-nitrogen bond never exchanges X_a for X_b

Figure II-7

NS Bond Rotation or Sulfur Inversion in S_7NSNR_2



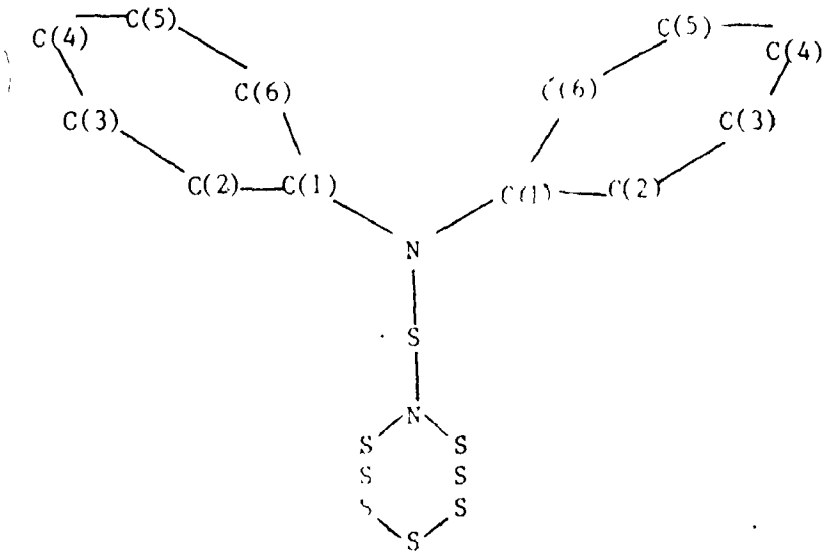
and vice versa in the same conformer. The necessary condition for diastereotopic X-groups is that there be no symmetry element which will relate the two groups. This is observed here, the σ-plane of the molecule tells us that X_{1a} or X_{1b} will be equivalent to X_{2a} or X_{2b}, respectively. The local σ-plane of the N<C framework which relates X_{1a} (or X_{2a}) to X_{1b} (or X_{2b}) is not a symmetry element of the molecule.

The correct NMR spectra for all derivatives are predicted by either slow nitrogen inversion or slow N — S bond rotation and slow sulfur inversion. The methyl groups should be equivalent and are found to be. The two methyl groups of the ethyl derivative should also be equivalent. The two methylene protons on each ethyl group are, however, not equivalent but each one is identical to the methylene proton with which it is reflected in the mirror plane of the molecule. Experimental results confirm these expectations. Behaviour of the isopropyl compound can be explained in the same way except in this case the methyl groups are different in each alkyl group. The ^{13}C NMR spectra for the cyclohexyl derivative provides final confirmation of this explanation. The six carbon atoms in each ring are different, and each give their own resonance in the NMR spectrum. The two groups are themselves identical however (Figure II-8). The chemical shifts of carbons 3(or 5), 5(or 3) and 4 are all very close to one another (+26.2, +26.0, +25.5 ppm, respectively).

To decide which of the processes described above are responsible for making the X-groups disastereotopic, comparisons can be made to similar processes reported in the literature. While little

Figure II-8

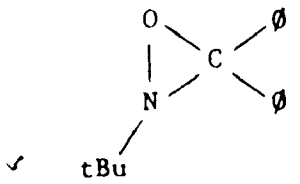
Assignment of ^{13}C NMR of $S_7NSN(cHex)_2$



information is available concerning the energy required from inversion at divalent sulfur, much work has been done on the pyramidal stability of tri co-ordinate sulfur in sulfoxides[107] and sulfonium salts[108]. It has been suggested[109] that the barrier to inversion of divalent sulfur will be higher than the quite substantial values found for the tri co-ordinate compounds studied (ca. 25 to 42 kcal/mole). It is expected therefore that the process of inversion at sulfur will be slow and that this may contribute to the fact that the two X groups in Figure II-7 are not equivalent. It should be noted that while this is a necessary condition, it is not sufficient, in that there must also be slow NS bond rotation for the groups to remain different. As has been mentioned in the introduction (section I-1), this second requirement, that of slow NS bond rotation, is a rather common occurrence when electronegative groups are attached to the sulfur atom.

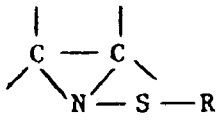
It is expected that bond rotation may be slow if there is a significant amount of pπ-dπ bonding in the N — S bond.

Nitrogen inversion has been studied in many compounds showing that fairly large energies are required only in molecules containing bulky substituents or having much ring strain in the transition state. In general, however, nitrogen inversion is much easier than sulfur inversion, the energies required for the process being typically 5.8 kcal $mole^{-1}$ (NH_3) or 7.46 kcal $mole^{-1}$ (Me_3N)[109]. A barrier as high as 28.4 kcal $mole^{-1}$ for XXI has been measured. In this case ring



XXI

strain, steric hindrance and heteroatomic substitution all restrict inversion[110]. Heteroatomic substitution hinders nitrogen inversion only if the heteroatom does not interact with the p-orbital on nitrogen. This has been postulated[109] as being the reason for the low energy of inversion for 1-sulfenyl aziridines XXII, the p-electron

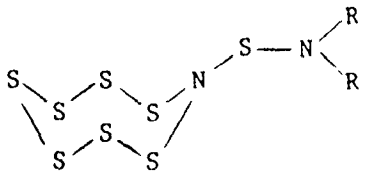


XXII

density being involved in a pπ-dπ bond with sulfur. Interaction with

a pπ-pπ system will also lower the activation energy of nitrogen inversion. Amides or N-aryl amines are found to have considerably lower energy barriers to inversion for this reason[110]. In these cases where nitrogen is involved with π-bonding, the pyramid at nitrogen becomes flattened and the sums of the angles about nitrogen approach 360°.

In looking now at compound XIX it is difficult to



XIX

predict whether there will be strong pπ-dπ interaction giving a low nitrogen inversion barrier. Most likely, the bonding situation in these molecules will be similar to that described in the introduction for N,N'-thiobisdimethylamine. In this molecule the nitrogens were approaching planarity which suggests that the nitrogens in the N,N'-dialkyl-N',N'-cycloheptathiosulfoxylic diamides will be rapidly inverting.

Since there has been no kinetic data collected for the NMR effects observed for these molecules, it is difficult to say with certainty which of these processes (slow S- inversion and slow NS-rotation or slow N-inversion) causes the groups to be diastereotopic. In order to investigate further this question, crystals were grown of N,N-dimethyl-N',N'-cycloheptathiosulfoxylic diamide and

N,N'thiobisdicyclohexylamine for X-ray structural analysis.

II-5 STRUCTURE OF N,N'-THIOBISDICYCLOHEXYLAMINE

The only structural information which has been reported in the literature for molecules containing the C_2NSNC_2 linkage is an electron diffraction study[21] done on the methyl derivative. Since the errors quoted in electron diffraction studies are usually quite large, the compound N,N'- thiobisdicyclohexylamine was prepared for analysis by X-ray crystallography. This compound was chosen since it was crystalline at room temperature (MP = 149°C). The crystallography was performed by Dr. D.R. Slim at this university. The unit cell dimensions were : -monoclinic, a = 13.75(2), b = 6.194(5), c = 13.74(2), β = 91.23 (7), space group I2*. The final unweighted R factor was 0.0525. Bond angles and lengths are given in Table II-4, the atoms being labelled in Figure II-10.

In general, this structure is very similar to that found by electron diffraction for the methyl derivative. The nitrogen atoms are somewhat more planar in the cyclohexyl than the methyl derivative (sum of N angles = 358.9(9)°, 352.3(2.8)°, respectively), but the difference is not significant. The sulfur-nitrogen bond length appears to be shorter in the cyclohexyl compound (1.657(4)Å) than in the methyl compound (1.688(6)Å). While this difference is significant if one

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* I2 is an alternative setting for the standard space group C2.

Table II-4

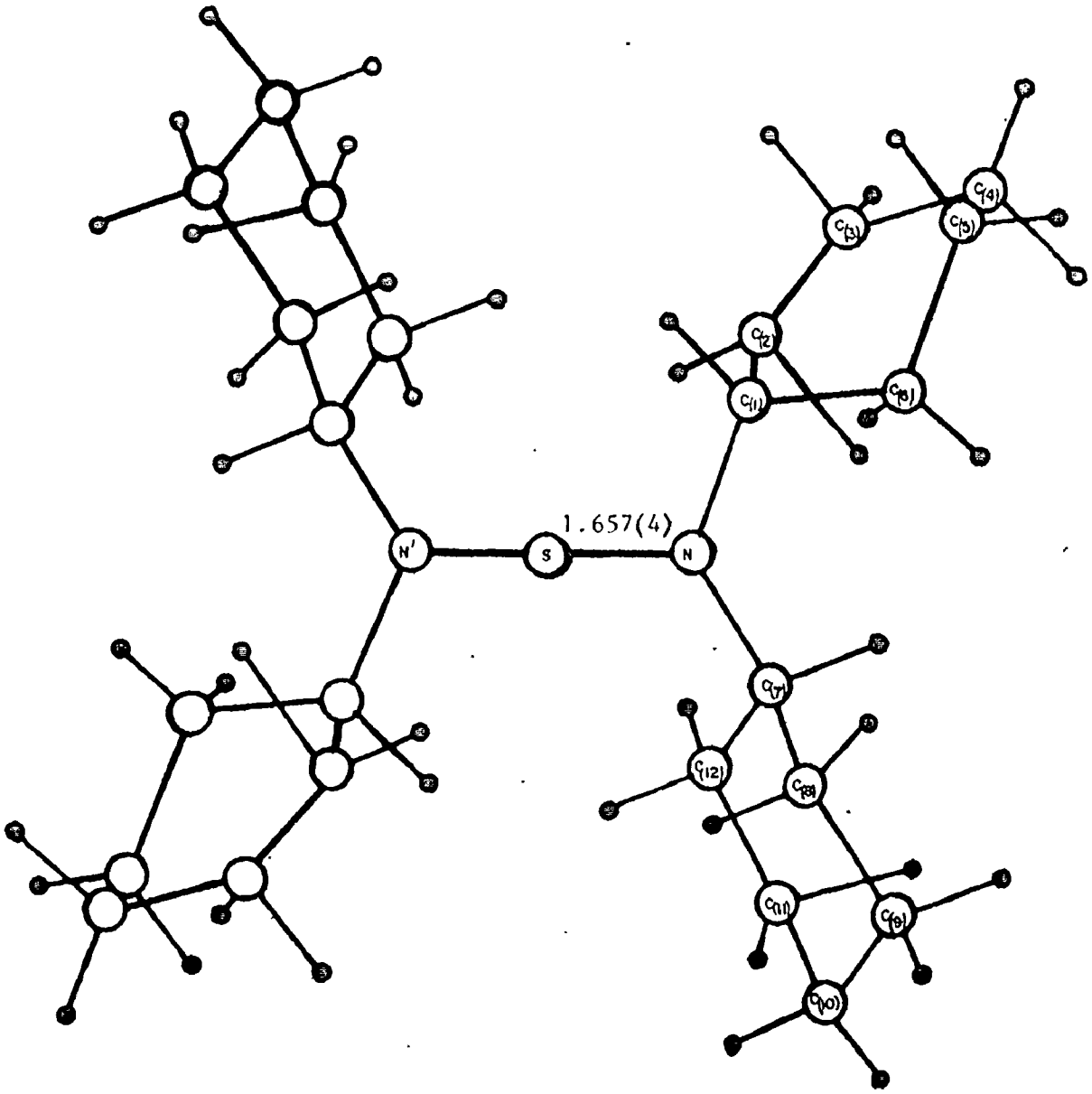
Bond Lengths and Bond Angles for

N,N'-Thiobisdicyclohexylamine

Bond Lengths (Å)		Bond Angles (°)	
S-N	1.657(4)	N-S-N'	110.7(2)
N-C(1)	1.456(6)	S-N-C(1)	119.7(3)
N-C(7)	1.477(5)	S-N-C(7)	121.3(3)
C(1)-C(2)	1.507(7)	C(1)-N-C(7)	117.9(4)
C(1)-C(6)	1.501(8)	C(6)-C(1)-C(2)	111.5(4)
C(2)-C(3)	1.520(8)	C(1)-C(2)-C(3)	111.4(4)
C(3)-C(4)	1.485(11)	C(2)-C(3)-C(4)	111.3(5)
C(4)-C(5)	1.495(10)	C(3)-C(4)-C(5)	112.5(6)
C(5)-C(6)	1.539(8)	C(4)-C(5)-C(6)	111.3(5)
C(7)-C(8)	1.520(8)	C(5)-C(6)-C(1)	110.2(5)
C(7)-C(12)	1.500(7)	C(12)-C(7)-C(8)	112.0(4)
C(8)-C(9)	1.534(7)	C(7)-C(8)-C(9)	109.1(5)
C(9)-C(10)	1.494(9)	C(8)-C(9)-C(10)	111.9(5)
C(10)-C(11)	1.504(8)	C(9)-C(10)-C(11)	111.6(4)
C(11)-C(12)	1.528(7)	C(10)-C(11)-C(12)	110.2(5)
		C(11)-C(12)-C(7)	110.6(4)

Figure I-9

Molecular Structure of N,N'-Thiobisdicyclohexylamine

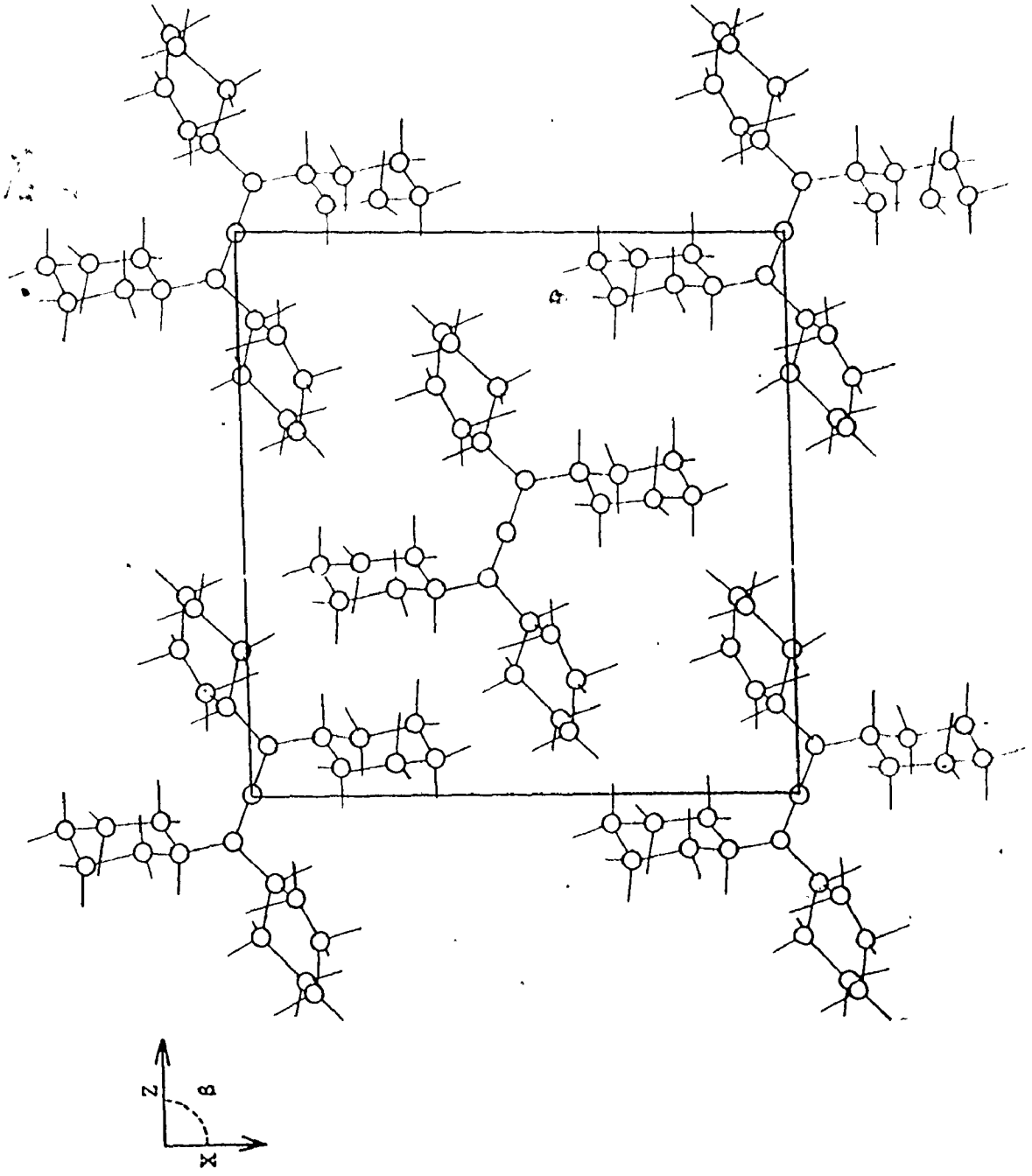


Bond Lengths and Bond Angles shown in Table II-3.

Figure II-10

I_2 Unit Cell of N,N'-thiobisdicyclohexylamine

(viewed down the y axis)



uses the errors quoted, the errors on the electron diffraction study seem optimistic and the bond lengths of these two compounds may not be significantly different. It should be noted that the NS bond length in the cyclohexyl compound is smaller than that of a single bond length (1.70 to 1.74 Å) discussed in the introduction.

The orientation of the $N\begin{smallmatrix}C\\C\end{smallmatrix}$ planes with respect to the NSN plane is in agreement with the low energy conformer found for $((CH_3)_2CH)_2N)_2S$ (using NMR) or $((CH_3)_2N)_2S$ (using electron diffraction). The planar nitrogen and short N-S bond lengths suggest that the variable temperature effect observed in the NMR of $((iPropyl)_2N)_2S$ is due to hindered N-S rotation as suggested and not to nitrogen inversion.

The short NS bond lengths suggest that there is a π-interaction between the two nitrogen atoms and the sulfur atom. The symmetry of the C_2NSNC_2 framework, however, rules out the possibility of pπ-pπ bonding between sulfur and nitrogen but is consistent with a pπ-dπ interaction. A dπ-pπ bonding situation is shown in Figure II-11. There are four electrons to be shared over the three orbitals. A simple LCAO-MO picture similar to that drawn in section I-1 (Figure I-3) can be used to describe the π-system here and is shown in Figure II-12. The molecular orbital picture suggests that a considerable amount of stabilization is attained by delocalization of the nitrogen electron pairs into the vacant sulfur d-orbital. Two electrons are placed in a strongly bonding molecular orbital and two in a non-bonding or weakly anti-bonding molecular

Figure II-11

dπ-pπ Bonding in N,N'-Thiobisdialkylamines

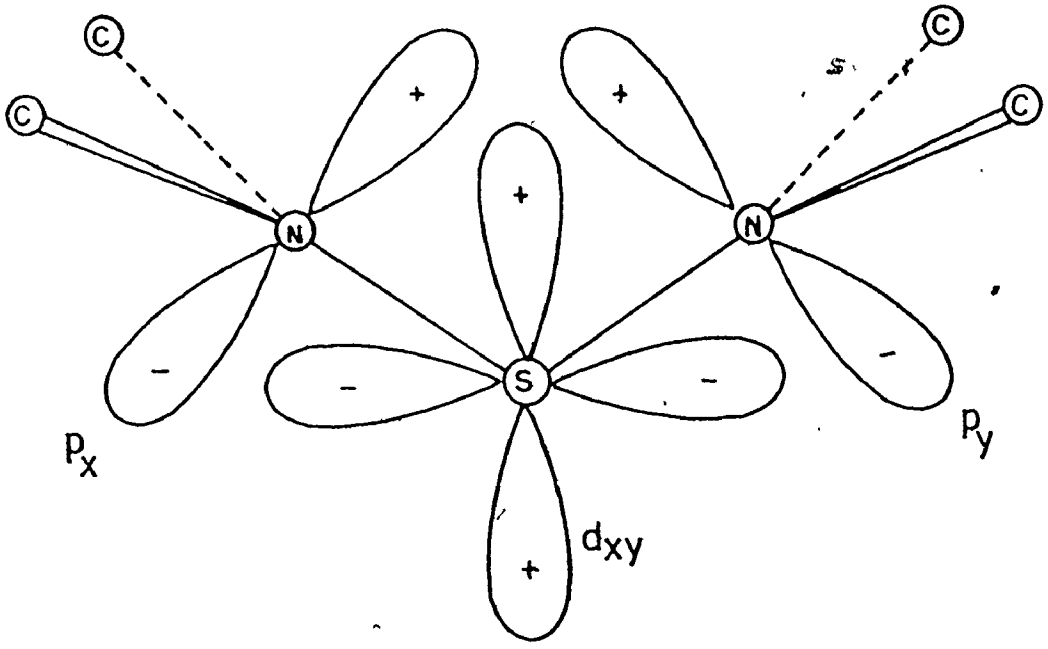
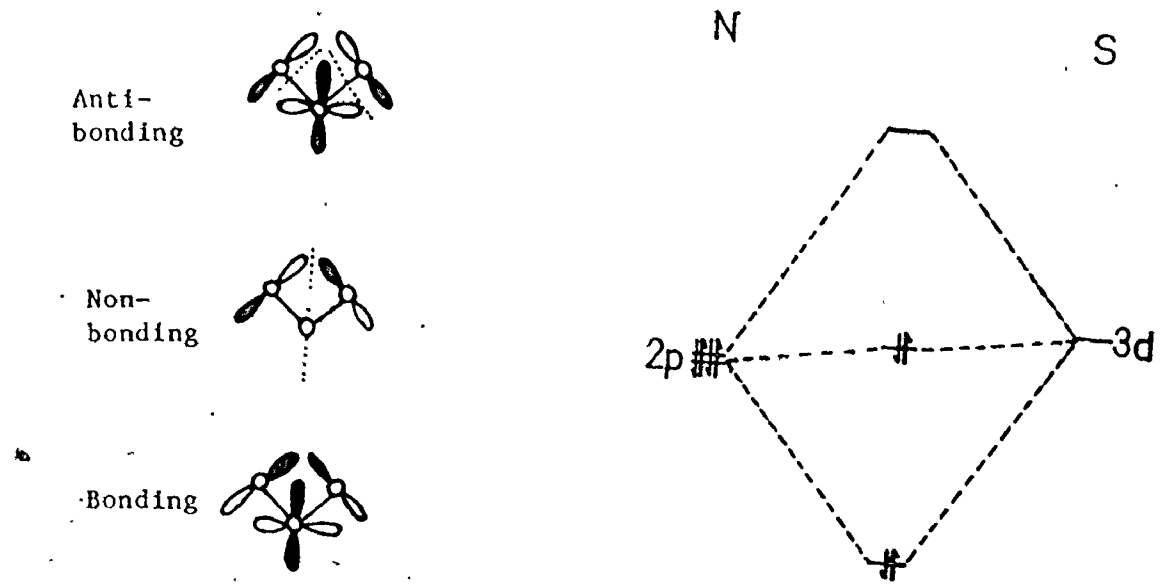


Figure II-12

LCAO-MO Diagram - π Bonding in N,N'-Thiobisdialkylamines



orbital for a total bonding interaction.

Turning again to the vibrational spectra of these molecules. This structure determination is more consistent with one of the previous assignments of the S-N stretching frequency of the N,N'-thiobisdialkylamines. The SN bond length - SN stretching frequency correlation proposed by Bannister et al[13] suggests that for a bond length of 1.657 (4) Å, the stretching frequency should be approximately 865 cm^{-1}. This is more in agreement with Török

et al[68] in their assignment of the bands in the regions 950 cm^{-1} (to the SN stretches) and at 650 cm^{-1} (to the NC_2 symmetric stretch) than the alternate assignment in reference (67).

II-6 STRUCTURE OF N,N-DIMETHYL-N',N'-CYCLOHEPTATHIOSULFOXYLIC DIAMIDE AND INTERPRETATION OF NMR SPECTRA

To confirm that the bonding in N,N-dimethyl-N',N'-cycloheptathiosulfoxylic diamide is similar to that described for the C_2NSNC_2 linkage in the N,N'-thiobisamines, an X-ray crystal structure determination was performed on $S_7NSN(CH_3)_2$ (again by Dr. D. Slim at this university). The unit cell dimensions are: - space group P_{bca}, orthorhombic, a = 8.129 (3), b = 23.892 (9), c = 11.407 (4). The final unweighted R factor was 0.0510. Table II-5 contains a list of the bond lengths and bond angles found for the molecule which is shown in Figure II-13. The molecules are shown stacked in the unit cell in Figure II-15. There are two distinct parts to the molecule, the sulfur nitrogen ring and the $N-S-N\begin{smallmatrix}C\\C\end{smallmatrix}$ side chain. The former will be discussed with respect to the structure of S_7NH and the latter with respect to the $N-S-N\begin{smallmatrix}C\\C\end{smallmatrix}$ structure just described for N,N'-thiobisdicyclohexylamine.

The structure of S_7NH was recently re-determined by Steudel[5] with the results presented in Figure II-14. The major differences in the two structures are the shorter NS bond lengths and the shorter lengths of the two sulfur-sulfur bonds to S (4) (Figure II-13) in $S_7NSN(CH_3)_2$. The former effect is best explained by enhanced $p\pi-d\pi$ bonding, a common feature of saturated nitrogen-

Table II-5

Bond Lengths and Bond Angles for $S_7NSN(CH_3)_2$

Bond Lengths (Å)			Bond Angles (°)			
S(1)	S(2)	2.013(2)	N(1)	S(1)	S(2)	109.0(2)
S(1)	N(1)	1.605(6)	S(1)	S(2)	S(3)	109.7(1)
S(2)	S(3)	2.038(2)	S(2)	S(3)	S(4)	105.6(1)
S(3)	S(4)	1.911(2)	S(3)	S(4)	S(5)	102.9(1)
S(4)	S(5)	1.943(2)	S(4)	S(5)	S(6)	106.8(1)
S(5)	S(6)	2.039(3)	S(5)	S(6)	S(7)	110.0(1)
S(6)	S(7)	1.993(3)	S(6)	S(7)	N(1)	106.9(2)
S(7)	N(1)	1.588(6)	S(7)	N(1)	S(1)	114.9(3)
			S(7)	N(1)	S(8)	122.0(3)
S(8)	N(1)	1.734(5)	S(1)	N(1)	S(8)	122.2(3)
S(8)	N(2)	1.607(5)	N(1)	S(8)	N(2)	110.6(3)
N(2)	C(1)	1.345(10)	S(8)	N(2)	C(1)	120.5(6)
N(2)	C(2)	1.404(11)	S(8)	N(2)	C(2)	121.7(5)
C(1)	H(1)	0.98 (8)	C(1)	N(2)	C(2)	112.3(7)
C(1)	H(2)	0.94 (7)	N(2)	C(1)	H(1)	105 (5)
C(1)	H(3)	0.96 (8)	N(2)	C(1)	H(2)	103 (5)
C(2)	H(4)	0.93 (8)	N(2)	C(1)	H(3)	109 (4)
C(2)	H(5)	0.95 (6)	N(2)	C(2)	H(4)	111 (5)
C(2)	H(6)	0.91(10)	N(2)	C(2)	H(5)	112 (4)
			N(2)	C(2)	H(6)	100 (6)
			H(1)	C(1)	H(2)	123 (7)
			H(1)	C(1)	H(3)	117 (7)
			H(2)	C(1)	H(3)	99 (6)
			H(4)	C(2)	H(5)	107 (6)
			H(4)	C(2)	H(6)	119 (8)
			H(5)	C(2)	H(6)	109 (8)

Figure II-13

Molecular Structure of $S_7NSN(CH_3)_2$

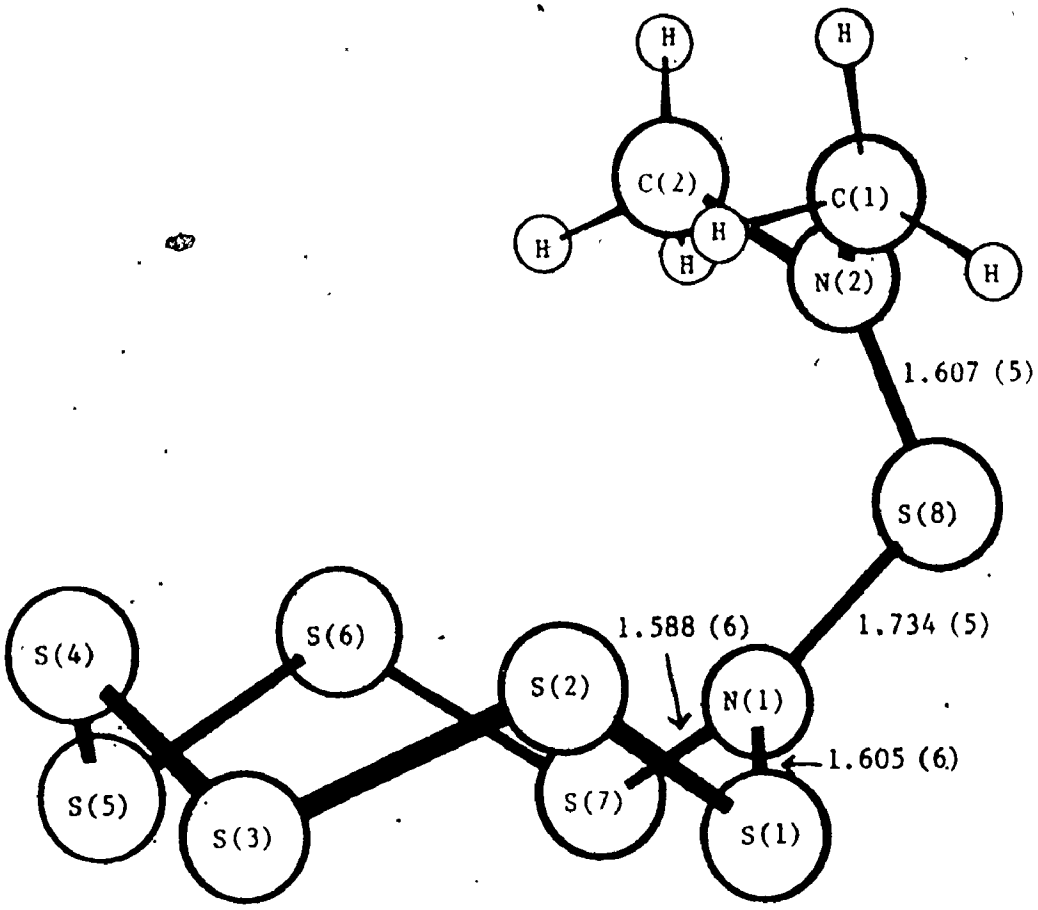


Figure II-14

Molecular Structure of S_7NH

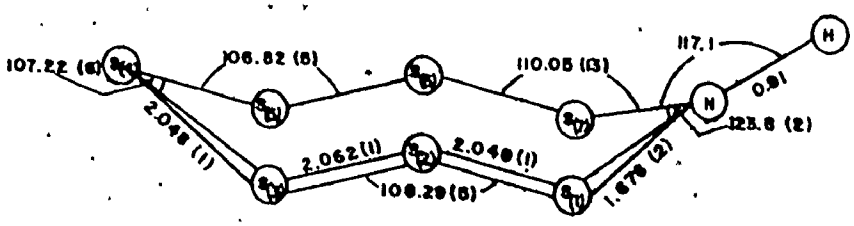
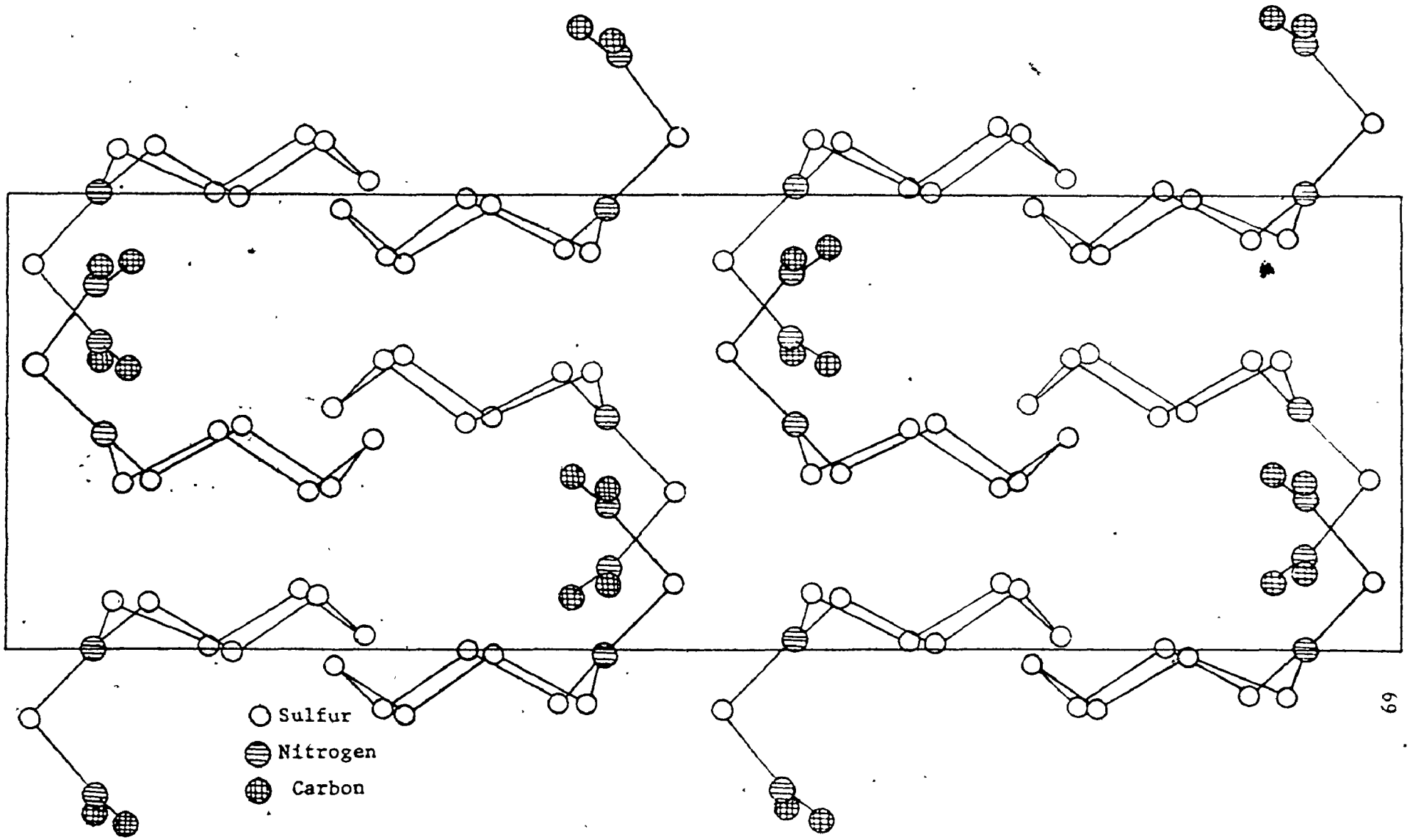


Figure II-15

P_{bca} Unit Cell of $S_7NSN(CH_3)_2$



sulfur frameworks. The extra N-S π-bonding is possibly due to the inductive effect of nitrogen pulling electrons from the polarizable sulfur atom in the side chain (S(8), Figure II-13) through the σ N-S bond. This would expand the nitrogen lone pair p-orbital giving better overlap with the d-orbitals on the sulfur atoms in the ring. The high acidity of the proton in S_7NH confirms that the ring is indeed electron withdrawing as suggested above. In S_7NH, the hydrogen is not capable of donating electron density to the ring making the N-S bonds considerably longer (1.676 (2) Å) than in the derivative described above (1.597 (6) Å).

The effect of the short N-S bonds in this compound appears to be transmitted around the ring to influence the sulfur-sulfur bonds to S (4) (Figure II-13). A sulfur-sulfur single bond length is reported in a review by Steudel[111] to be approximately 2.05 Å and to be dependent on the dihedral angle between substituents attached to each sulfur atom. Interactions between filled p-orbitals on sulfur result in shorter bond lengths when the dihedral angle is 90°. It should be noted that molecular geometries of compounds containing sulfur-sulfur bonds (ex. disulfides, S_{12}, S_8) are governed by this dihedral angle dependence. It may be this effect which causes the S-S bonds to S (4) to be short in the ring of $S_7NSN(CH_3)_2$. In shortening the N-S bonds as compared to S_7NH, the geometry of the ring must change either by slightly increasing all of the dihedral angles or by shortening the S-S bonds at the opposite side of the ring and keeping the dihedral angles close to 90°. A

comparison of the dihedral angles found in S_7NH and $S_7NSN(CH_3)_2$ (Table II-6) suggests that perhaps the optimum situation exists when both of these effects occur to some extent. The sum of the dihedral angles in the ring of $S_7NSN(CH_3)_2$ is larger than the sum of the dihedral angles in S_7NH. The S-S bonds to the sulfur atom opposite to the nitrogen in the ring are also considerably shorter in $S_7NSN(CH_3)_2$ (1.927 (2) Å) than in S_7NH (2.048 (1) Å)[5].

Table II-6

Ring Dihedral Angles in S_7NH and $S_7NSN(CH_3)_2$

Angle	S_7NH[5]	$S_7NSN(CH_3)_2$
S(7)N(1) - S(1)S(2)	96.5 (2)°	101.6(2)°
N(1)S(1) - S(2)S(3)	94.8 (1)°	102.1(2)°
S(1)S(2) - S(3)S(4)	99.39(5)°	100.8(2)°
S(2)S(3) - S(4)S(5)	93.53(6)°	92.7(2)°
S(3)S(4) - S(5)S(6)	93.55(6)°	94.8(2)°
S(4)S(5) - S(6)S(7)	99.39(5)°	102.8(2)°
S(5)S(6) - S(7)S(1)	94.8 (1)°	96.5(2)°
S(6)S(7) - N(1)S(1)	96.5 (2)°	98.5(2)°
	Sum 768.4°	789.8°

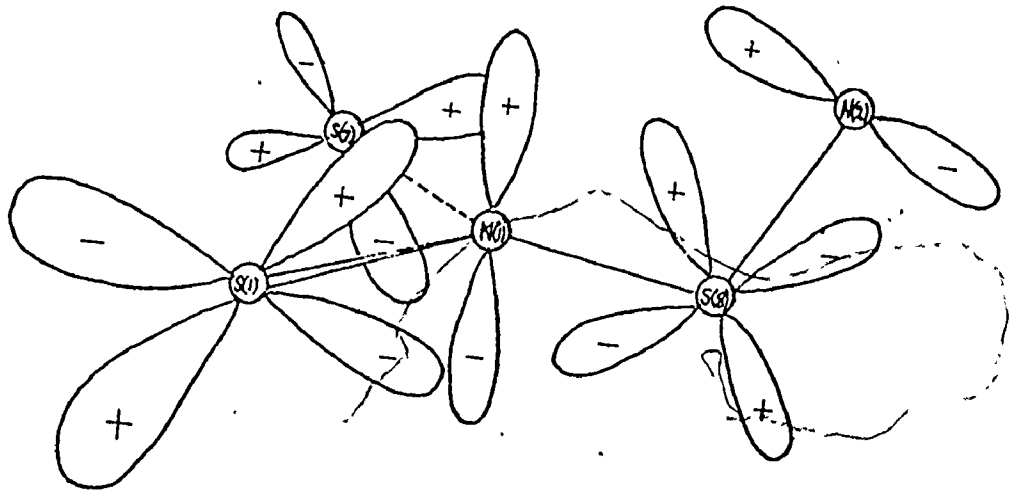
The $N - S - N\begin{matrix}C\\C\end{matrix}$ framework of this molecule is quite different from that found in the crystal structure of the N,N'-thiobisamine. The N-S bond adjacent to the ring is long (1.734 (5) Å) but in the range expected for a true single σ-bond.

The other N-S bond in this linkage is much shorter (1.607 (5) Å) than that found in the N,N'-dialkylthiobisamines (R = cyclohexyl (1.657 (4) Å, R = methyl (1.688 (6) Å). Both nitrogens are planar within experimental error so it can be postulated that pπ-dπ bonding may be involved here. The orientation of the CNC plane is perpendicular to the NSN plane as it is in the structure of N,N'-thiobisdicyclohexylamine.

The rationalization of the assymmetric NSN linkage in this molecule is as follows. It is assumed that all of the sulfur atoms bonded to nitrogen are about equally capable of accepting nitrogen pπ-electron density into their vacant d-orbitals. The amount of electron density which is available at nitrogen will be a function of the σ-environment, the electronegative nitrogen atom being able to extract electron density from sulfur through the σ-bonds. The amount of this electron density which can be shared with each particular sulfur atom, however, will depend on how many other sulfur atoms are competing for the same nitrogen lone pair. Figure II-16 shows the symmetry of the orbitals which would be involved in this molecule. The lone pair at N(1) should be easily accessible, since the atom is surrounded by three sulfur atoms. Sulfur atoms S(1), S(7) and S(8) (Figure II-16) are all competing for this lone pair in a p-type orbital. S(1) and S(7) are more effective since the d-orbital on S(8) will be accepting pπ-electron density from N(2) as well as N(1). The lone pair on N(2) should be reasonably accessible for pπ-dπ bonding due to inductive donation of electron density from

Figure II-16

π-Bonding in $S_7NSN(CH_3)_2$

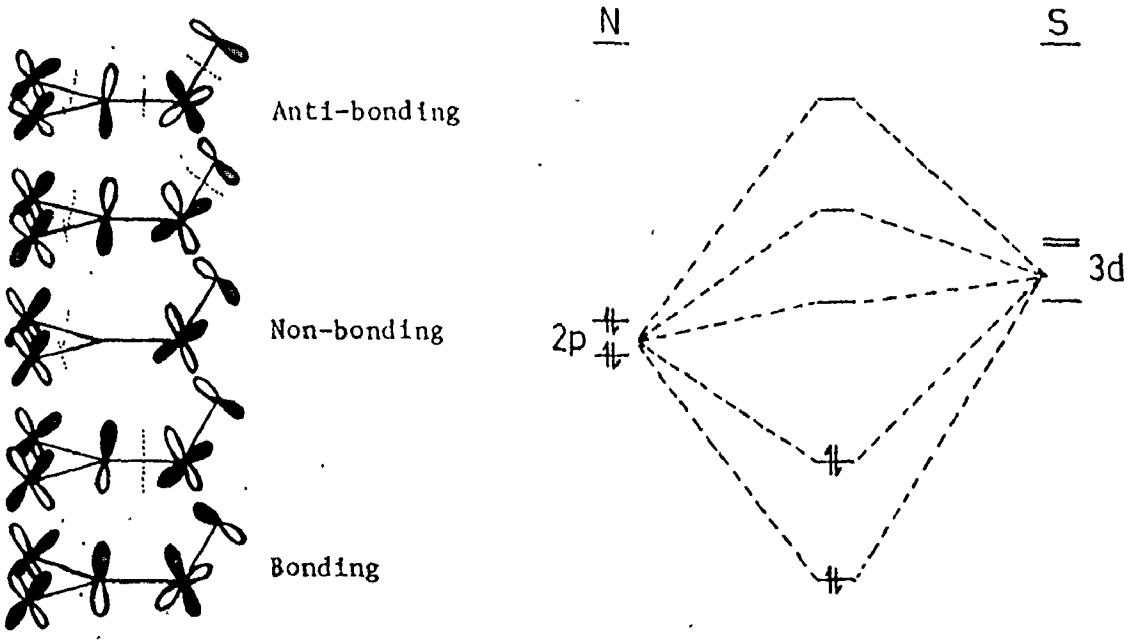


S(8) to N(2). The overall bonding expected would therefore involve strong bonds between N(1) and S(1), N(1) and S(7), N(2) and S(8) and only weak π-bonding between S(8) and N(1). This synergic type of bonding would seem reasonable. A similar explanation is used to describe the bonding of π-acid ligands or olefins to transition metals.

A simple LCAO-MO picture, similar to that described for the N,N'-thiobisamine (Figure II-12), can be drawn for this molecule (Figure II-17). While this is only a qualitative

Figure II-17

LCAO-MO Diagram for $S_7NSN(CH_3)_2$



approximation, it is interesting to note that when the four electrons from the nitrogen atoms are placed into the lowest energy molecular orbitals, a strongly bonding situation is predicted. The only node in the overlap of the filled orbitals occurs between the central sulfur and nitrogen atoms, which is in fact the long S(8) - N(1) bond.

In light of the structure described above, it is now easy to interpret the NMR spectra of this type of compound. The nitrogen atom is planar, removing the possibility of slow nitrogen inversion

to produce the diastereotopic alkyl groups (section II-4). At room temperature, the N-S bond is not rotating fast on an NMR time scale. Neither is the sulfur atom inverting at room temperature. While the latter is not so surprising, the former (slow NS bond rotation) is somewhat unusual for a formal single bond. It is these two processes, however, that cause these compounds to exhibit anomalous NMR behaviour at room temperature.

II-7 BONDING IN SATURATED SULFUR-NITROGEN COMPOUNDS

The structure determinations just described illustrate the unusual nature of an apparent single N-S bond.

The existence of $p\pi$-$d\pi$ bonding is becoming more accepted in discussions of bonding in these types of systems (for example, reference (112)). Structural studies have shown that some generalizations can be made in the description of "single" S-N bonds. These are listed below.

(a) The geometry of the molecule usually meets the requirements for a $p\pi$-$d\pi$ bond between nitrogen and sulfur.

(b) Electronegative groups attached to sulfur enhance the π-bond strength, presumably due to contraction of the sulfur d-orbitals.

(c) Polarizable groups attached to nitrogen enhance the π-bonding, most likely due to expansion of the p-type orbital containing the lone pair of electrons.

(d) The restricted rotation about N-S bonds is not due to

lone pair - lone pair repulsions.

(e) Any structural restriction tending to make the nitrogen non-planar, lengthens the N-S bond.

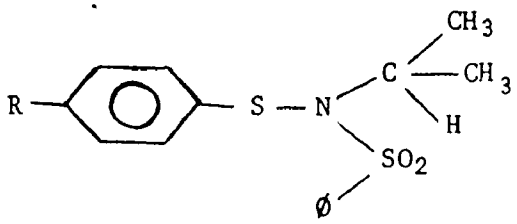
(f) A pπ-system which is attached to the nitrogen atom, would be expected to compete with the sulfur for the nitrogen p-electron density. This would weaken the N-S bond.

(g) The N-S bond contraction depends on the number of sulfur and nitrogen atoms in the system. A sulfur atom bonded to two electronegative substituents (one of them nitrogen) and-accepting pπ-electron density from only the one nitrogen atom would give a very short N-S bond (1.60 Å). A situation with one sulfur d-orbital and two nitrogen p-orbitals or one nitrogen p-orbital and two sulfur d-orbitals would give approximately the same amount of stabilization but this is now spread over two bonds.

(h) In an N-S-N system, the low energy conformer has p-orbitals and d-orbitals arranged such that only one d-orbital need be used to overlap with both nitrogen p-orbitals.

Item (a) has already been described in the discussion of the structures of $S_7NSN(CH_3)_2$ and N,N'-thiobisdicyclohexylamine. It is also the correct symmetry for the low energy conformer of other N,N'-thiobisamines or of the sulfenamides ($R - S - N\begin{smallmatrix}R'\\R''\end{smallmatrix}$). In all cases, diastereotopic groups attached to nitrogen are observed.

NMR studies on the N-sulfenyl sulfonamides[22] (XXIII) show the effect of increasing the electron withdrawing ability of the substituents attached to sulfur on the energy required to rotate

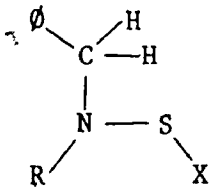


XXIII

the N-S bond (Item (b)). As the R-group is changed from $-O-CH_3$ to $-NO_2$ the coalescence temperature of the diastereotopic methyls increases from $-15^{\circ}C$ to $+32^{\circ}C$. The free energy of activation of this conformational change goes from 13.2 kcal $mole^{-1}$ to 15.6 kcal $mole^{-1}$. Similarly, for the sulfenamides[113] (XXIV to XXVII, Figure II-18), when the X group is electronegative (XXIV and XXV), the

Figure II-18

Restricted Rotation in Sulfenamides



Compound	R	X	Coalescence Temp ($^{\circ}C$)	$\Delta G^{\ddagger}$ kcal $mole^{-1}$
XXIV	$\emptyset CH_2$	CCl_3	28 ± 2	15.0 ± 0.2
XXV	Pr^i	CCl_3	47 ± 2	15.9 ± 0.2
XXVI	Pr^i	Ph	<-100	<9
XXVII	$\emptyset CH_2$	Me	<-100	<9

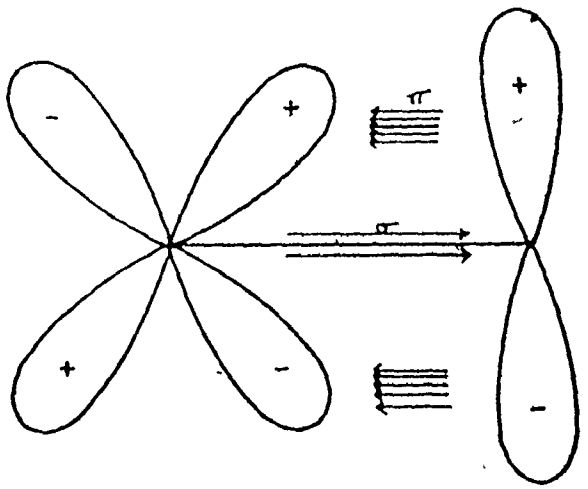
coalescence temperature and free energy of activation are high. When the X group is not electronegative, coalescence of the diastereotopic methylene protons is not observed even at $-100^{\circ}C$.

The dependence of π-bond strength on polarizable substituents of nitrogen is best illustrated by the comparison of the S_7NSNMe_2

and S_7NH structures as was discussed in section II-6. The extra sulfur atom attached to the nitrogen atom of the ring in $S_7NSN(CH_3)_2$ can donate electron density to nitrogen through the σ-bond system. This would expand the p-orbital containing the nitrogen lone pair and thus increase overlap with the sulfur d-orbitals. A sulfur-nitrogen bond can therefore be considered to be synergic in nature, with electron density being donated through the σ-bond from sulfur (electronegativity = 2.5, high polarizability) to nitrogen (electronegativity = 3.0). This electron density will then be donated from the filled p-orbital on nitrogen to the vacant d-orbital on sulfur (Figure II-19). This was mentioned in the review by Mitchell[114] as a factor which stabilizes bonds between second and third row non-metals

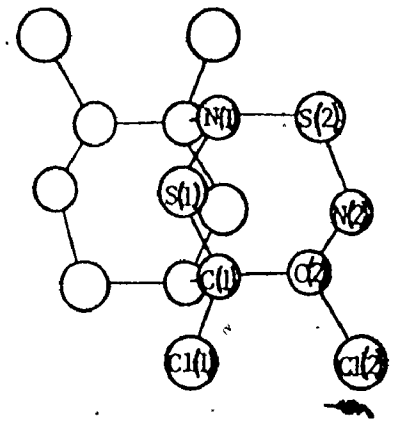
Figure II-19

Synergic Bonding in Saturated S-N Bonds



It is possible that the restricted rotation observed in S-N bonded species is a result of lone pair - lone pair repulsions since similar arguments have been suggested to describe slow bond rotation in hydroxylamines[115]. It is highly unlikely, however, that this is the major factor producing restricted rotation since this would not induce the nitrogen to become sp^2 hybridized. Also the dependence of the activation energy on the electronegativity of the substituents attached to sulfur is opposite to that expected if it were lone pair - lone pair repulsions which results in slow rotation. The very short N-S single bonds are also inconsistent with a lone pair - lone pair repulsion argument.

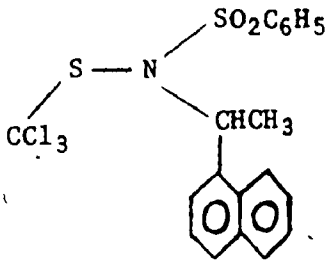
Structural studies performed on molecules in which the nitrogen atoms are not entirely sp^2 hybridized show that the N-S bonds are longer. The sum of the angles about N(1) in the tricyclic compound XXVIII is 335°. This is almost pyramidal with the NS bonds



XXVIII

being very long (1.705 (18) to S(1), 1.740 (14) to S(2)) in agreement with item (e)[2]. Presumably steric hindrance and ring strain

restrictions in the tricyclic compound demand the molecular structure found. The sum of the bond angles about nitrogen in N,N'-dithiobismorpholine XXIX is 344°. The N-S bond length in this compound is 1.686 (3) Å [4] which is intermediate between a true single N-S bond and the short bonds found in S_7NSNMe_2. If these N-S bond lengths are plotted as a function of the sum of the angles about nitrogen, an inverse relationship is found (Figure II-20). Only compounds in which there is a single N-S pπ-dπ interaction are included. Compound XXX was included as well although there are two N-S bonds to the



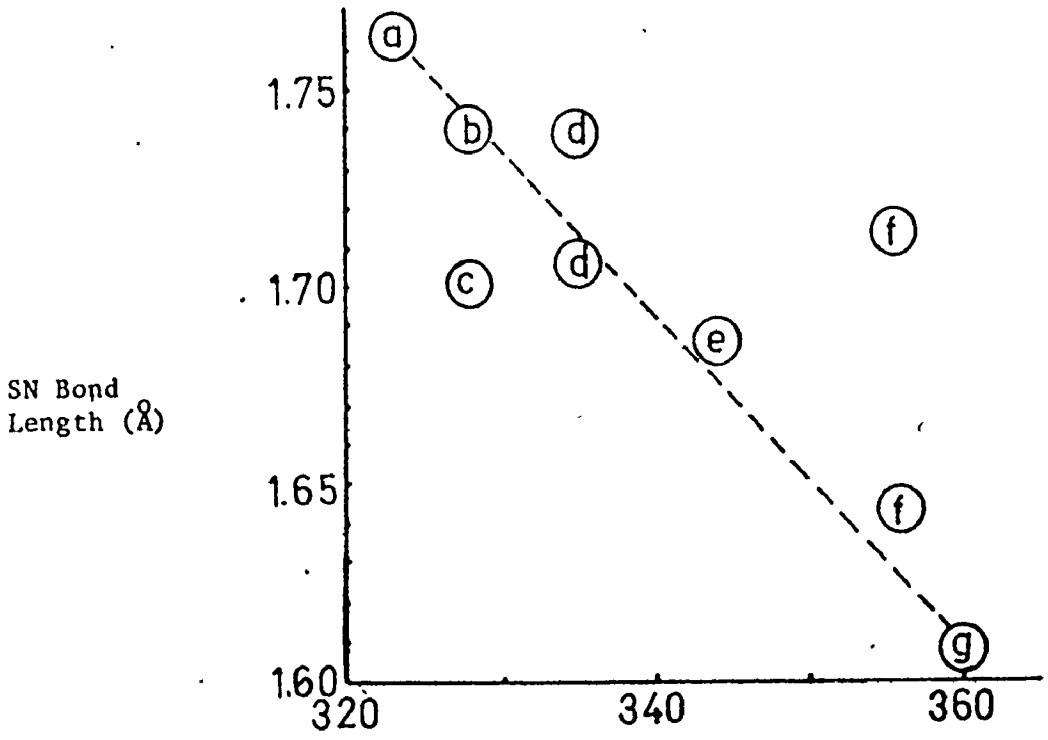
XXX

nitrogen atom since one of the bonds is quite long (1.713 (9) Å) [3] showing little donation to the sulfonyl sulfur atom.

Good examples to test the effect of a pπ- system competing for the nitrogen lone pair electrons do not exist in the structural literature. Most likely the effect which would be observed would be a lengthening of the N-S bond in comparison to a similar system in which no competing π-system is present. A structural determination should be performed on a molecule such as XXXI to study this effect. This could then be compared to the

Figure II-20

N-S Bond Length vs Sum of Bond Angles at Nitrogen

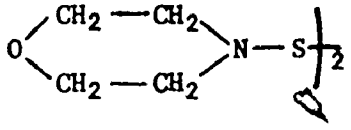


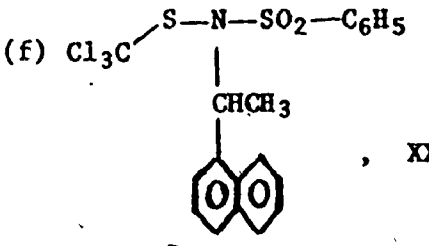
(a) $H_3N^+ — \bar{S}O_3$ (1)

(b) Pauling's Covalent Radii (15)

(c) Schomaker-Stevenson (16)

(d) $(SNCCl)_4$ XXVIII (2)

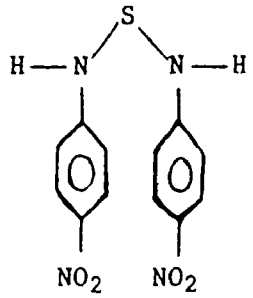
(e)  (4)

(f)  (3)

, XXX

(g) short exocyclic SN bond in $S_7NSN(CH_3)_2$

structure of the N,N'-thiobisdicyclohexylamine.



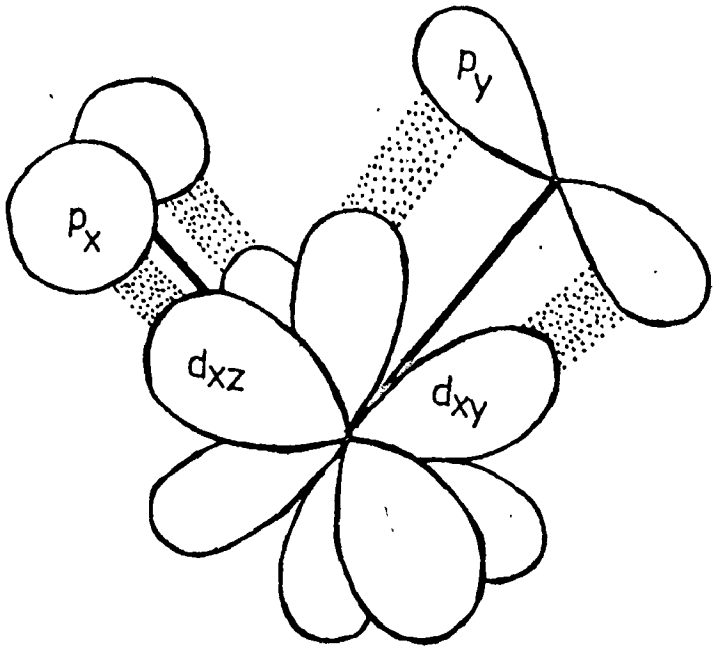
(melting point 208°C)[77]

XXXI

Items (g) and (h) will be discussed together since they are related. When two nitrogen lone pairs are donated to one sulfur atom, the symmetry is such that both are donated to the same d-orbital. This d-orbital is contained in the plane defined by the two N-S bonds. This is the conformation found for the N,N'-thiobisdicyclohexylamine (Figure II-9) as well as the S_7NSNMe_2 structure (Figure II-13). It appears that this situation is preferred to that in which each nitrogen lone pair is donated to its own vacant d-orbital (Figure II-21). This implies there is greater energy gain associated with one three-centre π-bond than with two two-centre π-bonds. The stabilization of each N-S bond is reduced in this observed π-bonding situation since the one sulfur d-orbital cannot accommodate all four electrons. The resulting N-S bonds are intermediate between a true single N-S bond (1.70 to 1.74 Å) and the N-S bond in $S_7NS-NMe_2$ where there is donation from one nitrogen to one sulfur atom (1.60Å) An example of this bonding situation is that of N,N'-thiobisdicyclohexylamine discussed earlier in this chapter.

Figure II-21

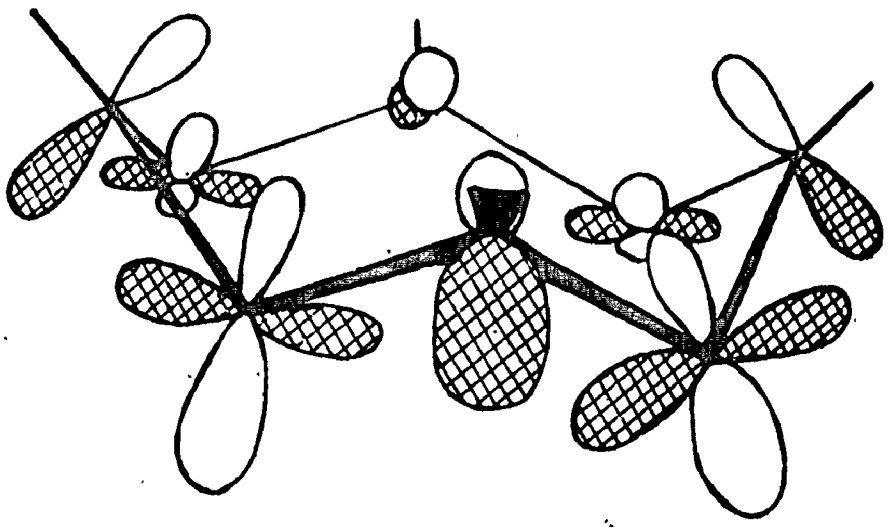
Overlap for Two Two-Centre pπ-dπ Bonds



A similar situation exists when there are two sulfur atoms competing for one lone pair. Upon sharing the pπ-electron density with both sulfur atoms, the two bonds are intermediate in length between a single NS bond and one with a full pπ-dπ bond. Only one sulfur d-orbital is required for each sulfur atom for complete delocalization. Even the sulfur imides can be regarded as having this kind of π-bonding. $S_4N_4(CH_3)_4$ for example requires only four sulfur 3d-orbitals and four nitrogen 2p-orbitals (Figure II-22). The observed bond length of 1.68 Å is again intermediate between

Figure II-22

Orbital Overlap in $S_4N_4Me_4$

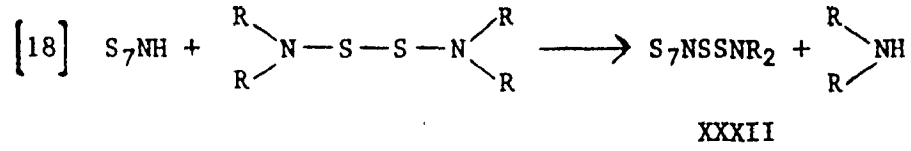


the single σ-bond length (1.70 to 1.74 Å) and that associated with σ- and π-bonds (1.60 Å).

Evaluation of the two structural determinations presented in this work along with structures in the literature illustrate the importance of pπ-dπ bonding in saturated sulfur-nitrogen systems. The eight points discussed in this section may be useful in understanding compounds containing formal sulfur-nitrogen single bonds.

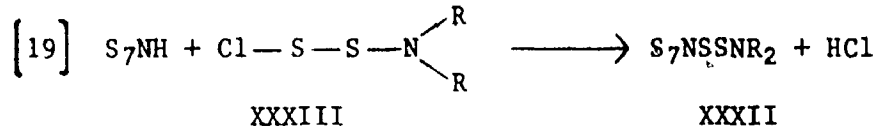
II-8 ATTEMPTED PREPARATION OF N,N'-DITHIOHEPTASULFURIMIDE-DIMETHYLAMINE (XXXII)

Preparation of compound XXXII was attempted by the following methods. Reaction [18] was an obvious route in light



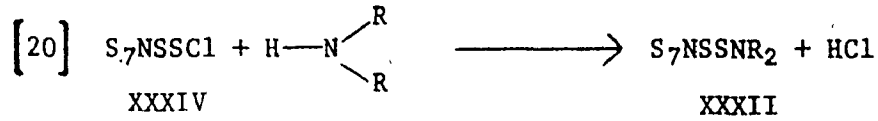
[18] $S_7NH + \begin{matrix} R \\ R \end{matrix}\!\!>\!N-S-S-N\!<\!\!\begin{matrix} R \\ R \end{matrix} \longrightarrow S_7NSSNR_2 + \begin{matrix} R \\ R \end{matrix}\!\!>\!NH$

XXXII



[19] $S_7NH + Cl-S-S-N\!<\!\!\begin{matrix} R \\ R \end{matrix} \longrightarrow S_7NSSNR_2 + HCl$

XXXIII XXXII



[20] $S_7NSSCl + H-N\!<\!\!\begin{matrix} R \\ R \end{matrix} \longrightarrow S_7NSSNR_2 + HCl$

XXXIV XXXII

of the method of preparation of S_7NSNMe_2. This reaction, however, was considerably slower than with the N,N'-thiobisamines. Many other reactions proceeded at the temperature necessary (60°C) for reaction [18]. At these temperatures, scission of the S-S bonds both of the chain or the ring could occur giving many products. When the reaction was monitored using ^1H NMR, many products were in fact observed. Preparation of S_7NSSNR_2 was in all likelyhood accomplished, but separation from the other products produced in the reaction (mostly N,N'-polythiobisamines) proved to be impossible using normal chromatography on silica or alumina. Perhaps application of molecular exclusion chromatography will enable this compound to be extracted from the complex reaction mixture.

Reactions [19] and [20] both appear to be straightforward

methods of preparation of compound XXXII. Problems in preparing pure XXXIII and XXXIV from condensation reactions between the amine (imide) and sulfur monochloride, however, made the final reaction mixture much more complex. There was no easy method to test the purity of XXXIV but the production of a red oil in these systems is usually indicative of polysulfides and other products. When this oil was reacted further with R_2NH, many products were formed. Even in reaction [19] using reasonably pure XXXIII ($R = (CH_3)_2CH-$, purified by fractional distillation), ^1H NMR showed that many products were present in resulting red oil. When this reaction was carried out in pyridine, one of the products isolated was found to be diisopropylammonium chloride (solubility in D_2O, ^1H NMR). This shows that the reaction is not proceeding entirely as expected. Chromatography was attempted on the red oil product mixtures but good separations were not attained even using pentane as eluent or columns over two meters in length.

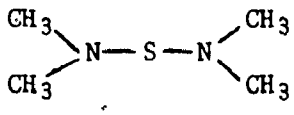
In general, the compound S_7NSSNR_2 is more difficult to prepare than the monosulfur analogue. Production of this compound competes much less favourably with side reactions in reaction [18] than for the preparation of S_7NSNR_2. These reactions, however, may be useful in preparing XXXII if better separation techniques can be found.

CHAPTER III

REACTION OF TRIPHENYLPHOSPHINE, DIPHENYLPHOSPHINOUS CHLORIDE, PHENYLPHOSPHONOUS CHLORIDE AND PHOSPHORUS TRICHLORIDE WITH N,N'-THIOBISDIMETHYLAMINE

III-1 INTRODUCTION

While there have been a considerable number of investigations into the reactions of N,N'-thiobisdimethylamine (tetramethylsulfoxylic diamide), III, with boron Lewis acids, few studies have been



III

made of similar reactions with phosphorus compounds. The reaction of PF_3 with N,N'-thiobisdimethylamine has been studied only superficially[80] and the reactions between chlorophosphines and the NSN linkage have not been reported in the literature.

III-2 TRIPHENYLPHOSPHINE AND N,N'-THIOBISDIMETHYLAMINE

Triphenylphosphine and N,N'-dithiobisdimethylamine, III, were found not to react upon heating to 50°C for 72 hours. The reaction mixture was monitored by ^1H NMR and the spectrum showed no change during this time.

III-3 DIPHENYLPHOSPHINOUS CHLORIDE AND N,N'-THIOBISDIMETHYLAMINE

Contrary to the non-reactivity of $(C_5H_5)_3P$ with N,N'-thiobisdimethylamine, diphenylphosphinous chloride reacted readily even at low temperatures.

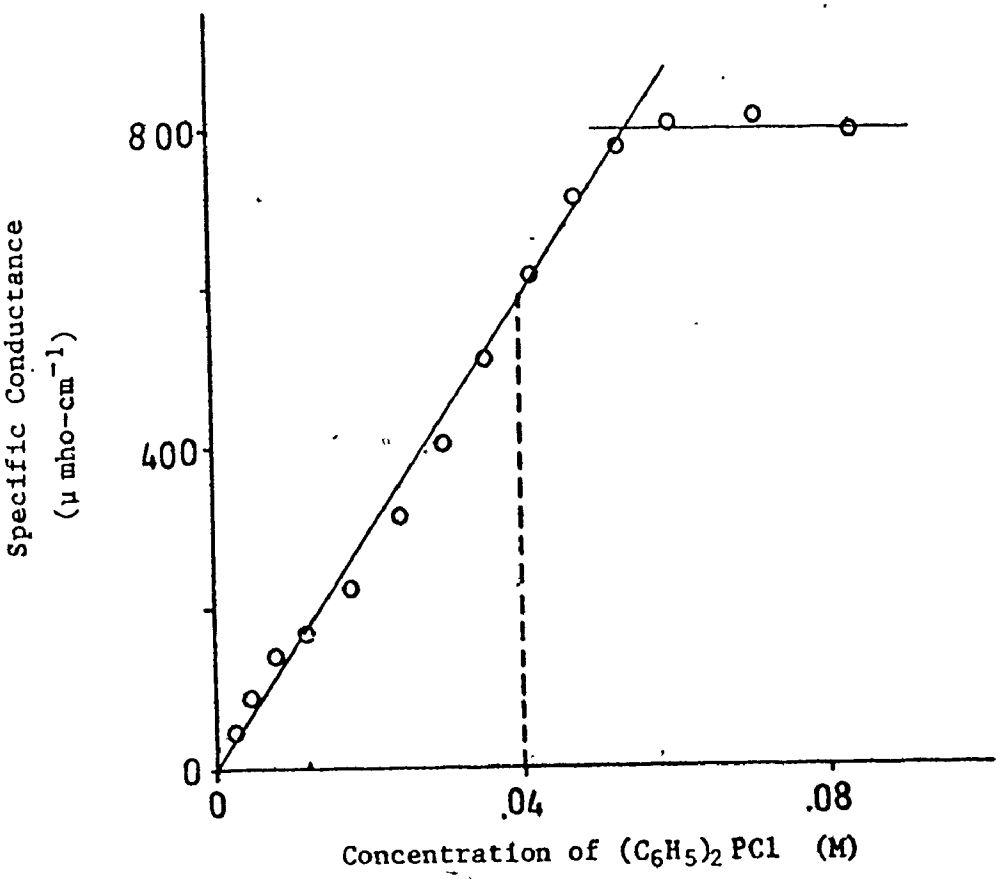
(i) Mole Ratio $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S$ = 1:1

When the N,N'-thiobisamine III was titrated with diphenylphosphinous chloride, the ^1H NMR singlet (δ = +3.03 ppm) corresponding to III was consumed upon reaching the mole ratio $\emptyset_2PCl$: III = 1:1. The reaction proceeded immediately, even at -60°C. The ^1H NMR spectrum then consisted of two doublets in the methyl region (δ = +3.16 ppm, J = 12.0 Hz, δ = +2.86 ppm, J = 1.5 Hz) and a complex pattern centred at δ = +7.8 ppm for the aryl protons. A ^{31}P NMR spectrum of a similarly mixed sample showed a broad peak (δ = -62.0 ppm, width at ½ height = 53 Hz) which sharpens when proton decoupled. Conductimetric measurements were carried out on the solution as a function of phosphine addition. The results are shown in Figure III-1. The sum of the conductivities of the reagents alone at that concentration (50 ($(C_5H_5)_2PCl$) + 0.0 (III) = 50 μ mho-cm^{-1}) was considerably less than the conductivity at the equivalence point ($\sim$600 μ mho-cm^{-1}). Upon reaching the mole ratio $(C_6H_5)_2PCl$: III = 1:1, the rate of increase of conductivity with addition of phosphine decreases rapidly. The fact that the inflection point is not exactly at 0.04 M is most likely due to secondary reactions or dissociation of products. Also the

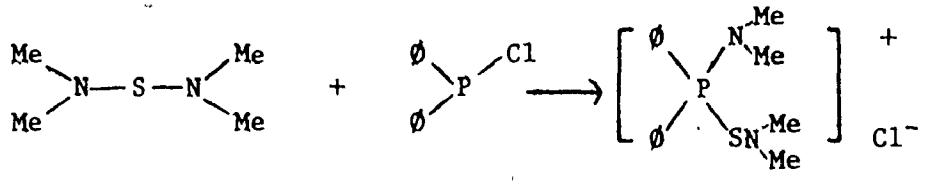
Figure III-1

Conductivity vs Addition of $(C_6H_5)_2PCl$ (25°C).

(0.4 M Solution of III in CH_2Cl_2)



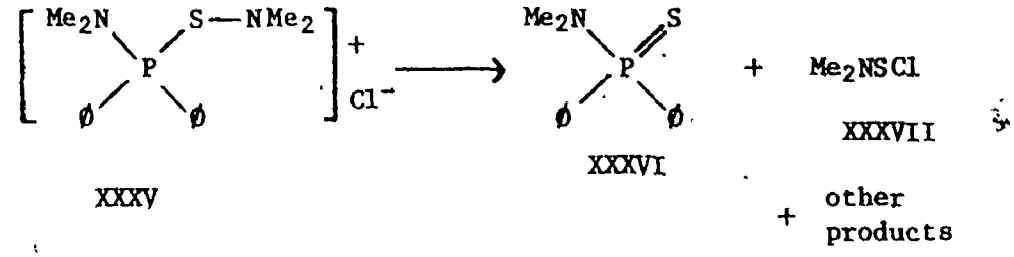
conductivity of the $(C_6H_5)_2PCl$ in CH_2Cl_2 (50 μ mhos-cm^{-1} at 0.04 M) suggests that some hydrolysis had taken place when the conductivity was measured. The above data is best explained by an insertion reaction of the phosphorus into the sulfur-nitrogen bond (reaction [21]). Species XXXV is consistent with the experimental results shown above. The proton NMR of the dimethylamino group attached

[21] 

XXXV

directly to phosphorus is shifted to low field most likely due to the inductive effect of the cationic phosphorus. The $^{31}P - {}^{1}H$ coupling constant of 12.0 (5) Hz is also consistent with this interpretation. The $^{31}P - {}^{1}H$ coupling through the P-S-N-C-H linkage is considerably smaller (1.5 (5) Hz) as would be expected. The ^{31}P chemical shift of XXXV is in the right region for a 4 coordinate phosphorus attached to one sulfur atom. The conductivity at the equivalence point ($\sim$600 micromho-cm^{-1}) is comparable to the conductivity of an equimolar solution of $[\phi_4P]^+ Cl^-$ (1150 micromhos-cm^{-1}).

Upon further standing, species XXXV decomposes to products as represented by reaction [22]. This reaction is quite slow at

[22] 

XXXV XXXVI XXXVII

room temperature with a half reaction time of about three days. Comparison of the ^{1}H and ^{31}P NMR data with that found in the literature confirms the existence of XXXVI (^{1}H NMR, methyl (δ = +2.45 ppm,

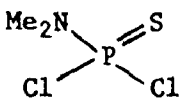
J = 14.5 Hz; lit.[116], δ = +2.39, J = 14.6 Hz), aryl (δ = +7.5 ppm, lit.[116], δ = +7.4 ppm); ^{31}P NMR (δ = -70.6 ppm, J = 14.0 Hz, lit.[116], δ = -70.9 ppm, J = 14.6 Hz)). Five of the seven peaks in the ^{31}P multiplet representing XXXVI were resolved. The ^{1}H NMR was also identical to that of an "authentic" sample of XXXVI which was isolated from another reaction and characterized by mass spectrometry (see section III-3ii).

Compound XXXVII gave a singlet in the ^{1}H NMR (δ = +3.12 ppm) which was identical to an authentic sample prepared by reaction [23]. Further characterization of XXXVII was effected by removing

[23] $Me_2NH + SCl_2(XS) \xrightarrow[\text{ether}]{Me_3N\ (XS)} Me_2NSCl + Me_3NH^+\ Cl^- \downarrow$

XXXVII

it from the reaction mixture of [21] by distillation and subsequent reaction with phosphorus trichloride (reaction [24]). Compound XXXVIII was identified by comparing the ^{31}P and ^{1}H NMR data to

[24] $Me_2NSCl + PCl_3 \longrightarrow$  $+ \ Cl_2 \uparrow$

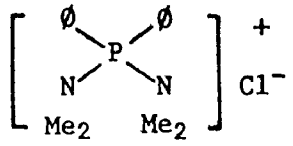
XXXVII

XXXVIII

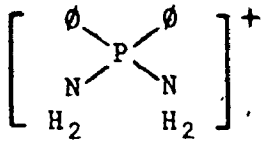
literature values (^{1}H NMR : δ = +3.00 ppm, J = 17.0 Hz, lit.[117] δ = +3.0 ppm, J = 17 Hz; ^{31}P NMR : δ = 65.1 ppm, J = 16.6 Hz, lit.[102] δ = -62.0 ppm). Evidence for the existence of chlorine was provided by the blackening of moistened starch-iodide paper by the fumes evolved upon warming the yellow CH_2Cl_2 solution.

The "authentic" sample of XXXVII behaved similarly in its reaction with PCl_3.

The NMR spectra of the reactant mixture after six days showed evidence of products other than those shown in reaction [22]. These consisted of the products characterized in the 2:1 = $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S$ mole ratio reaction (section III-3ii) as well as some other species. The ^1H NMR showed an extra doublet (δ = +2.61 ppm, J = 11.5 Hz) and the ^{31}P spectrum resolved 8 peaks in a complex multiplet (δ = -31.1 ppm, J = 11.5 Hz) and a broad peak (δ = -54.6 ppm). Although the evidence is not conclusive, it is tempting to assign the ^1H doublet and ^{31}P multiplet both with J = 11.5 Hz to species XXXIX since this fits the NMR data and would



XXXIX



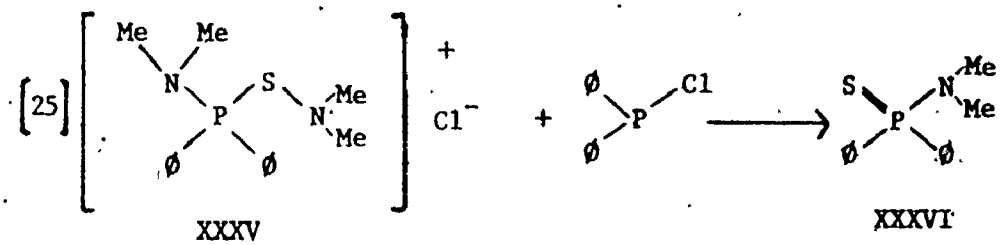
XL

balance equation [21]. The ^{31}P chemical shift of XXXIX has been predicted[118] to be about -40.0 ppm and the chemical shift found for XL[118] (δ = -31.9 ppm) is very close to that of the multiplet (δ = -31.1 ppm). It is expected that some XXXIX should be present since it has been shown[119] that exchange reactions of dimethylamino groups and halogens on triply connected phosphorus are quite fast. The other smaller peak at -54.6 ppm in the ^{31}P NMR spectra was likely due to further decomposition and was unassigned.

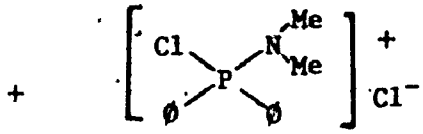
It should be pointed out that in all of these systems ($(C_6H_5)_nPCl_{3-n}$ - $((CH_3)_2N)_2S$) similar types of ligand scrambling reactions occurred. There seemed to be an initial period in which a specific reaction proceeded, then a slower rearrangement to give many products. Upon sitting even longer the solution turned dark brown, probably due to reactions involving the phenyl groups. The time period for the secondary reaction discussed above, [22], is suggestive that this reaction is of the rearrangement type.

(ii) Mole Ratio - $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S$ = 2:1

Upon mixing diphenylphosphinous chloride with N,N'-thiobisdimethylamine in the ratio of 2 to 1, the initial reaction is identical to the insertion discussed in reaction [21]. The two doublets corresponding to XXXV gradually disappear and are replaced by two other equivalent doublets. This half reaction time for this process was about 2 hours at room temperature. The reaction rate increased with the concentration of phosphine added. Reaction [25] represents the reaction that occurs.



XXXV XXXVI

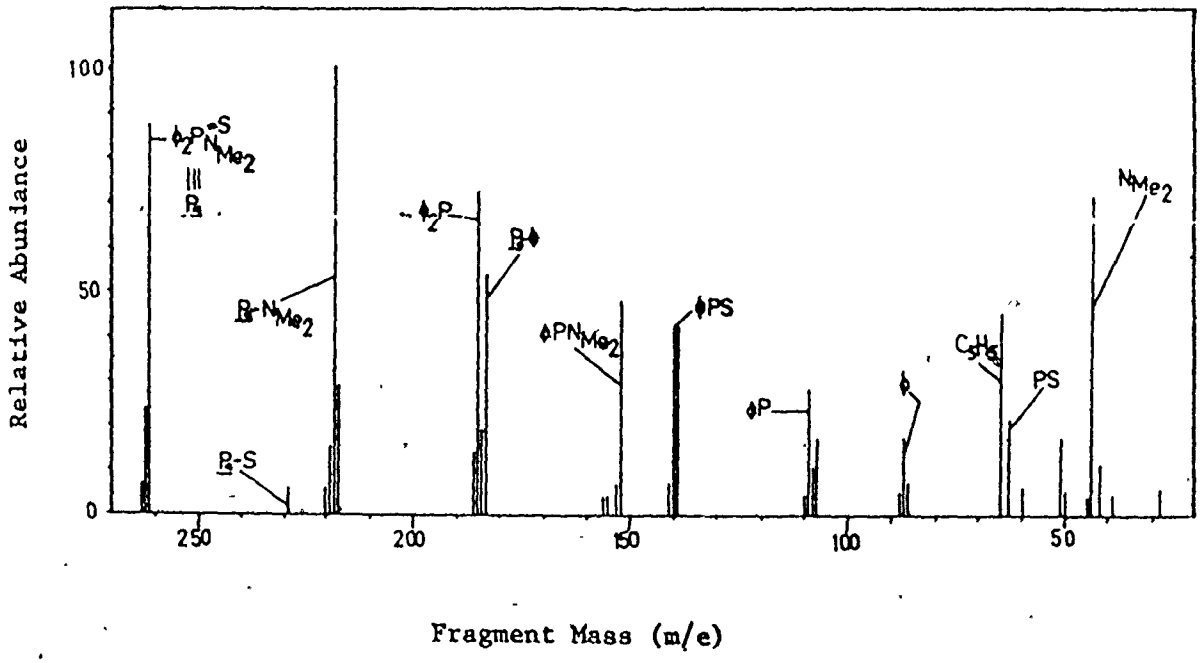


XLI

The existence of species XXXVI was again shown by the ^{1}H and ^{31}P NMR spectra as was discussed in section III-3i. This reaction mixture, however, was passed through a silica gel column and compound XXXVI was isolated as colourless crystals (M.P. = 91 to 92°C). The mass spectrum of these crystals is shown in Figure III-2 and confirms that XXXVI was indeed formed.

Figure III-2

Mass Spectrum of $(C_6H_5)_2P(S)(N(CH_3)_2)$



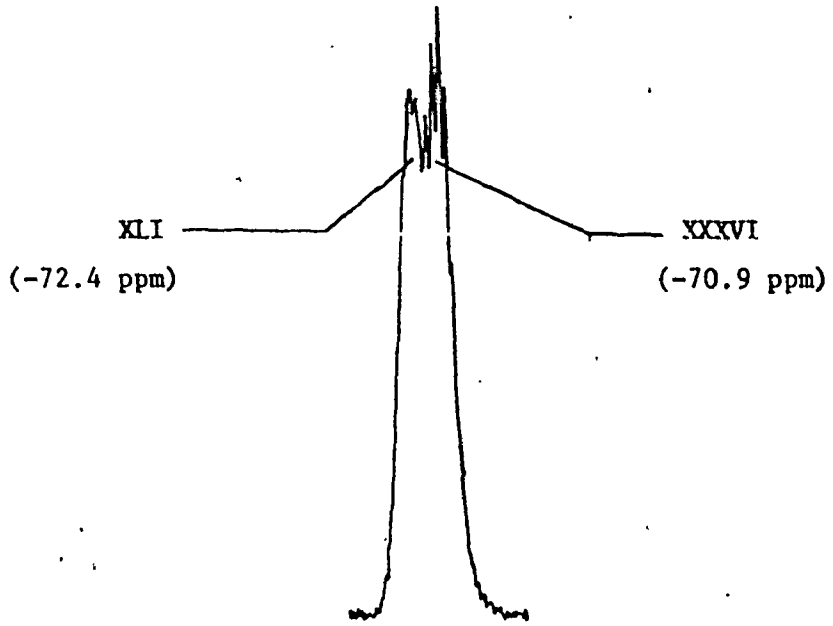
The phosphorus cation XLI was identified using ^{1}H NMR, ^{31}P NMR and conductivity measurements. The ^{1}H NMR spectrum consisted of a doublet in the methyl region (δ = +2.95 ppm, J = 15.5 Hz) and

an unresolved multiplet centred at +7.9 ppm for the aryl protons. The ^{31}P NMR spectrum of this compound was a partially resolved multiplet (δ = -72.4 ppm, J $\cong$ 15 Hz) which overlaps slightly with the multiplet of XXXVI at -70.9 ppm (Figure III-3).

Figure III-3

Overlapping ^{31}P NMR Resonances

of XXXVI and XLI



The ^{31}P chemical shift agrees well with that reported for the hexachloroantimonate salt in nitromethane (δ = -72.5 ppm)[118]. A specific conductivity of 750 micromhos-cm^{-1} for a 0.04 M solution

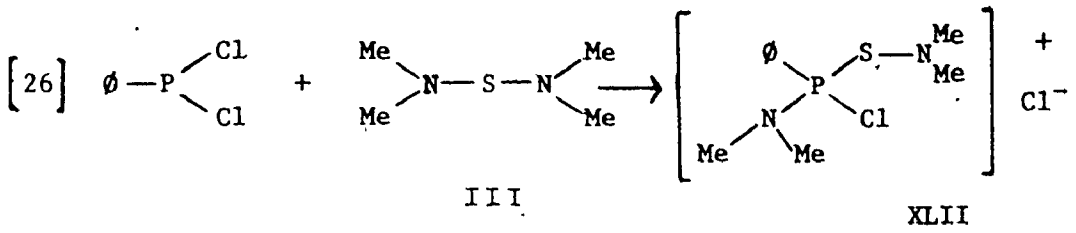
is in good agreement with conductivities (κ) of the similar salts $(C_6H_5)_4P^+ Cl^-$ (κ = 1150 μ mhos-cm^{-1}) and $(C_6H_5)_2P(NMe_2)(SNMe_2)^+Cl^-$ (XXXV) (κ = 600 - 800 μ mhos-cm^{-1}).

The utilization of chromatography in these systems was discontinued when it was discovered in the literature[120] that these compounds are highly poisonous. Any further manipulation of this type of compound was done with extreme care.

III-4 PHENYLPHOSPHONOUS DICHLORIDE AND N,N'-THIOBISDIMETHYLAMINE

(i) Mole Ratio $(C_6H_5)PCl_2$: $((CH_3)_2N)_2S$ = 1:1

The insertion reaction of phosphorus into the sulfur-nitrogen bonds which was suggested in the last section (III-3) has also been found to occur when $(C_6H_5)PCl_2$ is reacted with N,N'-thiobisdimethylamine (reaction [26]). In the ^1H NMR at -60°C



III XLII

two doublets (δ_1 = +3.06, J_1 = 14.0 Hz; δ_2 = +2.87, J_2 = 7.0 Hz) replace the singlet (δ = +3.03) corresponding to III in the methyl region as the phosphine is added in small amounts. Again in this cation, the dimethyl-amino group attached directly to the phosphorus can be identified by its larger ^{31}P coupling constant (14.0 Hz) and its more negative chemical shift (δ = +3.06 ppm). It may be noted that the long range coupling through the P-S-N-C-H linkage

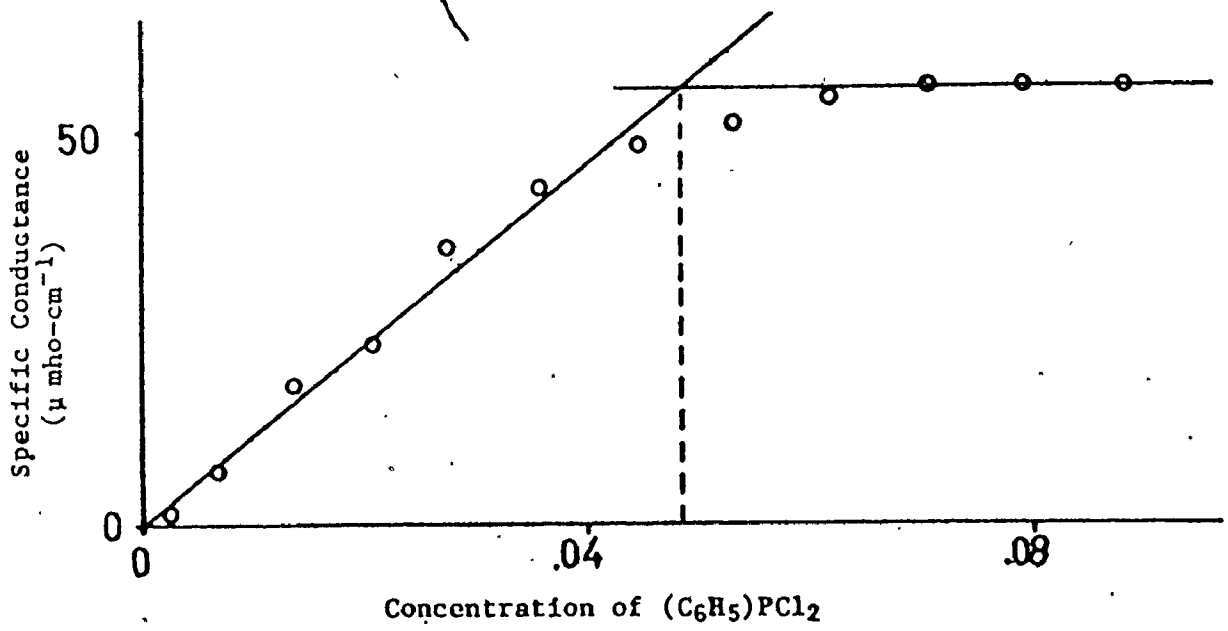
(J = 7.0 Hz) is larger than in the analogous diphenyl phosphine cation XXXV (J = 1.5 Hz). This pair of doublets continues to grow at the expense of the singlet until the mole ratio $(C_6H_5)PCl_2$: $((CH_3)_2N)_2S$ = 1:1 is reached, at which point other products form. The ^{31}P NMR spectra of species XLII consisted of a broad peak at -54.3 ppm, a chemical shift which is consistent with the 4 co-ordinate phosphorus attached to sulfur. The coupling to the hydrogen atoms on the methyl groups or the phenyl group was not resolved.

Conductivity measurements were also carried out on a 0.04 M solution of III (in CH_2Cl_2 at -78°C) as a function of added phosphine. The results are shown graphically in (Figure III-4). The rate of increase in conductivity with respect to addition of

Figure III-4

Conductivity vs Addition of $(C_6H_5)PCl_2$

(0.04 M Solution of III in CH_2Cl_2)



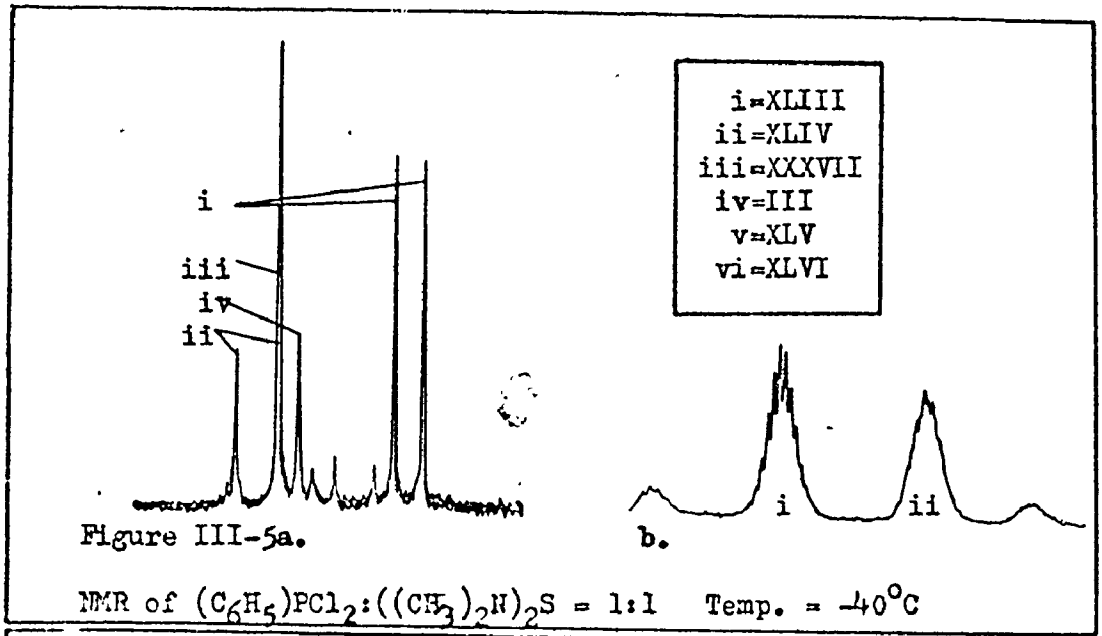


Figure III-5a.

NMR of $(C_6H_5)PCl_2$:$((CH_3)_2N)_2S$ = 1:1 Temp. = -40°C

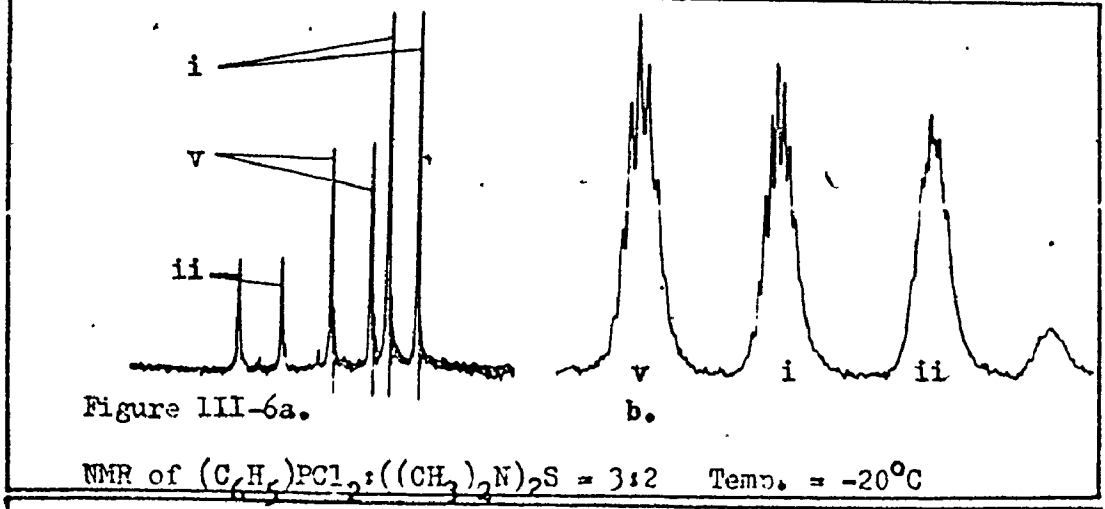


Figure III-6a.

NMR of $(C_6H_5)PCl_2$:$((CH_3)_2N)_2S$ = 3:2 Temp. = -20°C

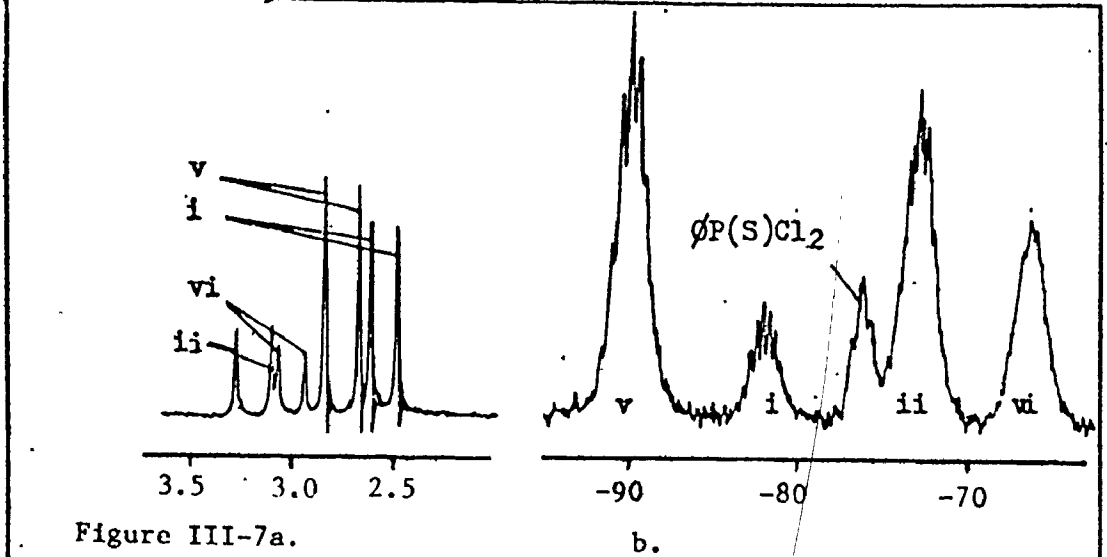
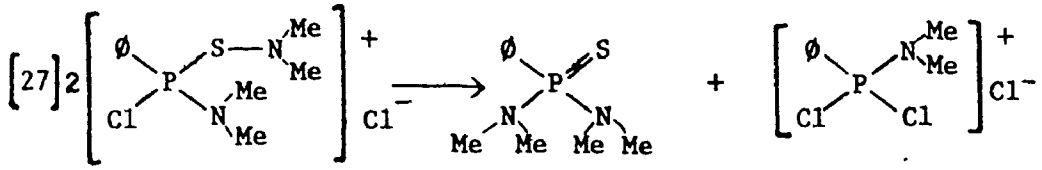


Figure III-7a.

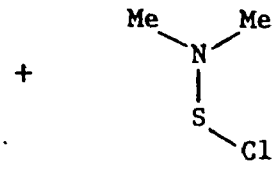
NMR of $(C_6H_5)PCl_2$: $((CH_3)_2N)_2S$ = 3:2 Temp. = +20°C

phosphine decreases sharply in the region of mole ratio $(C_6H_5)PCl_2$: $((CH_3)_2N)_2S$ = 1:1. This is consistent with reaction [26] showing the coupling of one molecule of phosphine with one molecule of thiobisamine to produce a salt. The specific conductivity of 50 μ mhos cm^{-1} at -78°C for a 0.4 M solution could not be compared to an equimolar solution of $(C_6H_5)_4P^+ Cl^-$ since the solubility of this compound in CH_2Cl_2 at -78°C is too low and precipitation occurs. It would be expected that the conductivity of these solutions be considerably lower than equivalent solutions at room temperature.

Compound XLII is unstable above -50°C and will react further to give a number of other products (reaction [27]). In the methyl



XLII XLIII XLIV



XXXVII

region of the ^1H NMR, the two doublets corresponding to XLII give way to the appearance of two more doublets, one twice the intensity of the other and a singlet (Figure III-5a). Similarly the broad unresolved peak (corresponding to XLII) in the ^{31}P NMR spectrum goes to two peaks of equal intensity (Figure III-5b). Compound

XLIII can be unambiguously identified by comparison of experimental NMR data with that reported in the literature (^{1}H NMR - doublet, δ_{methyl} = +2.56 ppm, J = 12.0 Hz; lit.[116] δ_{methyl} = +2.50 ppm, J = 12.0 Hz, δ_{aryl} = +7.38 ppm) (^{31}P NMR - 13-plet, δ = -81.5 ppm, J = 12.2 Hz, lit.[116] δ = -81.7 ppm, J = 12.0 Hz).

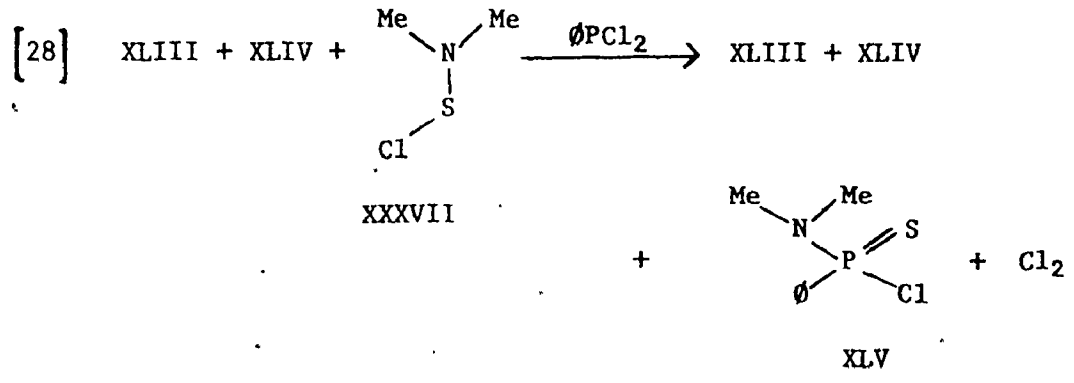
The singlet in the ^{1}H NMR spectrum (δ = +3.12 ppm) can be assigned to compound XXXVII in agreement with the NMR data found for an authentic sample as described in section (III-31).

The cation XLIV has not been reported in the literature and therefore cannot be assigned in this manner. The ^{1}H NMR resonance of this species, however, suggests this structure. The low field chemical shift (δ = +3.19 ppm) indicates that there is a positive charge associated with the molecule. At 100 MHz, one peak of the doublet (J = 17.5 Hz) is hidden by the singlet corresponding to XXXVII but the peak is easily observed by recording at 60 MHz. The relative intensities of the peaks corresponding to XLIII and XLIV (2:1) also suggests that reaction [26] represents what is truly occurring. Although the intensities of the ^{1}H NMR peaks corresponding to XLIII and XLIV were two to one, the peaks in the ^{31}P NMR spectra of a similarly prepared sample showed that the concentrations of XLIII and XLIV were equal. This showed that there were twice as many methyl groups per phosphorus atom in compound XLIII than in compound XLIV. Since XLIII has four methyl groups, there must be one dimethylamino group in compound XLIV. The ^{1}H - ^{31}P coupling

is of relatively little use in assigning this peak (δ = -73.0 ppm) since coupling is observed not only with the dimethylamino group but also with additional protons, probably the phenyl protons. Significant coupling may be expected due to delocalization of the positive charge on the phosphorus atom into the aryl ring. Confirmation of this explanation from the aryl region of the ^1H NMR should be possible. However, assignment of the aryl absorbances of compound XLIV in the complex pattern given by the mixture of this compound and also compound XLIII proved to be impracticable.

(ii) Mole Ratio $(C_6H_5)PCl_2$: $((CH_3)_2N)_2S$ = 3:2

When another half equivalent of $(C_6H_5)PCl_2$ is added to the products of reaction [27] at -20°C, the following reaction [28] occurs immediately. The ^1H and ^{31}P NMR spectra of the products of



this reaction are shown in Figure III-6. In the ^1H NMR spectrum, the singlet corresponding to XXXVII disappears and the doublet (δ = +2.76 ppm, J = 17.0 Hz) corresponding to XLV appears. Although the NMR spectrum of this compound has not been reported, an

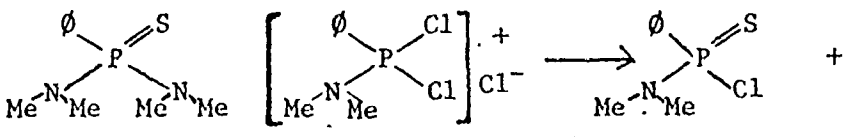
authentic sample was prepared by another reaction (discussed later in section IV-3, reaction [51]) and identified using mass spectrometry. The ^{1}H NMR spectrum of that sample was identical to one of the constituents observed in the mixture of products from reaction [28].

The ^{31}P NMR spectrum of XLV in the mixture from reaction [28] also agreed with the ^{31}P spectrum of the authentic sample. The ^{31}P septet is found at -89.1 ppm with the same coupling constant observed in the ^{1}H spectrum (17.0 Hz). The chemical shift is quite negative for a 4 co-ordinate phosphorus suggesting the presence of a double bonded sulfur substituent. The septet shows there is only one dimethylamino group.

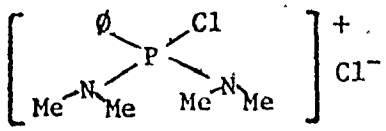
The chlorine produced in reaction [28] was identified by the yellow colouration of the methylene chloride solvent and the fact that moistened starch-iodide paper held above the warmed solution turned black. Similar tests on methylene chloride solutions containing only halophosphines were negative.

When the solution from reaction [28] is allowed to sit at room temperature, some disproportionation reactions occur as shown in reaction [29]. Species XLIII, XLIV and XLV have all been

[29]



XLIII XLIV XLV



identified using their ^{1}H and ^{31}P NMR resonances as discussed above.

The ^{1}H NMR spectrum of XLVI (Figure III-7a) showed a doublet (J = 13.0 Hz) at low field (δ = +3.01 ppm), the chemical shift being indicative of a cationic species. The ^{31}P NMR chemical shift (δ = -66.4 ppm, Figure III-7b) suggested that this species did not likely contain a doubly bonded sulfur substituent. The ^{1}H coupling to the peak assigned to XLVI was consistent with the other salt XLIV in that the coupling observed was not entirely due to dimethylamino groups but also involved the aryl protons.

It may be noted that in (Figure III-7b), the ^{31}P NMR spectrum shows that there is phenylphosphonothioic dichloride produced from the rearrangement reactions taking place. The coupling of the aryl protons to phosphorus which was suggested for the ^{31}P NMR of XLIV and XLVI can be observed in this species.

III-5 PHOSPHORUS TRICHLORIDE AND N,N'-THIOBISDIMETHYLAMINE

(i) Mole Ratio PCl_3 : $((CH_3)_2N)_2S$ = 1:2

Phosphorus trichloride behaves slightly differently in its reaction with N,N'-thiobisdimethylamine, III, than do the other halophosphines in that the first product observed in the NMR is that which results from two successive insertion reactions [30].

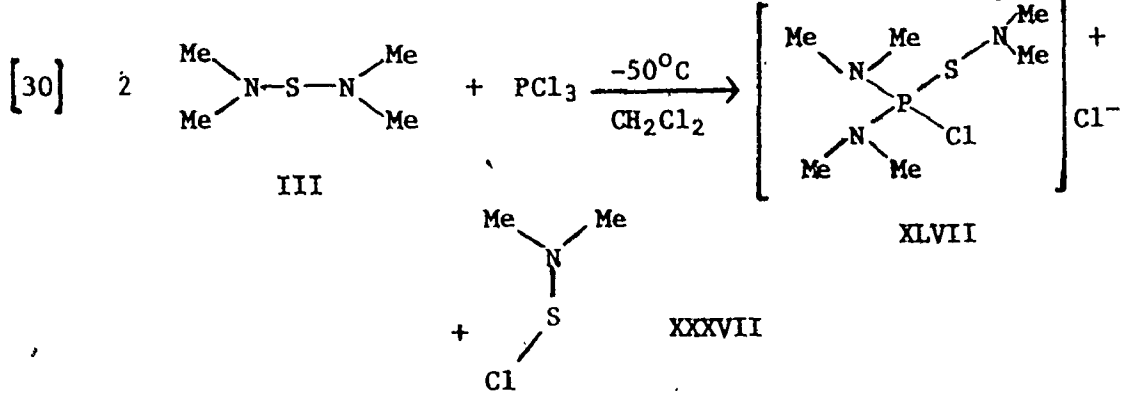
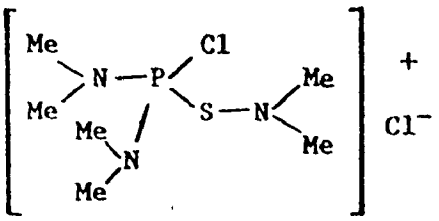
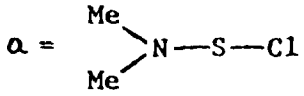
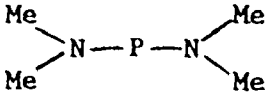


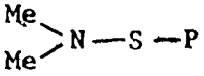
Figure III-8

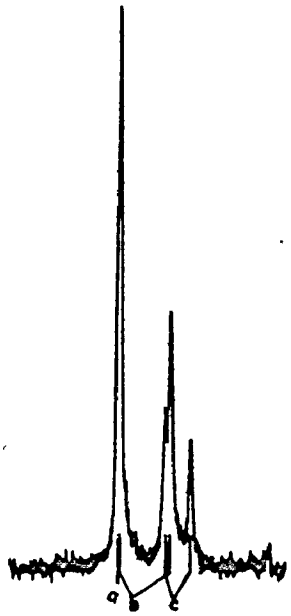
^1H and ^{31}P NMR of 

(a) ^1H NMR (100 MHz)

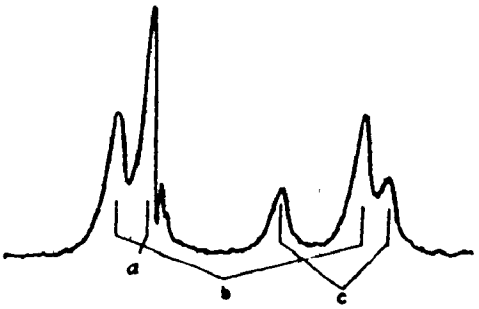
a = 

b =  J_b = 14.0 Hz

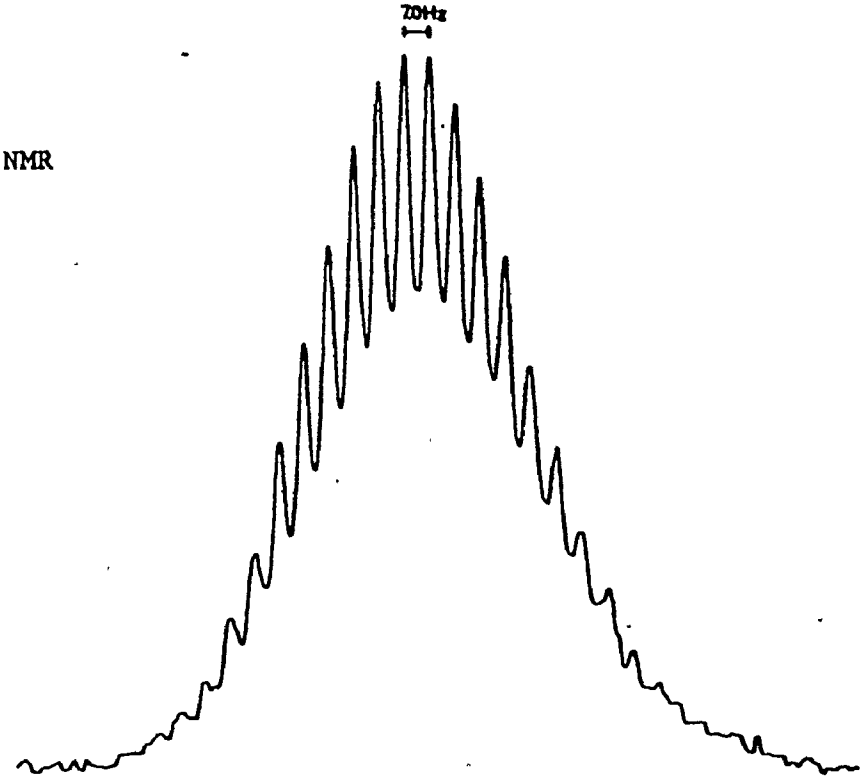
c =  J_c = 7.0 Hz



(b) ^1H NMR (60 MHz)



(c) ^{31}P NMR

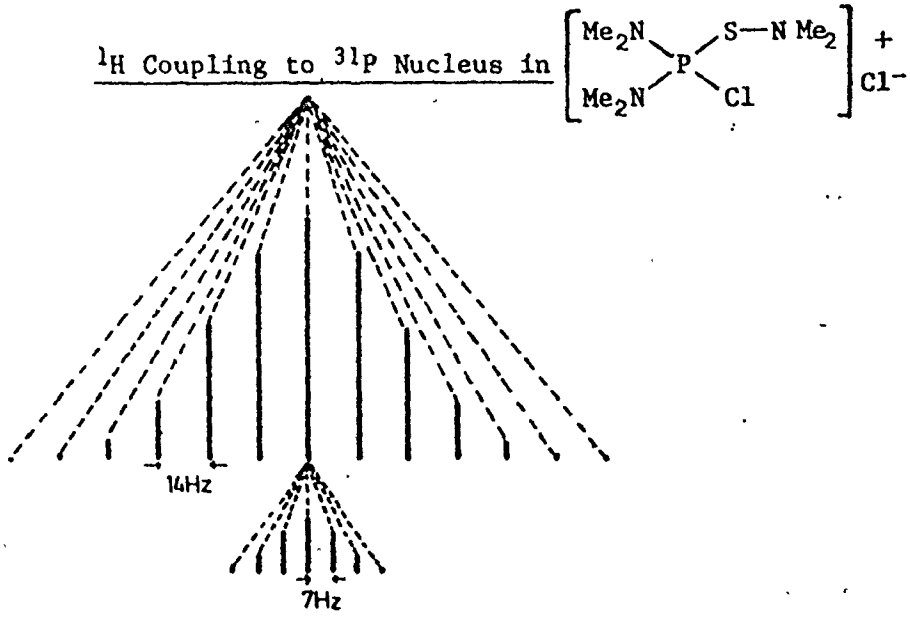


Species XXXVII was identified using ^{1}H NMR (δ = +3.11 ppm) as in the last two sections (III-3, III-4).

The ^{1}H NMR spectrum of XLVII consisted of two doublets, one (δ = +3.07 ppm, J = 14.0 Hz) twice the intensity of the other (δ = +2.98 ppm, J = 7.0 Hz). At 100 MHz, one peak of the low field doublet falls directly under the singlet corresponding to XXXVII (Figure III-8a). At 60 MHz, however, both doublets are clearly visible (Figure III-8b).

The ^{31}P NMR spectrum of species XLVII is quite unique because the ^{1}H coupling through the P-N-CH_3 linkage (14.0 Hz) is twice that of the P-S-N-CH_3 linkage (7.0 Hz). The resultant spectrum is a 31 line multiplet (δ = -80.2 ppm) of which about twenty lines can be resolved (Figure III-8c). The theoretical intensities for the peaks can be found from a completed first order "stick" diagram such as Figure III-9 and are found to be

Figure III-9

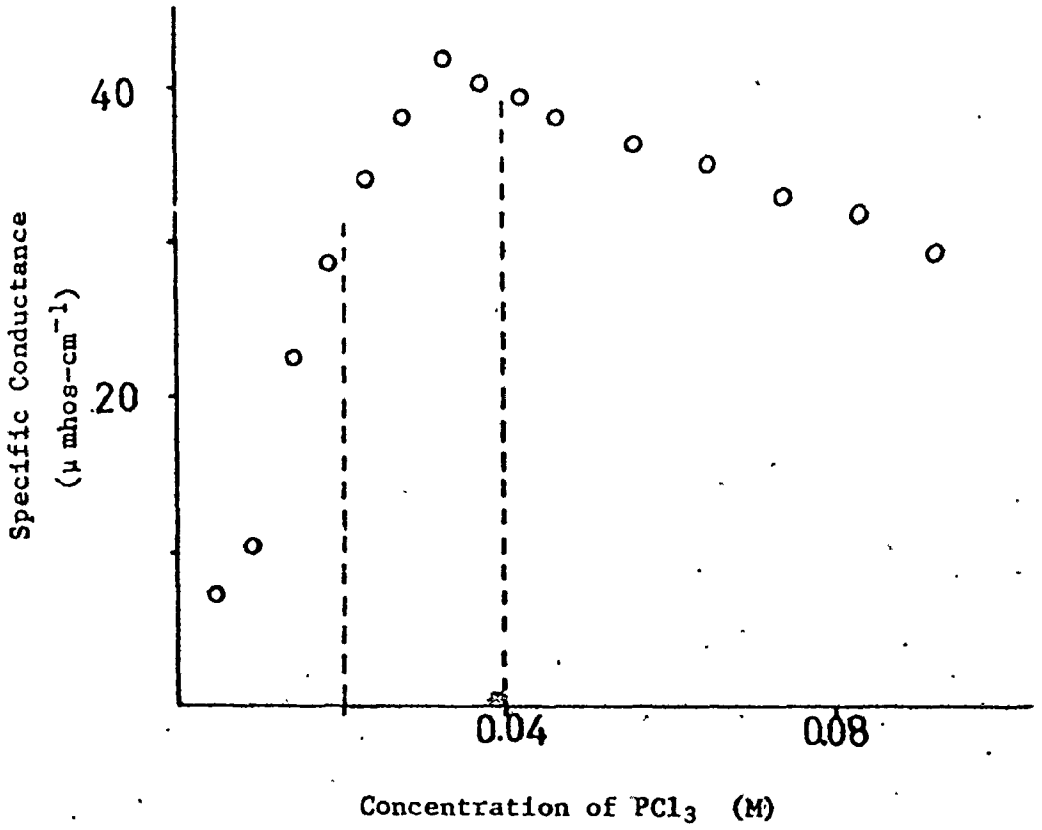


(27984 , 27027, 24354, 20449, 15972, 11583, 7766, 4797, 2712, 1391, 642, 261, 92, 27, 6, 1) starting from the centre peak.

Conductivity measurements were also obtained for this system at -78°C. The results are shown below in Figure III-10. Again the maximum specific conductivity measured occurs at a ratio

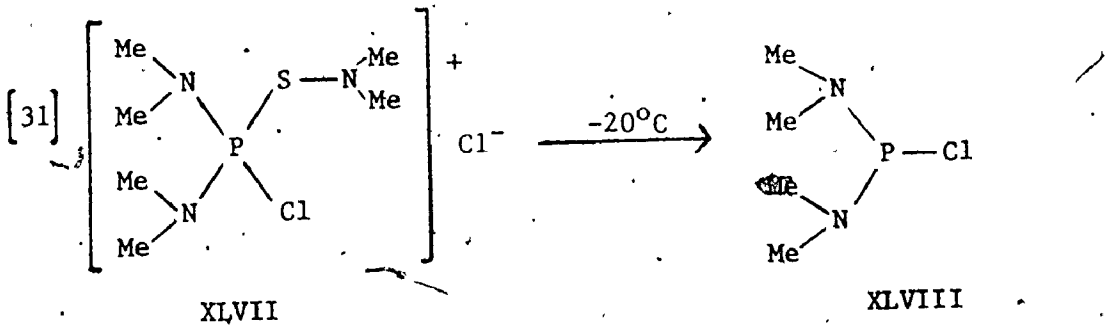
Figure III-10

Conductivity vs Addition of PCl_3
(0.04 M Solution of III in CH_2Cl_2)

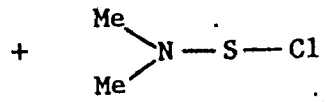


above the predicted stoichiometry (in this case PCl_3 : $(((CH_3)_2N)_2S$ = 1:2). It is clear, however, that the conductivity maximum occurs before the 1 to 1 molar ratio is reached.

When species XLVII is allowed to warm up to -20°C in CH_2Cl_2 it reacts further as shown by reaction [31]. Compound XLVIII was identified using ^1H NMR, the experimental data agreeing



XLVII XLVIII

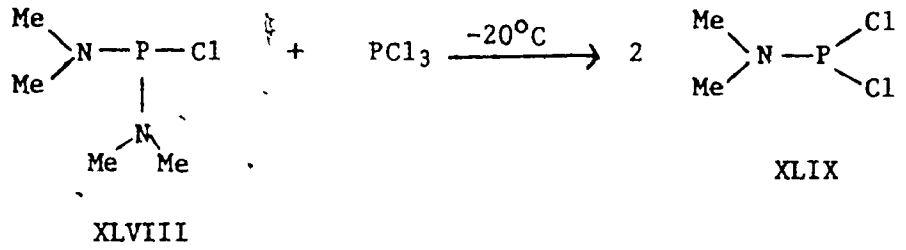


XXXVII

well with the literature (δ = +2.71 ppm, J = 12.0 Hz, lit.[121] δ = +2.74 ppm, J = 12.3 Hz).

(ii) Mole Ratio PCl_3 : $((CH_3)_2N)_2S$ = 1:1

When more PCl_3 is added to the products of the decomposition of XLVII (reaction [31]) a disproportionation of XLVIII occurs with PCl_3 (reaction [32]). This reaction has been shown to occur by Van Wazer et al[119]. Compound XLIX was identified by comparison of ^1H and ^{31}P NMR data with literature values (^1H - doublet, δ = +2.77 ppm, J = 12.5 Hz, lit.[122] δ = +2.82 ppm, J = 13.0 Hz)

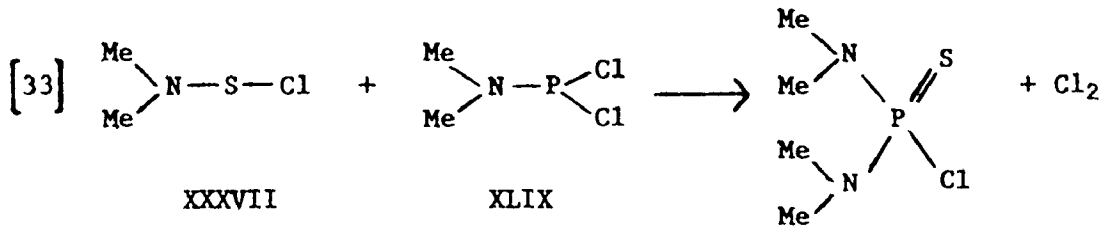
[32] 

XLVIII XLIX

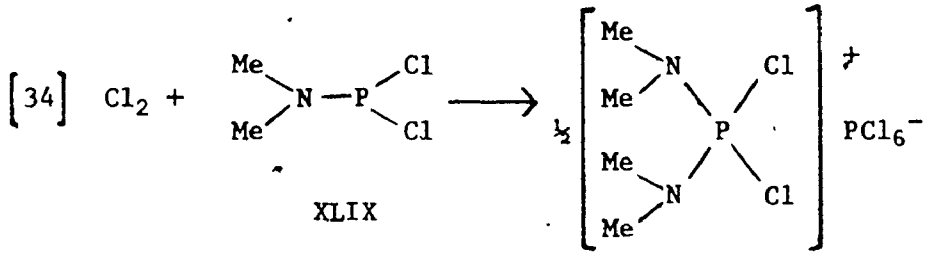
(^{31}P broad, δ = -164 ppm, lit.[102] δ = -166.0 ppm). Note that the ^{31}P chemical shift of XLIX is well out of the region of tetra-co-ordinate phosphorus. Coupling of the ^{31}P nucleus to the methyl groups was present since the peak sharpened when proton decoupled but the expected septet was not resolved. The reason for this is possibly that the ^{31}P chemical shift of this compound may be dependent on concentration, ionic strength, etc. In the time required to obtain a few hundred scans for reasonable resolution the chemical shift may have changed slightly.

(iii) Mole Ratio PCl_3 : $((CH_3)_2N)_2S$ = 3:2

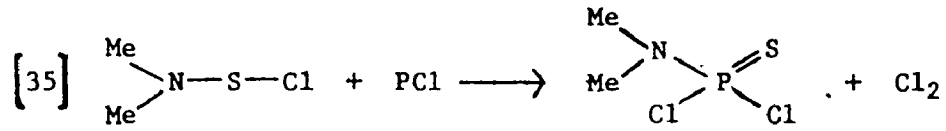
When the mixtures of the 1:2 and 1:1 reactions are allowed to warm to room temperature, further reaction takes place. The overall reaction requires that the reagents PCl_3 and III be present in the ratio 3:2, respectively, to go to completion. Although the reaction is quite complicated, some of the steps can be defined using ^{1}H and ^{31}P NMR. Three of the reactions occurring are presented below, [33], [34], [35]. The chlorine was identified again by colour in methylene chloride and by the moistened starch-iodide test. Compounds L and XXXVII were identified by their ^{1}H NMR and ^{31}P NMR



XXXVII XLIX L



XLIX LI



XXXVII XXXVIII

spectra and this information is given in Table III-1.

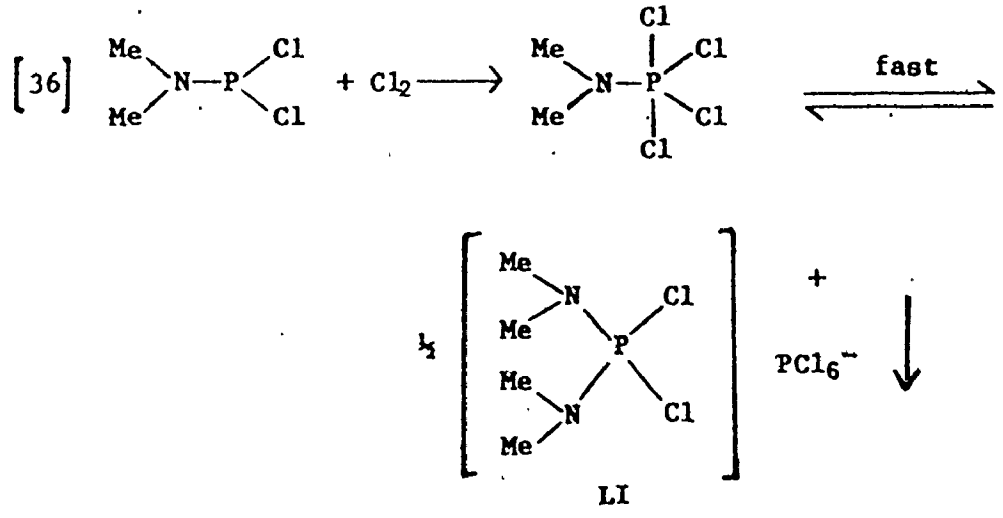
Compound LI occurred as a white air sensitive solid which precipitated out of the $CHCl_3$ or CH_2Cl_2 solution. Precipitation, the appearance of a yellow colour (Cl_2) and of the NMR spectrum assigned to compound LI are concurrent. For this reason it is thought that reaction [34] to produce LI can occur only after reaction [33] has proceeded to some extent. No peaks in the ^1H or ^{31}P NMR could be definitely assigned to this species although some

Table III-1

^{1}H and ^{31}P NMR Data for Compounds L and XXXVIII

Compound		^{31}P NMR (expt.)		^{31}P NMR (lit.)		Ref.
		δ	J	δ	J	
L	13-plet	-91.2	15.4	-91.4	--	102
XXXVIII	septet	-59.2	19.0	-62.0	--	102
		^{1}H NMR (expt.)		^{1}H NMR (lit.)		Ref.
		δ	J	δ	J	
L	doublet	2.73	15.5	2.73	15.4	123
XXXVIII	doublet	3.01	17.5	3.02	17.2	123

small transient peaks were observed. The compound appeared to precipitate immediately upon formation. This reaction may be best regarded as involving an equilibrium [36] which leads to the precipitation of LI.



The structure proposed for LI is based on Raman spectra and elemental analysis. The Raman spectrum of LI is shown below in Table III-2. Note that the strongest peaks in the spectrum

Table III-2

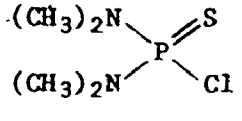
Raman Spectrum of $\left[((CH_3)_2N)_2PCl_3\right]^+PCl_6^-$

Frequency (cm^{-1})		Assignment of PCl_6^- Peaks[124]		
126				
242		(1)	238 (w)	ν_5
282 (broad)		(4)	283 (m w)	ν_2
			285	ν_4
362		(10)	360 (s)	ν_1
398			444	ν_3 Raman inactive
488				
524		(1)		
627				
733				
1456				
2824	CH stretching modes			
2846				
2876				
2971				
2990				
3006				

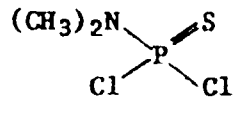
correspond to the strong Raman active vibrational modes of PCl_6^-. Final confirmation of the structure presented for LI was obtained by chemical analysis, experimental values agreeing well with calculated values (Found C - 11.78%, H - 3.16%, N - 6.79%, P - 13.84%, Cl - 63.82%, Calculated C - 11.07%, H - 2.79%, N - 6.46%, P - 14.28%, Cl - 65.40%).

If there is a slight deficiency of PCl_3 for complete reaction, when the reaction is complete there is unreacted XXXVII and less than one mole of XXXVIII per mole of L. For this reason reaction [35] is thought to occur as the final (or slowest) reaction in the system. Reaction [35] is also found to occur as one step in a similar reaction (reaction [52]) which will be discussed in section IV-4. It was found to require temperatures near -10^oC or higher for the reaction to proceed at a reasonable rate.

The overall reaction is given by equation [37].

[37] $3PCl_3 + 2((CH_3)_2N)_2S \longrightarrow$  + $\frac{1}{2}$ PCl_6^-

III L LI

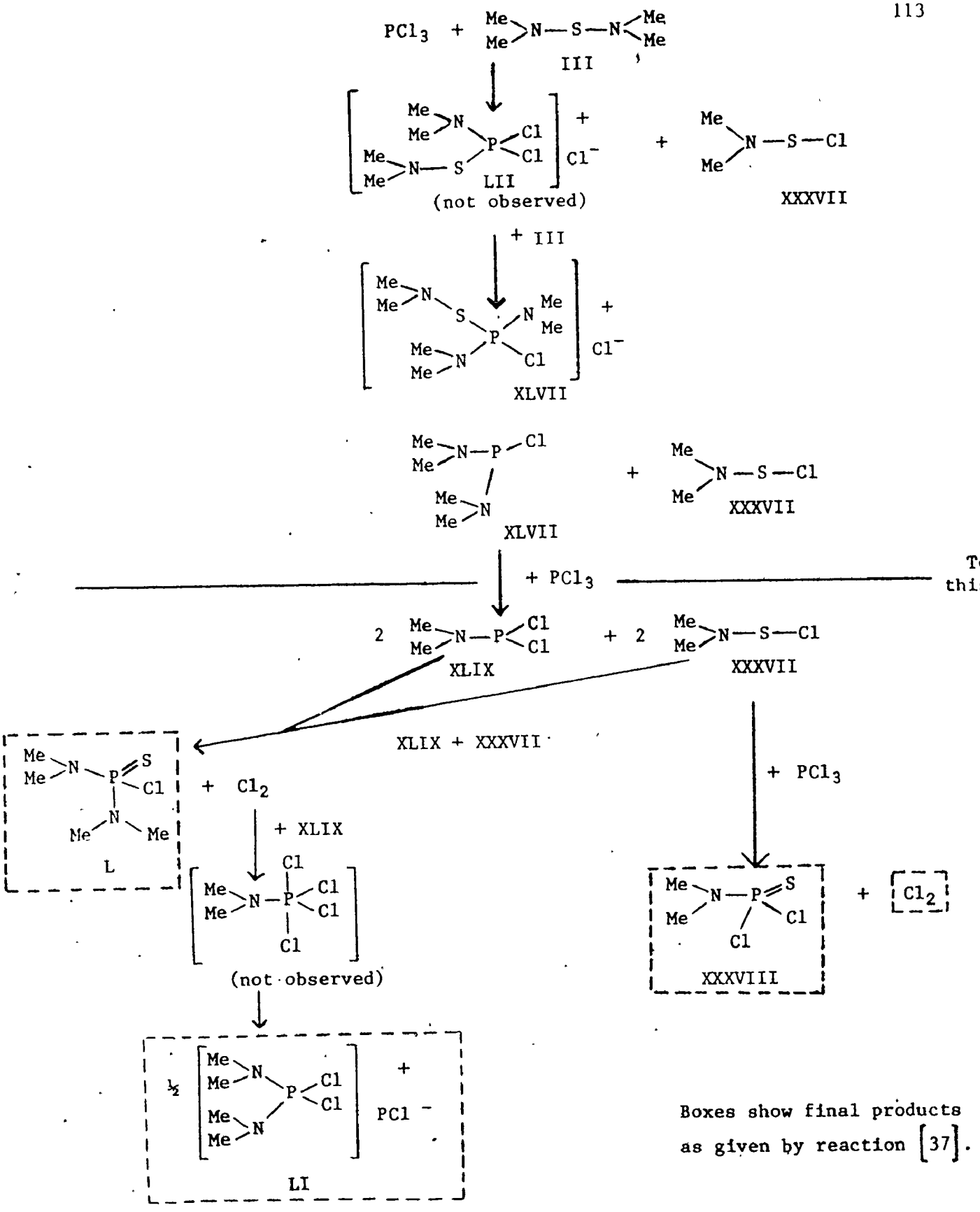
+  + Cl_2

XXXVIII

Since all of the products have now been described and a reaction suggested to account for their formation, it is now possible to

Figure III-11

Reaction of PCl_3 and N,N'-Thiobisdimethylamine



Boxes show final products as given by reaction [37].

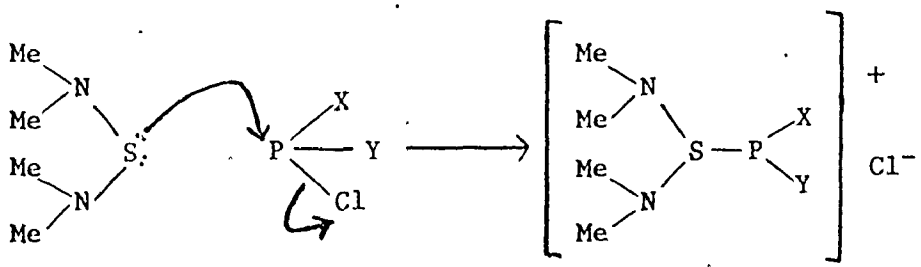
write a reaction scheme (Figure III-10) which is consistent with the experimental results.

III-6 DISCUSSION OF MECHANISM

In all of the systems discussed above (sections III-2 to III-4), a phosphorus atom has been inserted into a sulfur-nitrogen bond. Equivalent reactions do not occur if the phosphine has electron releasing groups (e.g. PEt_3) or electron withdrawing substituents (e.g. $P(OMe)_3$). The requirement for the insertion reaction to occur seems to be that there is a good leaving group (in this case Cl^-) attached to the phosphorus. The sulfur atom in the N,N'-thiobisamines has been shown to have Lewis base activity towards boron halides. This could result from a $p\pi$-$d\pi$ donation from nitrogen to sulfur, placing a slightly negative charge on the sulfur atom.

In light of these two factors, it is most logical to suggest that the initial attack of the thiobisamine on phosphorus involves donation of electron density from sulfur to phosphorus and subsequent loss of chloride ion (reaction [38]).

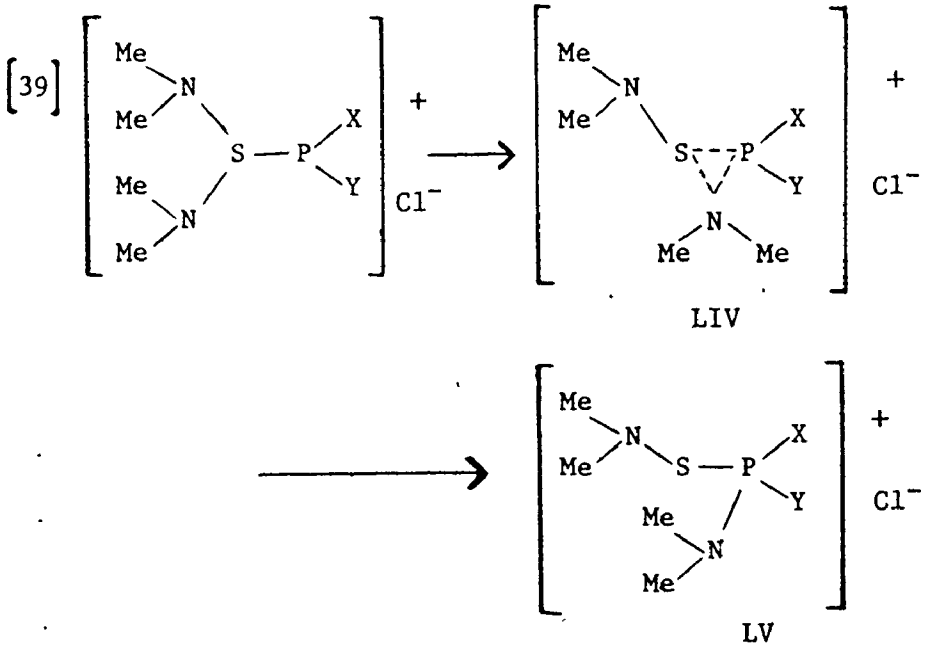
[38]



LIII

The resulting species LIII could then undergo a ligand

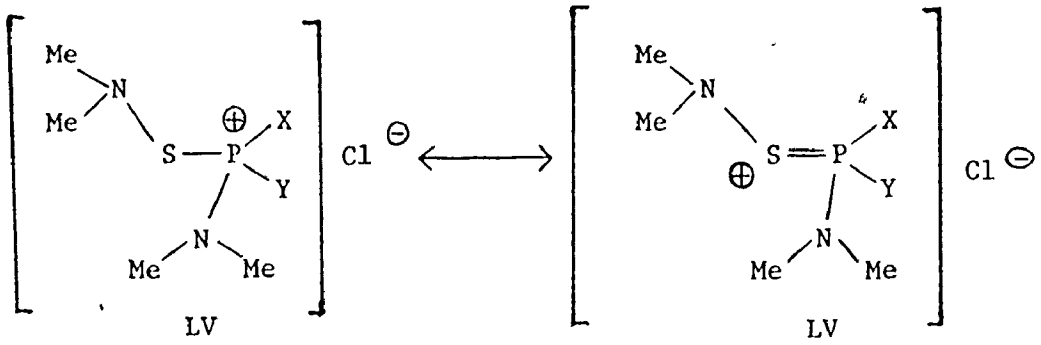
migration reaction through a 3-centre transition state, LIV, (analogous to transition metal insertion reactions) to give the insertion product LV (reaction [39]).



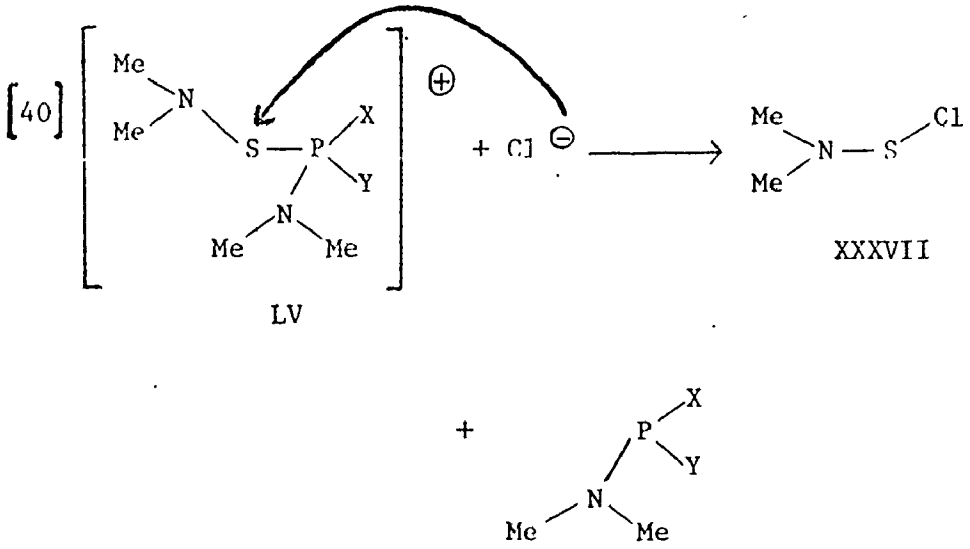
The second step in these reactions, that being the reaction of another mole of halo-phosphine with the initial insertion product (LV), is different if X = Y = phenyl than in the other two cases (X = Y = Cl; X = Cl, Y = Ø). The latter case involved loss of $Me_2N-S-Cl$, XXXVII, from the initial insertion product, LV. This probably occurs via attack of chloride ion on the slightly positive sulfur atom. Resonance structures can be written (Figure III-12) which will illustrate this. If attack on sulfur by chloride ion does occur, the products can be obtained in the following manner (reaction [40]). It should be pointed out that

Figure III-12

Canonical Forms of Initial Insertion Product



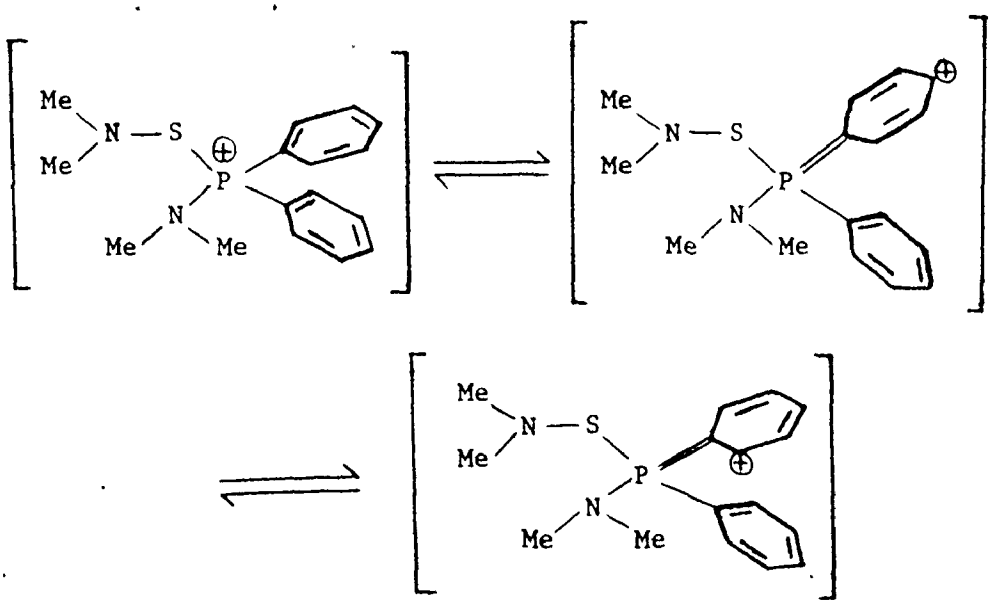
the stability of the insertion product LV increases as the number of



phenyl groups attached to phosphorus increases. The insertion product LV, when X = Y = ∅ is stable for days at room temperature whereas when X = Y = Cl it loses XXXVII immediately and a second insertion reaction occurs. The reason for this stability could be delocalization of the positive charge on phosphorus into the phenyl rings (Figure III-13) making the sulfur less susceptible to attack by chloride. There could also be more steric interference

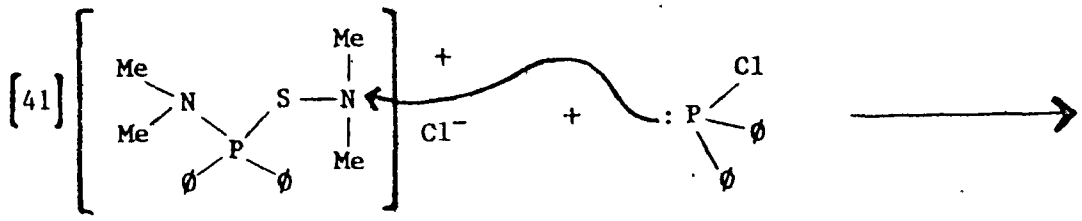
Figure III-13

Delocalization of Positive Charge in XXXV

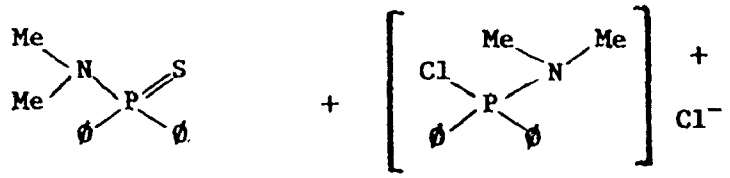


to this reaction as the number of phenyl groups increases.

The second reaction observed, when X = Y = Ø, differs from that discussed above. It is a nucleophilic attack of phosphine on the dimethylamino group attached to sulfur (reaction [41]). As mentioned earlier, this reaction is dependent on the concentration



XXXV



XXXVI XLI

of phosphine, the rate being faster when an excess of phosphine is available. This reaction is much slower than the loss of $Me_2N—S—Cl$ from the insertion product LV of PCl_3 or $\emptyset PCl_2$. It is, however, considerably faster than the decomposition of XXXV from $P\emptyset_2Cl$ as shown by reaction [22]. This reaction is actually quite similar to the final step in the Michaelis-Abrusov[125] rearrangement reaction [42]. Here the attacking species is X^-

[42] $(R_3O)_3P + R'X \longrightarrow \left[(RO)_2\overset{O—R}{\overset{|}{P}}\,R'\right]^+ X^- \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}R' + RX$

instead of $\emptyset_2PCl$ as in reaction [41].

Another reaction which is mechanistically interesting is that associated with [43]. Perhaps the most obvious mechanism

[43] $\begin{matrix}X\\ \diagdown\\ P—Cl\\ \diagup\\ Y\end{matrix} + Cl—S—N\begin{matrix}\diagup Me\\ \diagdown Me\end{matrix} \longrightarrow \begin{matrix}X\\ \diagdown\\ P\\ \diagup\\ Y\end{matrix}\!\!=\!\!S\;\; N\begin{matrix}\diagup Me\\ \diagdown Me\end{matrix} + Cl_2$

which could be proposed is the direct loss of chlorine from the reaction with a fast rearrangement of the intermediate LVII produced (reaction [44]). This rearrangement is quite common in

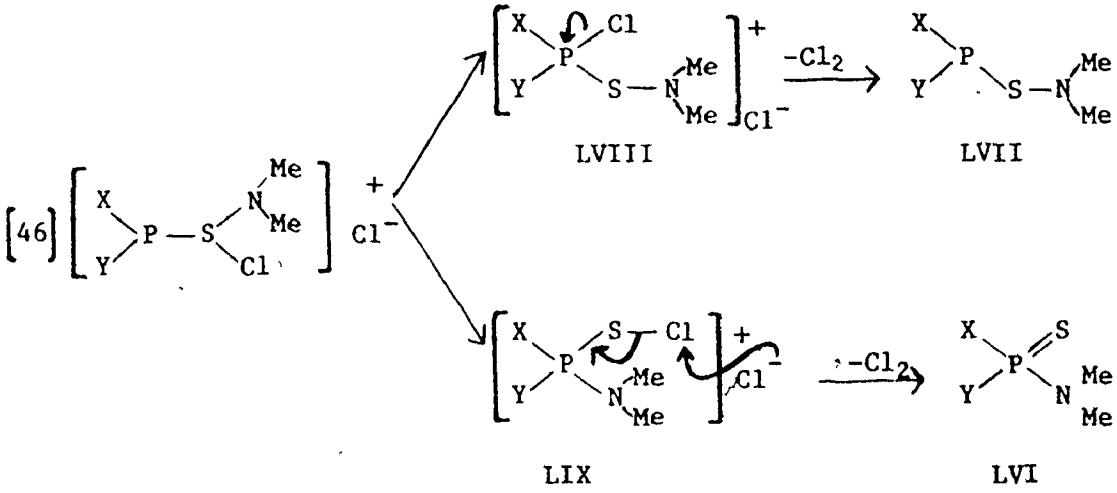
[44] $\begin{matrix}Me\\ \diagdown\\ N—S:\\ \diagup\\ Me\end{matrix}\;\;\begin{matrix}\\ \\ Cl\end{matrix} + \begin{matrix}Y\\ |\\ P—X\\ |\\ Cl\end{matrix} \longrightarrow \underset{LVII}{\begin{matrix}Me\\ \diagdown\\ N—S—P\\ \diagup\\ Me\end{matrix}\!\!\begin{matrix}Cl_2\\ +\\ X\\ \diagdown\\ Y\end{matrix}} \longrightarrow \underset{XVI}{\begin{matrix}S\\ \|\\ P\\ \diagup\;\diagdown\\ Me\;\;Me\end{matrix}\!\!\begin{matrix}X\\ \diagdown\\ Y\\ \diagup\\ N\end{matrix}} + Cl_2$

phosphorus chemistry. The free acid, monoesters and diesters of

phosphorus acid all undergo this type of rearrangement [45]. The completely substituted ester, however, does not.

[45] 

In light of the insertion reactions discussed earlier, there are two more possibilities for this reaction. These both involve electrophilic attack of phosphorus on sulfur and then insertion into either the sulfur-chlorine bond to give LVIII or the sulfur-nitrogen bond to give LIX (reaction [46]). Either of the two

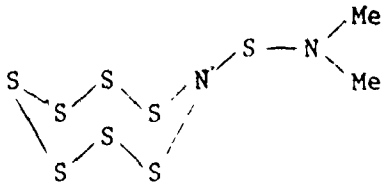
[46] 

insertion products could result in the production of chlorine. Insertion into the sulfur-chlorine bond would require a rearrangement (LVII → LVI) similar to the one discussed above (reactions [44] and [45]).

Since none of the possible intermediates (LVII, LVIII, LIX) were observed experimentally, it is not possible to definitely decide which of the above three mechanisms, if any, is correct.

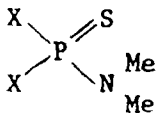
III-7 REACTION OF PHOSPHORUS TRIHALIDES (X = Cl, Br) WITH $S_7NSH(CH_3)_2$

In chapter II, another molecule was discussed which contained the N-S-N linkage, namely N,N'-dimethyl-N',N'-cycloheptathiosulfoxylic diamide, XIX. Preliminary investigations have shown that



XIX

halophosphines react with this molecule in a manner similar to that just discussed. When PX_3 (X = Cl, Br) was added to a methylene chloride solution of S_7NSNMe_2, reaction [47] occurs. The trichloride

[47] $S_7NSNMe_2 + PX_3 \xrightarrow[X = Cl,\ Br]{}$  + other product(s)

LX

took about 3 hours to react completely at room temperature whereas the tribromide reacted immediately even at -20°C. Species LX with X = Cl has been discussed before (it is actually compound XXXVIII) and was again identified using ^1H and ^{31}P NMR. The equivalent bromine compound was presumably made since the singlet corresponding to (XIX) went to a doublet (δ = +2.88 ppm, J = 18.0 Hz) at the reactant ratio of 1 to 1. Literature values have not been quoted for the ^1H NMR of this compound. While there is no direct evidence as to the mechanism of this reaction,

production of LX does suggest it proceeds in a manner similar to the N,N'-thiobisdimethylamine reaction.

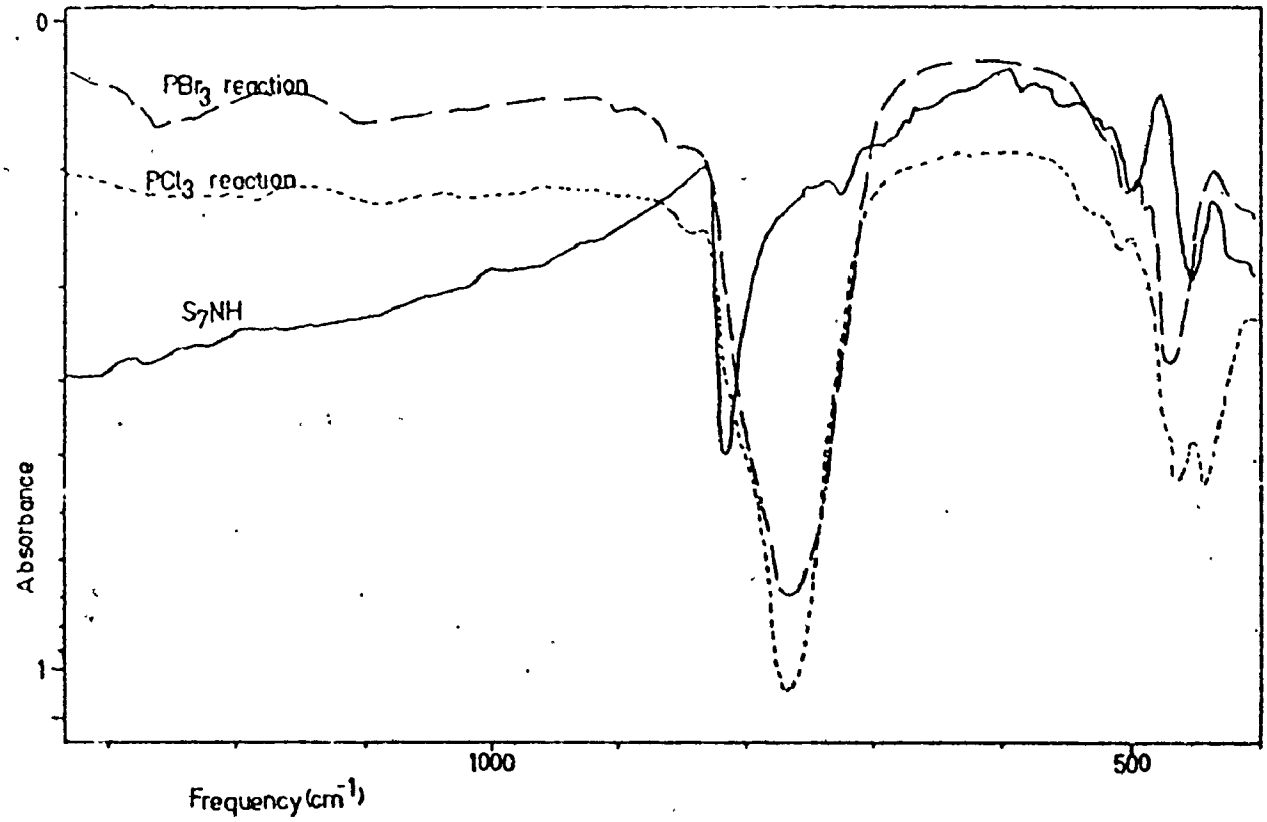
Some effort was made to characterize the "other products(s)" of reaction [47] since it was thought that this may be a synthetic route to the halo derivatives of heptasulfurimide (i.e. S_7NX). These compounds have not as yet been reported in the literature. The "other product(s)" consisted of a red oil which was very soluble in CS_2 but less soluble in other organic solvents. It was purified from the phosphorus compound LX using adsorption chromatography on silica gel. The sample then consisted of a clear red oil with no ^1H or ^{31}P NMR spectrum. It slowly decomposed even at -20°C so the compound was kept at dry ice temperatures under a nitrogen atmosphere. An infra-red spectrum in the region 400 to 1300 cm^{-1} is given in Figure III-13. The only bands observed could be associated with the sulfur-nitrogen stretching modes ($\sim$775 cm^{-}), sulfur-sulfur stretching modes (461 cm^{-1}) and possibly sulfur-halogen vibrations when X = Cl (437 cm^{-1}). It is interesting to note that the N-S bond stretching frequencies are considerably lower (790, 760 cm^{-1}) than in S_7NH (816 cm^{-1}).

The mass spectrum of this oil even at low ionization potential showed strong peaks only for fragments corresponding to S_yX_2 (X = Cl, Br, y = 1,2,3,4), SyX (X = Cl, Br, y = 1,2,3,4), Sy (y = 1 + 8) and NS.

Raman spectroscopy was useful in studying this oil since S_8 and the sulfur imides all have characteristic ring breathing

Figure III-14

Infra-red Spectrum of S_7NH and "Other Product(s)" of Reaction [47]



modes which are strongly Raman active. The Raman spectrum of the oil suggested contamination by elemental sulfur due to a strong absorbance at 219 cm^{-1}. It is interesting to notice, however, that there may be another 8-membered ring present since there is another similar absorption in that region (206 to 208 cm^{-1}). Table III-3 shows the similarities of the Raman spectra of the resulting oils to that obtained for S_7NH after taking into account contamination by sulfur.

At present, the identities of the "other product(s)" in reaction [41] remain unknown. There are considerable difficulties in obtaining the products of this reaction in the pure form. Perhaps variation of halophosphine or reaction conditions will one day result in reaction [47] being used to prepare S_7NX (X = Cl, Br). In any event, the insertion of phosphorus into sulfur-nitrogen bonds will undoubtedly suggest new methods of preparation of many other compounds.

Table III-3

Raman Spectrum of "Other Product(s)" in Reaction [46]

in Comparion to S_8 and S_7NH

Red Oil (X = Cl)	Red Oil (X = Br)	S_7NH (126) Solid	S_7NH (126) CS_2	S_8 (127) Solid	S_8 (127) CS_2
		3528(m-s)			
830(vw)	827(vw)				
		496(m)	487(m)		
476(10)	467(10)	473(s)	478(m)	470(s)	475(sp)
464(5)	464(5)	456(m)	460(w)		
434(2)	432(2)	433(m)	440(m)	434(m)	437(w)
		424(sh)			
	363(w)				334(w)
	358(w)				299(w)
310(vw)	310(w)				
284(w)	284(w)	282(s)	272(m)		
262(2)	264(2)	261(w)			
		251(vw)	249(w)	243(w)	248(w)
248(1)	247(1)	247(w)			
219(6)	219(9)	220(vwsh)			
206(6)	208(3)	215(vvs)	212(vvs)	216(s)	218(s)
186(vw)					
180(vw)		171(w)	170(vw)	184(w)	184(w)
165(wsh)	162(wsh)	162(vs)	160(vs)		
152(8)	152(10)	158(vs)		152(s)	152(s)
135(vw)					
	122(vw)			114(w)	
		105(wsh)			
		91(vs)	89(s)	85(s)	86(s)
		71(s)			
		56(wsh)			
		50(vs)		49(s)	
		47(vs)			
		21(m)			

(v = very, s = strong, m = medium, w = weak, sh = shoulder)

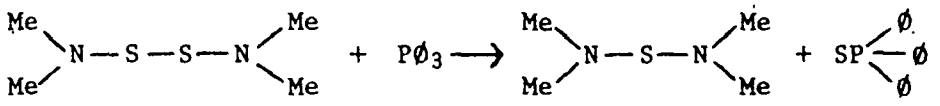
CHAPTER IV

REACTION OF TRIPHENYLPHOSPHINE, DIPHENYLPHOSPHINOUS CHLORIDE, PHENYLPHOSPHONOUS CHLORIDE AND PHOSPHORUS TRICHLORIDE WITH N,N'-DITHIOBISDIMETHYLAMINE

The previous chapter discussed the reaction of phosphorus compounds with the NSN linkage. The present chapter will be concerned with the reactions of the same phosphorus compounds with the dithiodiamine linkage, $\rangle N - S - S - N \langle$.

IV-1 TRIPHENYLPHOSPHINE AND N,N'-DITHIOBISDIMETHYLAMINE

In contrast with the non-reactivity of triphenylphosphine with N,N'-thiobisamines, the N,N'-dithiobisamines do undergo reaction [48]. This reaction goes to completion in

[48] 

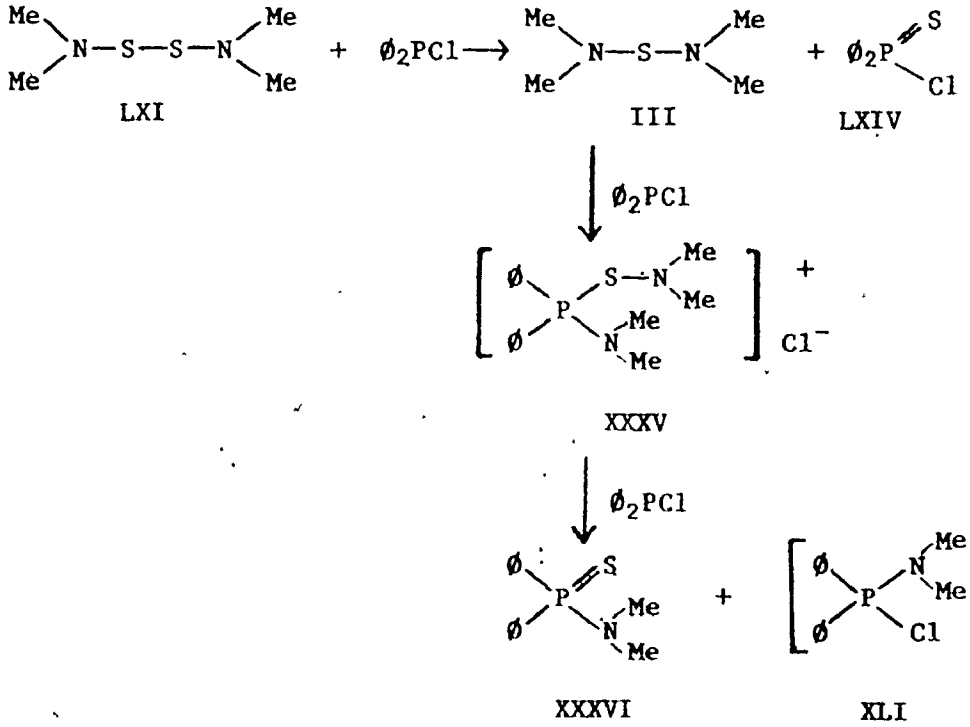
LXI LXII III LXIII

about four hours at room temperature. In the proton NMR, the singlet corresponding to LXI at +2.59 ppm is replaced by another singlet III at lower field (δ = +3.03 ppm). Any subsequent reaction of this solution with phenylphosphorus chlorides resulted in products forming as just described in Chapter III. The identification of triphenylphosphine sulfide was easily accomplished using ^{31}P NMR.

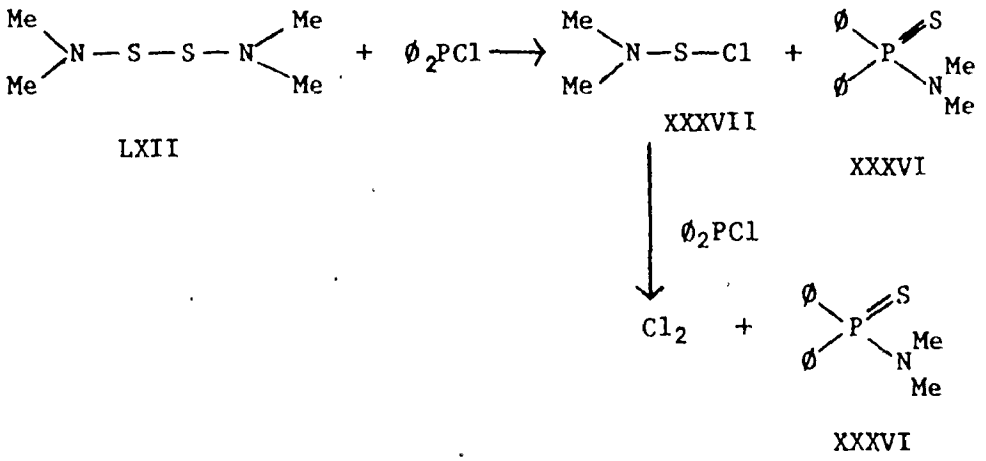
Upon reacting these reagents ($(C_6H_5)_3P$, LXI) in the 1 to 1 ratio described, the peak at +7.4 ppm corresponding to triphenylphosphine (lit. δ [102] = +5.6 to 8.0 ppm) is slowly lost and a peak at -41.4 ppm (LXIII, lit.[102] δ = -39.9 to -43.5 ppm) grows in intensity.

IV-2 DIPHENYLPHOSPHINOUS CHLORIDE AND N,N'-DITHIOBISDIMETHYLAMINE

Analysis of the reaction of diphenylphosphinous chloride with N,N'-dithiobisdimethylamine proved difficult until it was realized that two competing reactions were occurring. Reactions [49] and [50] are thought to occur concurrently. All of the

[49] 

[50]



products except chlorine were identified using ^{1}H NMR and ^{31}P NMR. The results of these measurements are recorded in Table IV-1. The arguments for assignments for all phosphorus compounds except diphenylphosphinothioic chloride, LXIV, are identical to those given in the section concerning reaction of diphenylphosphinous chloride with N,N'-thiobisdimethylamine (section III-3).

Differentiation between diphenylphosphinous chloride and diphenylphosphinothioic chloride, LXIV was not possible from the ^{31}P chemical shift of the two compounds. The two compounds resonate at almost exactly the same field strength, the former being at -81.2 ppm (lit. δ = -79.5 to -81.5 ppm)[102] and the latter (δ = -81.4 ppm) (lit. δ = -79.1 to -79.6 ppm)[102]. The shapes of the peaks and the peak widths, however, easily distinguish the two as shown in Figure IV-1. This difference is caused by different coupling of the phosphorus nucleii to the phenyl protons.

Table IV-1

^{1}H and ^{31}P NMR Data for Products of Reactions [48] and [49]

^{1}H NMR	Measured δ Methyl(ppm)	Measured J(Hz)	Literature δ Methyl(ppm)	Literature J(Hz)	Reference
XXV	+ 2.87	1.5	+ 2.86	1.5	(b)
	+ 3.18	12.0	+ 3.16	12.0	(b)
XXXVI	+ 2.48	14.5	+ 2.39	14.6	(116)
XLI	+ 3.08	16.5	--	--	
III	+ 3.03		+ 3.03		(a)
XXXVII	+ 3.12		+ 3.12		(a)
LXI	+ 2.59		+ 2.62		(a)

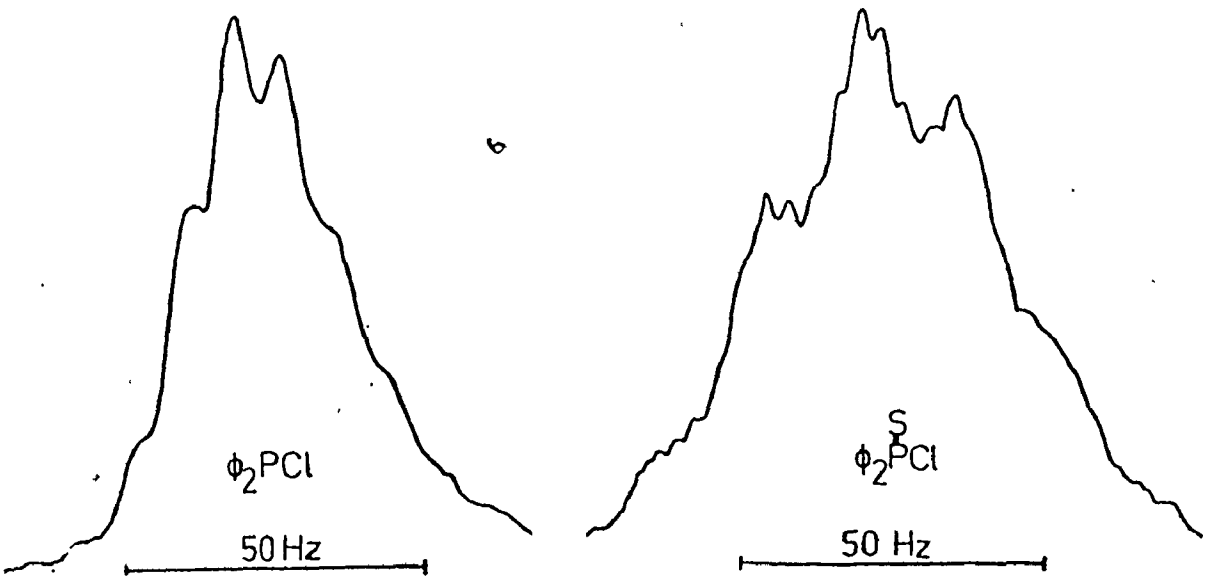
^{31}P NMR	Measured δ (ppm)	Measured J(Hz)	Literature δ (ppm)	Literature J(Hz)	Reference
LXIV	-81.4	--	-79.1 to -79.6	--	(102)
XXXV	-63.3	--	-62.0	--	(b)
XXXVI	-71.7	13.2	-70.9	14.6	(116)
XLI	-73.3	15.0	-72.5	--	(118)

(a) Authentic sample

(b) Sample prepared in Chapter III

Figure IV-1

^{31}P NMR Spectrum of Diphenylphosphinous Chloride and Diphenylphosphinothioic Chloride



Under room temperature conditions it was found that consumption of N,N'-dithiobisaiine proceeded at about the same rate for reaction [49] as reaction [50]. A few hours were required for complete reaction of a $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S_2$ = 3:1 mixture.

For a short period of time another singlet was observed in the ^1H NMR (δ = +2.72 ppm) of this reaction mixture at -10°C. This species was an intermediate in the reaction mixture but it was not clear if it was involved in reaction [49] or [50] or both. This species was not found in the ^{31}P NMR of this mixture,

presumably due to its short lifetime.

Conductivity measurements of the $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S_2$ = 2:1 mixture at room temperature showed that ionic species were present but in lower concentrations than in the $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S$ = 1:1 case (κ = 200 μ mhos cm^{-1} for a 0.4 M CH_2Cl_2 solution of $((CH_3)_2N)_2S_2$).

IV-3 PHENYLPHOSPHONOUS CHLORIDE AND N,N'-DITHIOBISDIMETHYLAMINE

The reaction of N,N'-dithiobisdimethylamine with phenylphosphonous chloride is much simpler than that of the monochloride and is represented in equation [51]. This reaction is

[51] ϕPCl_2 + LXI → XXXVII + XLV

XXXVII + ϕPCl_2 → Cl_2 + XLV

equivalent to reaction [50]. Both steps in reaction [51] are fast enough to be conveniently followed at -50°C using NMR, The second step is slightly slower than the first since in the course of the reaction, XXXVII can be observed as a product of the first step even when excess phenylphosphonous chloride is present.

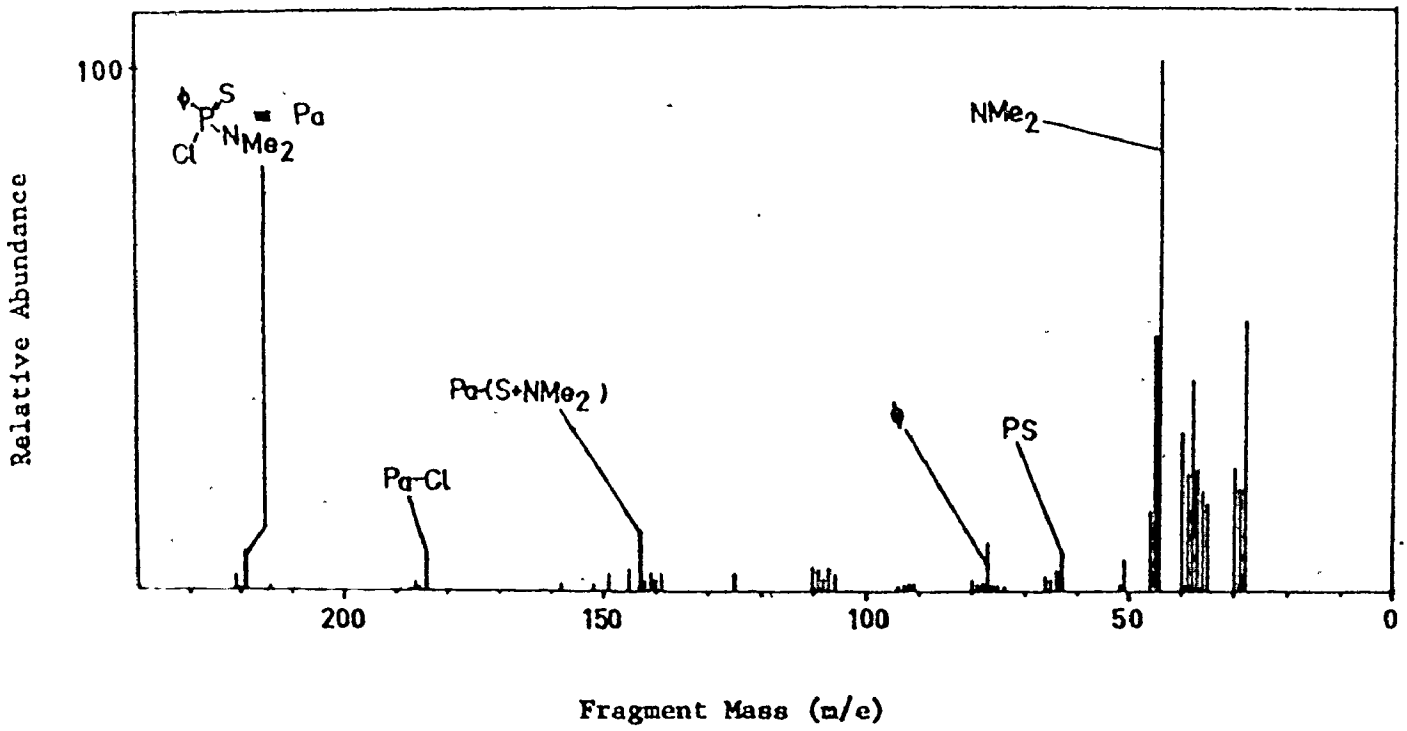
In reaction [51] the products were identified using ^1H NMR, ^{31}P NMR and mass spectrometry. The dimethylamino-sulfenyl

chloride, XXXVII, showed its characteristic proton NMR absorbance at low field (δ = +3.12 ppm)

As mentioned earlier (section III-5), there are no literature values to compare with the experimental data found for compound XLV (^{1}H NMR (δ = +2.76 ppm, J = 17.0 Hz), ^{31}P NMR (δ = -89.3 ppm, J = 16.6 Hz)). Reaction [51], however, presents a convenient method of preparation of this compound and this was used to obtain a sample for mass spectral analysis. The resulting spectrum is given in Figure IV-2. Chlorine was again easily detected.

Figure IV-2

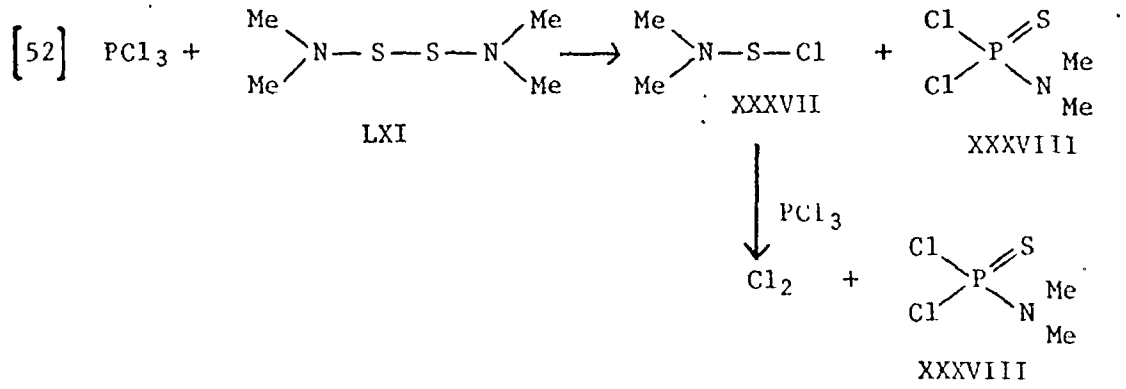
Mass Spectrum of $(C_6H_5)P(S)(N(CH_3)_2)(Cl)$



Conductivity measurements performed on a 0.4 M solution of $((CH_3)_2N)_2S_2$ in CH_2Cl_2 as $(C_6H_5)PCl_2$ is added showed that very few ionic species were formed (K = 6.5 μ mhos $-cm^{-1}$) was the maximum specific conductivity at $((C_6H_5)PCl_2 : ((CH_3)_2N)_2S_2 = 2:1$).

IV-4 PHOSPHORUS TRICHLORIDE AND N,N'-DITHIOBISDIMETHYLAMINE

The reaction between PCl_3 and LXI is exactly equivalent to that just discussed for $\emptyset PCl_2$ and LXI and is represented by

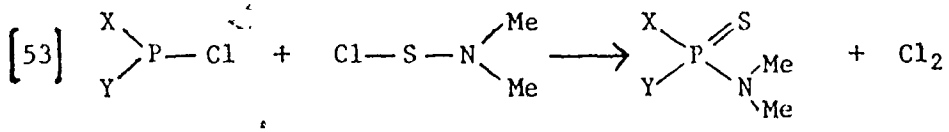


reaction [52]. Elemental chlorine and the amino-sulfenyl chloride were identified as just discussed for reaction [51] (section IV-3). Compound XXXVIII was identified by comparison of the experimental ^1H and ^{31}P NMR data with literature values (^1H NMR (doublet, δ = +3.01 ppm, J = 17.5 Hz, lit.[123] δ = +3.00 ppm, J = 17.8 Hz); ^{31}P NMR (septet, δ = -60.5 ppm, J = 18.0 Hz, lit.[102] δ = -62.0 ppm). The first step in reaction [52] was quite fast whereas the second step was slow even at -20°C. Conductivity of a 0.4 M solution of LXI in CH_2Cl_2 as PCl_3 was added, suggested that no ionic species were produced (maximum specific conductivity was 0.31 μ mhos $- cm^{-1}$

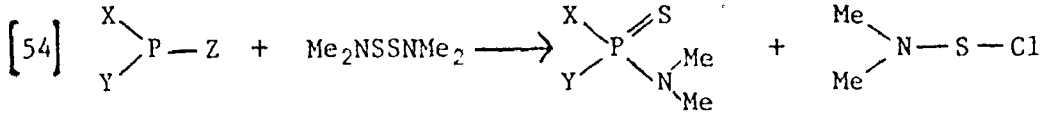
at PCl_3 : $((CH_3)_2N)_2S$ = 2:1).

IV-5 DISCUSSION OF MECHANISM

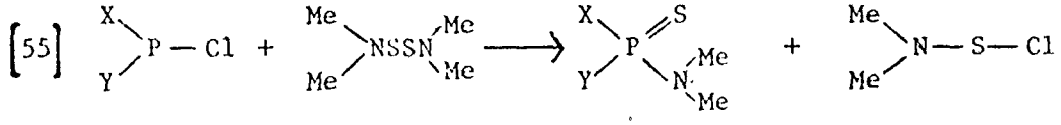
In the systems described in this chapter, there are basically three types of reactions occurring. Reaction [53]



[54]



[55]



has already been discussed in the last chapter (section III-6). Reactions [54] and [55] are actually competing reactions, the rates at which they occur depend upon the substituents. When X = Y = Z = Ø, only reaction [54] occurs. When X = Y = Ø and Z = Cl, reactions [54] and [55] occur at about the same rate. When one or no phenyl substituents are present, only reaction [55] is found to occur.

Intermediates are suggested in reaction [54] and [55] since it is difficult to visualize one step processes giving the products found. Since phosphorus has been found to attack sulfur in N,N'-thiobisdimethylamine, a similar reaction is possible here. This reaction occurs more slowly with N,N'-dithiobisdimethylamine

probably because there is less negative charge associated with the sulfur atoms in this molecule. The structure determination of the N,N'-dithiodimorpholine[4] suggests that the sulfur atoms in this molecule are accepting pπ-electron density from the nitrogen atoms. This would place a negative charge on the sulfur atoms. It is expected that in this case there is less negative charge associated with the sulfur atoms than in the N,N'-monothiodiamines. The latter molecules contain sulfur atoms which can accept electron density from two nitrogen p-orbitals. As halogens are added to the phosphorus atom, reactions [53] and [54] proceed more quickly. This is to be expected since the halogens, by pulling electron density from the central atom, make it more susceptible to nucleophilic attack.

The nature of any intermediate(s) formed in reactions [53] and [54] should be discussed in proposing a mechanism for these reactions. The intermediate suggested[96] for the desulfurization of organic disulfides by triphenylphosphine (section I-1cii) is possibly present in these reactions. This intermediate involves insertion of phosphorus into the sulfur-sulfur bond of the N,N'-dithiobisamine and may be the initial species formed in reaction(s) [53] and/or [54]. While this is the most probable reaction pathway, the possibility of sulfur-nitrogen insertion should also be investigated in light of the insertion reactions discussed in Chapter III.

Products from reactions [53] and [54] can therefore be

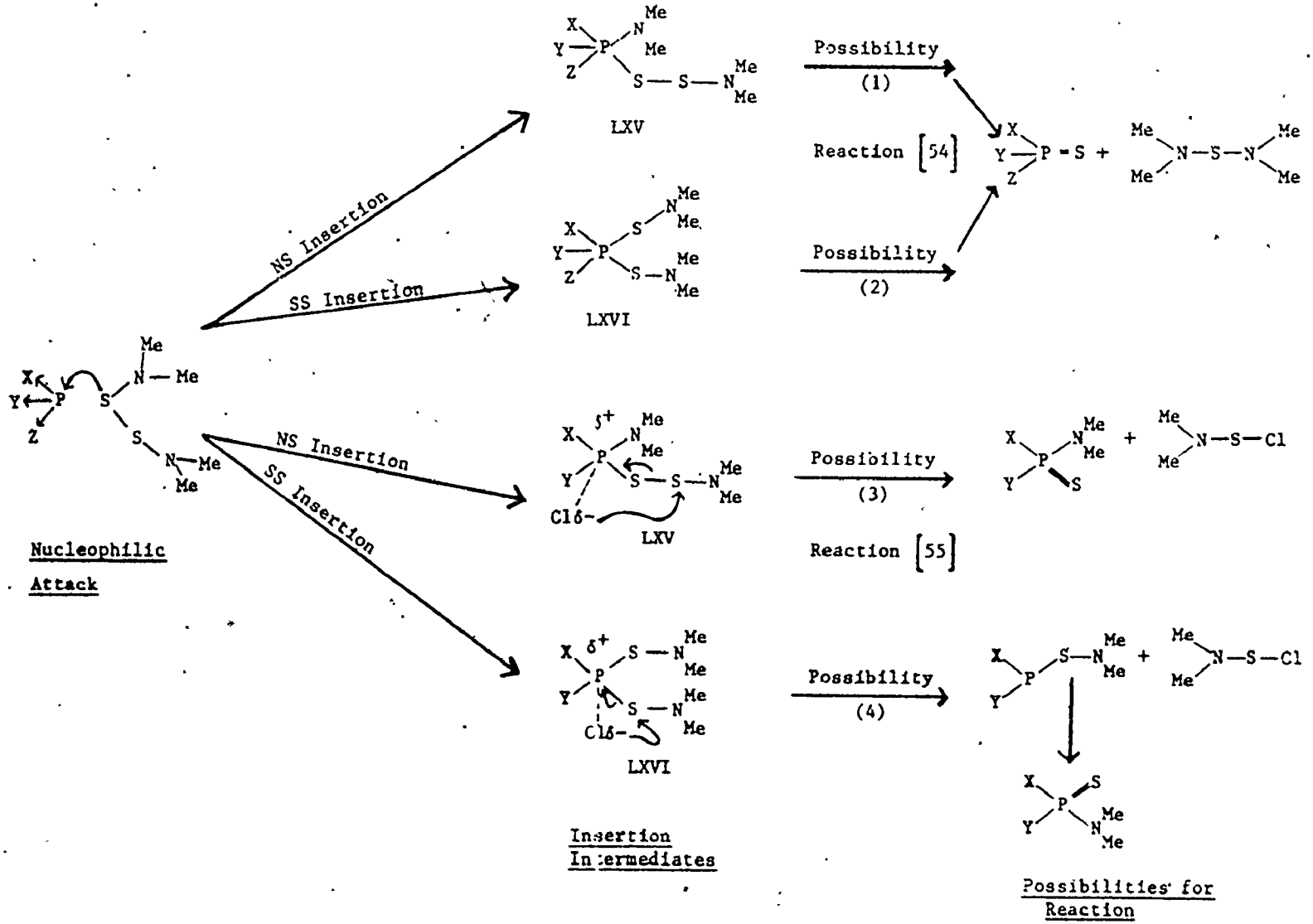
thought of as coming through an intermediate where phosphorus has inserted into either a nitrogen-sulfur or sulfur-sulfur bond. Figure IV-3 considers these possibilities for these two reactions.

If the possibilities given in Figure IV-3 are considered in turn, some suggestions as to the mechanism can be given. Possibility (1) involves production of thiobisamine from the dithiobisamine through an intermediate, LXV, derived by N-S bond insertion. It is very unlikely that this is happening since there is no reaction with triphenylphosphine and N,N'-thiobisdimethylamine although this contains a sulfur-nitrogen bond. The triphenylphosphine reaction with organic disulfides also suggests strongly that the S-S bond plays an active role in the mechanism. The intermediate suggested by possibility (1) (Figure IV-3) is also inconsistent with the singlet tentatively assigned to the transient intermediate observed in the ^1H NMR spectrum of the ($\emptyset_2PCl$: LXI) mixture. Another reason that this reaction is less likely is that the N-S bond in compound LXI should be stronger than in the monosulfur analogue (R_2NSNR_2). Here there is one sulfur atom accepting electron density from one nitrogen atom giving a reasonably strong N-S bond. Chapter II suggests that in the monosulfide, approximately the same amount of π-electron density as the disulfide is donated to the sulfur atom but from two nitrogen atoms. Each N-S bond is therefore stabilized by only about half as much as in the N,N'-dithiobisdialkylamines.

Possibility (2) (Figure IV-3) is more consistent with the

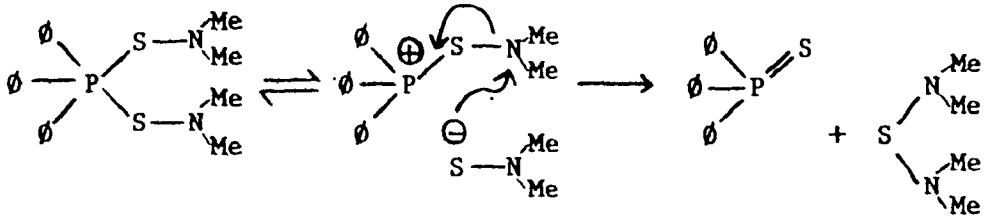
Figure IV-3

Insertion Mechanism for Reaction of Phosphines and Phosphorus Chlorides with N,N'-Dithiobisdimethylamine



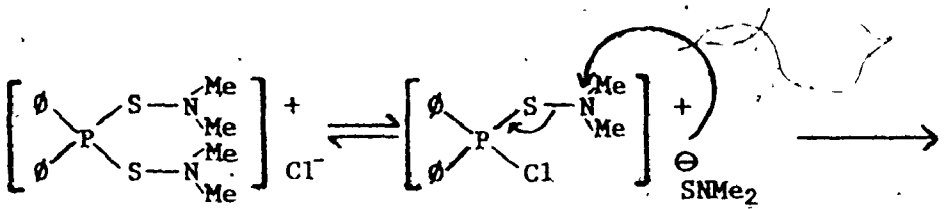
experimental evidence found in this system. It is expected that species LXVI could show only a singlet in the ^1H NMR (in $(C_6H_5)_2PCl \cdot ((CH_3)N)_2S_2$ reaction) since the molecule is symmetric and the hydrogen atoms are 3 bonds away from the phosphorus nucleus.

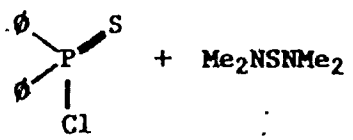
Reaction [54] could occur either as written (in possibility (2) Figure IV-1) or through an ionic intermediate such as LXVII shown in reaction [56]. When there is chloride available, initial

[56] 

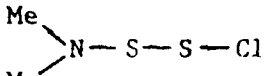
LXVII

formation of the intermediate may be facilitated by loss of chloride ion. Subsequent reactions may occur then by substituent exchange on the cation and reaction as above in the second step of [56] (reaction [57]).

[57] 



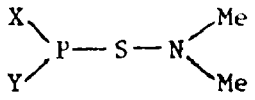
Possibilities (3) and (4) (Figure IV-3) show that reaction [55] can also occur via N-S or S-S insertion intermediates. The restriction that the ^1H NMR must be a singlet for the intermediate of the ϕ_2PCl = (III) system is removed for reaction [55] since it may be the intermediate only for reaction [54]. Intermediate LXV is at first attractive since no rearrangement is necessary after chloride ion attacks the sulfur atom in the β position to phosphorus (Scheme IV-1). It is hard to rationalize, however, the large difference in reactivity between the monochloride and di- or trichlorides of phosphorus. Both of the phenylphosphorus chlorides and PCl_3 reacted immediately with the N,N'-thiobisamine at -60°C whereas diphenylphosphinous chloride is comparatively unreactive with the disulfide even at -20°C. It is also to be expected that some of LXVIII would be produced in this mechanism via attack of



LXVIII

the sulfur atom adjacent to the phosphorus atom by chloride ion. This is not found although this type of reaction is common in the monothiobisdialkylamine system discussed in Chapter III. Of these two possibilities involving insertion of phosphorus into a sulfur bond, intermediate LXVI is therefore more likely to be present in the mechanism of reaction [55]. Subsequent reactions of this intermediate are also of the type suggested in Chapter III. Attack by chloride ion of sulfur attached to phosphorus (possibility

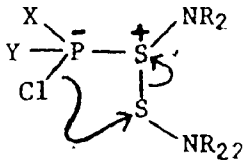
(4), Figure IV-3) with loss of amine sulfenyl chloride and rearrangement of LVII is exactly that suggested by reactions



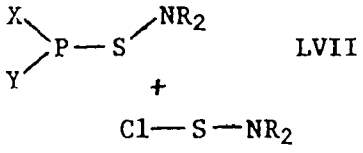
LVII

[40] and [44] in Chapter III. The increased reactivity as the number of chlorines on phosphorus goes from 1 to 2 or 3 is expected due to an increased positive charge on the phosphorus atom and on sulfur atoms directly bonded to it. This makes the sulfur atom more susceptible to attack by the negative chloride ion.

A third mechanism can be postulated to describe the formation of products in reaction [55]; this one not involving a phosphorus insertion reaction. After initial attack of $((CH_3)_2N)_2S)_2$ on the phosphine giving LXIX, a chloride ion could



LXIX



LVII

attack the sulfur atom β to the phosphorus giving the correct products. As the number of chlorine atoms on phosphorus increases, the reaction would proceed at a greater rate. This reaction may be then able to compete better with sulfur-sulfur insertion which leads to desulfurization of the N,N'-dithiobisdialkylamine

(reaction [54]). This mechanism, or the one mentioned above involving S-S insertion (possibility (4), Figure IV-3), are more likely than the third mechanism discussed for reaction [55].

Again in this system, the mechanisms of the reactions involved cannot be stated with certainty. What is shown clearly, however, is that N,N'-dithiobisdimethylamine reacts differently towards these phosphorus compounds than N,N'-thiobisdimethylamine. The reason for this appears to be the presence of the sulfur-sulfur bond. The reaction of $\emptyset_2PCl$ and $((CH_3)_2N)_2S_2$ only at $-10^{\circ}C$ shows that the nitrogen-sulfur bonds in the N,N'-dithiobis-dialkylamines are more stable towards these reagents than in the monothio analogue. Furthermore, the N-S bonds of the former compounds may not be involved in the initial reaction at all. Although the experimental evidence accumulated for this system is not definitive, it does suggest that the phosphorus atom attacks a slightly negative sulfur atom. From this point on, two reactions can occur depending on the charge distribution and the substituents on phosphorus in the resulting intermediate.

CHAPTER V

EXPERIMENTAL

V-1 SYNTHESIS

(a) Heptasulfurimide (Cyclothiazocene)

The method used in the preparation of S_7NH was similar to that described in Brauer[128]. Dimethylformamide (3.5 ℓ) was cooled in a 5ℓ three neck flask to -20°C using a dry ice-acetone bath. Ammonia was then bubbled into the vigorously stirred solution at a flow rate of >100 ℓ/hr for 30 minutes. Sulfur monochloride (350 ml) was then added in 15 ml aliquots from a 100 ml syringe equiped with a 18 G x 6" needle. The sulfur monochloride was injected into the flask below the surface of the solvent. The reaction is quite vigorous and gloves, etc. are necessary for this part of the preparation. When the solution has cooled again to -20°C, another aliquot of S_2Cl_2 is added. Care must be taken that the addition of S_2Cl_2 does not occur faster than the solution can be kept saturated in NH_3. The S_2Cl_2 addition should take place over a period of about two hours. If the reaction appears to decrease in vigor as addition of S_2Cl_2 proceeds, the solution should be allowed to saturate in NH_3 before S_2Cl_2 addition continues. Once the sulfur monochloride has been added, bubbling of NH_3 is continued for 15 minutes. The ammonia addition, stirring and cooling then are stopped and the deep blue solution is allowed to stand for another 30 minutes. The

solution is then slowly added to 50 ℓ of 1% hydrochloric acid in a 100 ℓ container with constant stirring. This pink-purple mixture was neutralized with 10% HCl, the colour changing to brown and then at the equivalence point to an orange colour. This suspension was allowed to settle overnight and the solution decanted leaving a yellow solid. This solid was spread on paper towels and allowed to dry for 24 hours. The dry solid was then soxlet extracted with tetrahydrofuran (1 ℓ). The tetrahydrofuran was removed using a rotary evaporator and the brown oil dissolved in a minimum amount of hot methanol. Upon cooling, pale yellow platelets crystallized from the solution. These crystals were then vacuum dried and recrystallized from benzene or carbon disulfide to remove final traces of elemental sulfur. Typical yield was 30 g of very pale yellow cubic crystals (melting point 113°C; lit. M.P. 113°C[128]).

(b) Preparation of the N,N'-Thiobisdialkylamines (N,N,N',N'-Tetraalkylsulfoxylic Diamides)

(i) Alkyl = methyl

Dimethylamine was rapidly bubbled into a 4 ℓ three neck flask containing 3 ℓ of diethyl ether. The flask was equipped with a mechanical stirrer to ensure good agitation. The solution was cooled to 0°C using an ice bath. Sulfur dichloride (19 ml, 0.3 moles) was diluted with ether (200 ml) and added dropwise to the solution from a 500 ml separatory funnel. The amine was added through a Claisen adaptor so that excess amine could escape through the second opening.

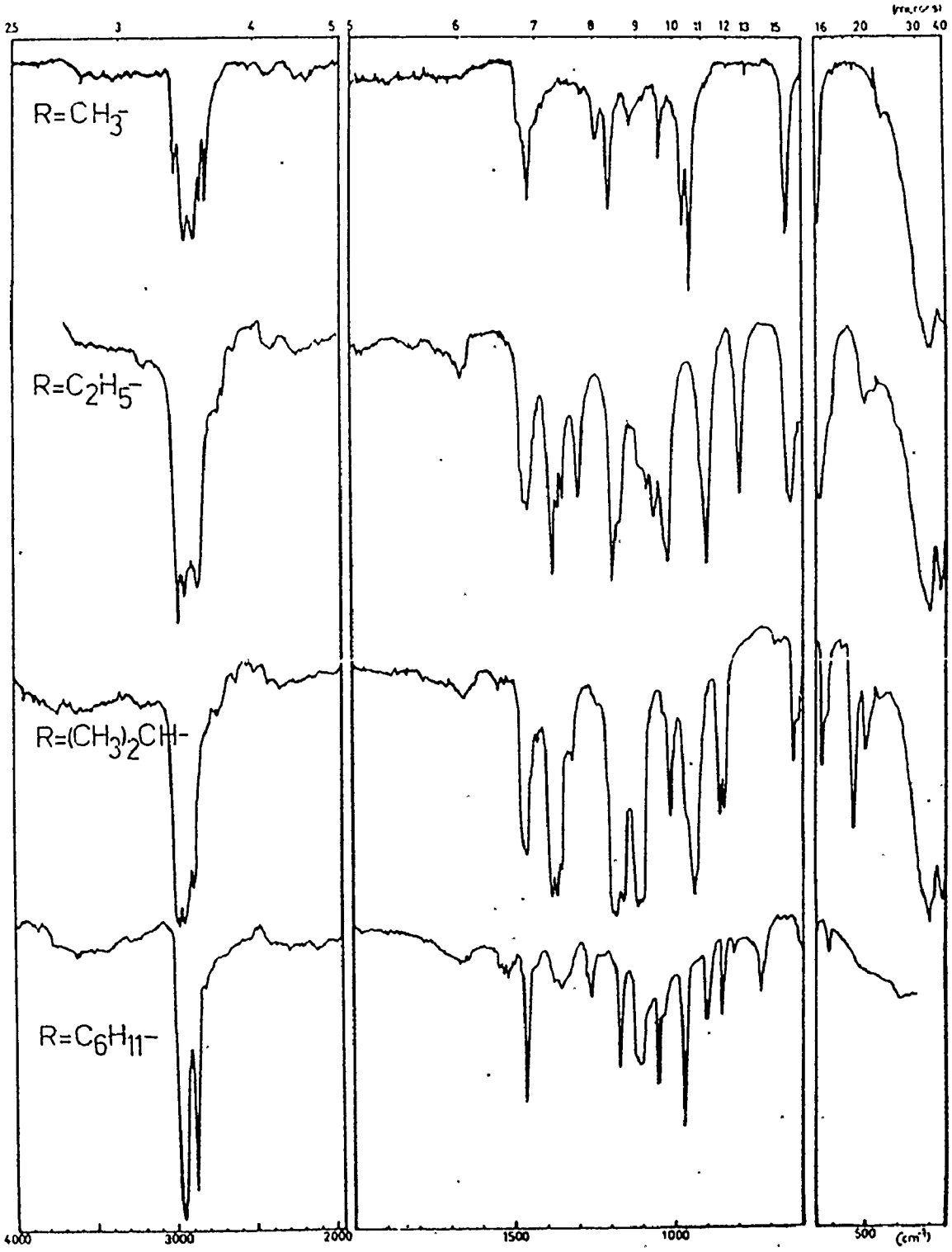
Once the S_2Cl_2 was added, cooling, addition of amine and stirring were discontinued. After standing for 30 minutes, the white solid $\left[((CH_3)_2NH_2)^+ Cl^-\right]$ was filtered off leaving a pale yellow solution. Most of the solvent and excess amine were removed using a rotary evaporator. The remaining solvent was removed on the vacuum line by cooling the flask containing the product to -25°C. The N,N'-thiobisdimethylamine crystallizes and the ether can be distilled off. The product was then warmed to room temperature and distilled on the vacuum line leaving behind traces of the impurity N,N'-dithiobisdimethylamine. The purity was checked using ^1H NMR to ensure that all of the ether had been removed. The yield was approximately 35 g (38 ml, 0.29 moles) of a clear colourless liquid. The product was stored at -20°C at which temperature it freezes, then sublimes to the walls of the container giving large colourless crystals (melting point 20°C, literature[59] 20°C). The infra-red spectrum was recorded and is shown in Figure V-1a. Care should be taken to avoid contact with skin or clothing because of the lingering offensive odour of this compound.

(ii) Alkyl = ethyl, isopropyl

This reaction was carried out similarly to the methyl derivative. Dialkyl amine (ethyl 1.2 moles, 124 ml; isopropyl 1.2 moles, 169 ml) was added to 3 ℓ of cooled ether (0°C) in a 4 ℓ three neck flask. The SCl_2 (19 ml (0.3 moles) in 200 ml ether) was added dropwise from a pressure equalizing dropping funnel equipped with a nitrogen inlet. The nitrogen was passed through the system

Figure V-1

Infra-red Spectra of R_2NSNR_2



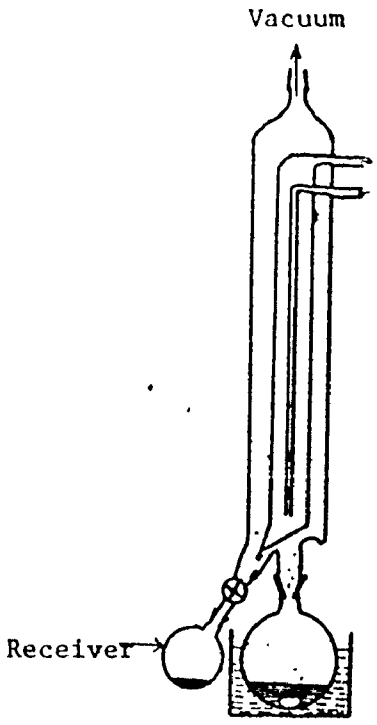
and out via a drying tube in the flask. After the SCl_2 was added, the solution was allowed to warm to room temperature without stirring for 30 minutes, then filtered, leaving a pale yellow solution. The solvent was removed using a rotary evaporator initially and a vacuum system to remove the last traces. The pale yellow liquid was then distilled using a cold-finger condenser attached directly to the vacuum line (Figure V-2). The temperatures at which the compounds distilled were ethyl, 30°C and isopropyl, 40°C. The compounds were checked for purity using ^1H NMR ((ethyl, CH_3, triplet, δ = +1.15 ppm, J = 8.0 Hz; CH_2 , quartet, δ = +3.12 ppm, J = 8.0 Hz)(isopropyl; CH_3, doublet, δ = +1.12 ppm, J = 6.5 Hz, CH, septet, δ = +3.39 ppm, J = 6.5 Hz)). Infra-red spectra were recorded and are shown in Figure V-1. The clear colourless liquids were then stored at -20°C. Very high yields of the pure products were obtained (ethyl, 0.29 moles, 51 g; isopropyl, 0.27 moles, 62 g). Care should be taken to avoid contact with skin or clothing because of the lingering offensive odour of these compounds.

(iii) Alkyl = Cyclohexyl

Dicyclohexylamine (0.8 moles, 159 ml) was added to 3 ℓ of cooled ether (0°C) in a 4 ℓ three neck flask. SCl_2 was diluted with ether (0.2 moles, 12.7 ml in 200 ml ether) and added dropwise from a pressure equalizing dropping funnel equipped with a nitrogen inlet. The outlet was a drying tube attached to the flask. After the SCl_2 had been added to the vigorously stirred mixture, it was allowed to

Figure V-2

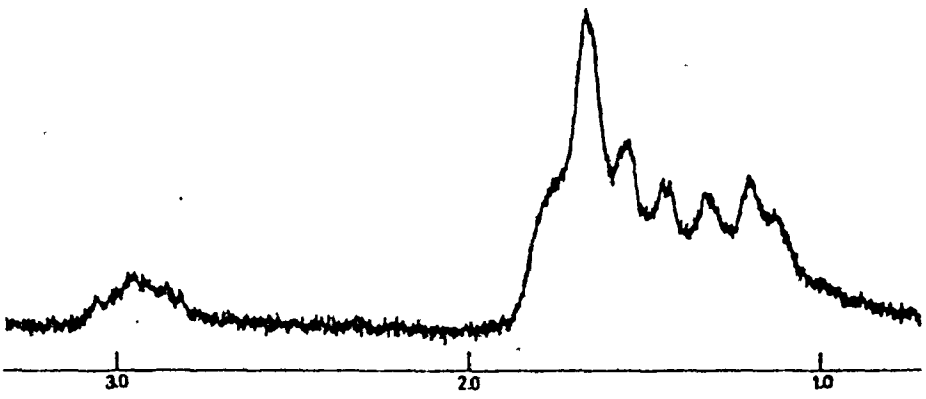
Cold-Finger Condenser Used for Distillation of High Boiling Point Liquids



warm to room temperature without stirring for 30 minutes. The mixture was filtered giving a pale yellow solution. The solvent was removed using a rotary evaporator giving a yellow oil. This oil was dissolved in a minimum amount of benzene at 50°C from which the product was crystallized. Two more recrystallizations from benzene yielded 30 g (37%) of clear colourless crystals (melting point 149°C, literature[59] 150°C). The ^{1}H NMR spectrum was recorded and is shown in Figure V-3. The infra-red spectrum was also recorded and is shown in Figure V-1d.

Figure V-3

^{1}H NMR Spectrum of $((C_6H_{11})_2N)_2S$



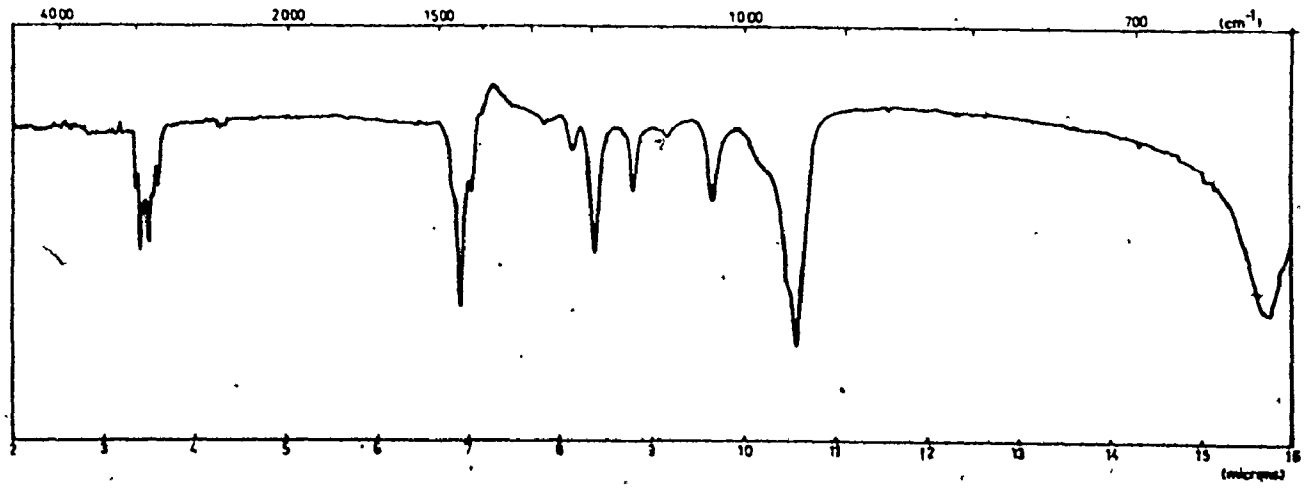
(c) Preparation of N,N'-Dithiobisdimethylamine

Dimethylamine was rapidly bubbled into 3 ℓ of cold (0°C)

ether in a 4 ℓ three neck flask. The gas was added through a gas inlet fitted through a Claisen adaptor to allow the excess amine to escape. This was continued for 15 minutes at which time sulfur monochloride (16 ml, 0.2 moles) diluted with ether (200 ml) was added dropwise from a 500 ml separatory funnel to the well stirred mixture. At this time, the stirring, cooling and amine addition were discontinued and the mixture allowed to stand for 30 minutes. The white precipitate was filtered leaving a pale yellow solution. The solvent was removed using the rotary evaporator and the resulting yellow liquid distilled at 50°C using the cold-finger condenser shown in Figure V-2. An infra-red spectrum was recorded and is shown in Figure V-4. The ^1H NMR spectrum was a singlet at -2.62 ppm.

Figure V-4

Infra-red Spectrum of $(CH_3)_2NS_2N(CH_3)_2$

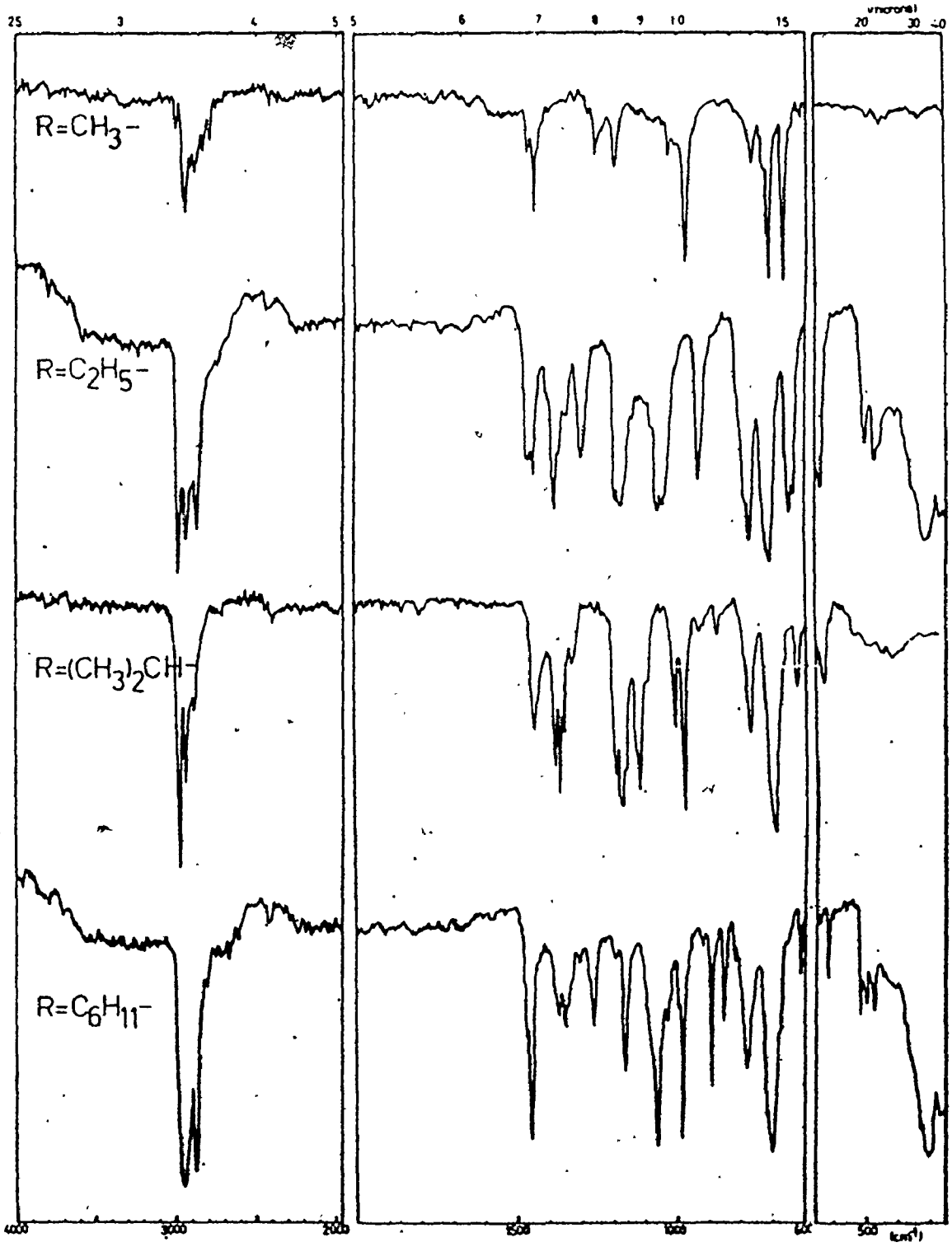


(d) Preparation of the N,N-Dialkyl-N',N'-Cycloheptathiosulfoxylic Diamide

(i) Alkyl = Methyl, Ethyl, Isopropyl

Heptasulfurimide (0.01 mole, 2.39 g) was ground to a powder and added to a well stirred 5 to 8 fold excess (about 10 ml) of the N,N'-thiobisdialkylamine at 40 to 50°C. The mixture was stirred for one hour leaving a red coloured solution. In the methyl case, a basic gas ($(CH_3)_2NH$) bubbled from the solution while the reaction proceeded. Excess $(R_2N)_2S$ was distilled off using the vacuum line. The resulting red oil was then passed through a silica gel column (1.0 m x 2.5 cm of 80 to 200 mesh silica gel) using hexane as eluent. Approximately 750 ml of solvent was taken off the column, then 40 fractions (25 to 50 ml) were taken into 125 ml flasks. The fractions were placed in the fume hood overnight during which time the hexane evaporated. The first compound off the column was the product, being very pure in the first flask in which it was observed. The major contaminant was the pale yellow oil consisting of $R_2NS_xNR_2$ ($x = 1,2,3,4 \ldots$) which came off the column immediately after the product. Flasks containing reasonably pure product were washed with pentane and the solutions combined. The solution was warmed to boiling and reduced in volume until a stream of nitrogen passed into the flask caused precipitation. The solution was then reheated to dissolve the sample, stoppered and cooled

Infra-red Spectra of $S_7NSN(R_2)$



at -20°C. Within two hours, crystals developed. After another recrystallization, the pale yellow crystals were filtered and dried in vacuo (melting points, methyl = 55°C, ethyl = 30°C, isopropyl = 66°C). Care must be taken in handling of crystals of the ethyl compound due to the low melting point. The ^1H NMR spectra of these compounds are discussed in section II-4. The infra-red spectra of the compounds are shown in Figure V-5. IR spectra of the methyl and isopropyl derivatives shown are drawn from solution spectra in CS_2 and CCl_4 in order to show all the bands. The ethyl derivative was melted, then its spectrum recorded as a thin film between two KBr discs. The frequencies of the observed bands are reported in Table II-3.

(ii) Alkyl = Cyclohexyl

Powdered S_7NH (0.01 mole, 2.39 g) and excess N,N'-thiobisdicyclohexylamine (powdered, 0.03 mole, 11.8 g) were added to benzene held at 50°C. The mixture was stirred for 1.5 hours after which the reaction mixture had become a red solution. The solvent was removed in vacuo leaving a red oil. This oil was passed through a silica gel column (1.0 m x 2.5 cm of 50 to 200 mesh) using hexane as eluent. Approximately 500 ml of hexane was collected from the column, then 40 fractions (25 to 50 ml) were taken into 125 ml flasks and the solvent allowed to evaporate overnight. The first compound off the column was the N,N-dicyclohexyl-N',N'-

cycloheptathiosulfoxylic diamide, $S_7NSN(C_6H_{11})_2$. Again the second product off the column was a yellow oil, the compounds $R_2NS_xNR_2$ ($x = 1,2,3,4 \ldots$). The crystals obtained for $S_7NSN(C_6H_{11})_2$ were recrystallized twice from hot pentane. This yielded approximately 2 g of pale yellow crystals (melting point 97° to 98°C). The ^1H and ^{13}C NMR spectra were recorded for this compound and are discussed in section II-4. A few crystals of the compound were dissolved in CS_2 and then the CS_2 was removed on the vacuum line. The IR spectrum of the resulting oil was recorded as a thin film between KBr plates and is given in Figure V-5. Frequencies are given in Table II-3.

(e) Preparation of $(CH_3)_2NSCl$

Dimethylamine was bubbled into a solution of ether (200 ml) for 15 minutes. This solution was then added dropwise to a well agitated excess of sulfur dichloride (200 ml) in a 1 ℓ, 3 neck flask held at 0°C under a nitrogen atmosphere. The flask is then transferred to the vacuum line and the sulfur dichloride distilled to another vessel. The red-brown oil was then distilled using the apparatus described in Figure II-2 to give a pale yellow liquid. The purity of this compound was checked using ^1H NMR (singlet $\delta = +3.12$ ppm).

(f) Preparation of $((CH_3)_2CH)_2N)SSCl$

A solution of isopropyl amine in ether (14.1 ml (0.1 mole) in

200 ml) is added dropwise to a well agitated excess of S_2Cl_2 (250 ml) in a 1 ℓ, 3 neck flask at 0°C under a nitrogen atmosphere. Excess S_2Cl_2 is then fractionally distilled using the apparatus in Figure V-2 and a fractionating column. The solution is brought to 40°C at which temperature the S_2Cl_2 distills. The ether is distilled right into the vacuum line cold trap. The temperature is then raised to 55°C at which the product distills. The ^1H NMR spectrum of the distillate was recorded until the product was found to be distilling off in reasonable purity. Undoubtedly, there was some contamination by S_2Cl_2. The ^1H NMR spectrum showed the usual isopropyl pattern (CH_3, doublet, δ = +1.28 ppm, J = 6.5 Hz, CH, septet, δ = +3.70, J = 6.4 Hz).

(g) Attempted Preparation of S_7NSSNR_2

(i) R = CH_3, S_7NH and $((CH_3)_2N)_2S_2$

Powdered S_7NH (2.39 g, 0.01 moles) was added to an excess of $((CH_3)_2N)_2S_2$ (15.2 ml, 0.10 moles) in a 50 ml flask. The mixture was stirred under a nitrogen atmosphere on a water bath. At about 50°C, the mixture began to turn red and some gas ($(CH_3)_2NH$) was evolved. The reaction was monitored using ^1H NMR until most of the peak at +3.12 ppm ($((CH_3)_2N)_2S_2$) had disappeared. At this point, the deep red solution was placed on the vacuum line and the excess $((CH_3)_2N)_2S_2$ was distilled off. The red oil was then passed through a silica gel column (2.5 cm x 200 cm of 80 to 200 mesh silica gel) using pentane as eluent. Approximately 40 fractions (50 ml) were

removed after an initial volume of eluent (1250 ml) had been removed. The solvent was allowed to evaporate overnight and the ^1H NMR recorded of the resulting residues. These showed that although the product ratios changed somewhat, separation of the compounds produced could not be effected by this method.

(ii) $\underline{S_7NH + ((CH_3)_2CH)_2NSSCl}$

S_7NH (1.1 g) 4.6 m moles) and $((CH_3)_2CH)_2NSSCl$ (0.83 ml, 4.6 m moles) were each diluted with 50 ml of pyridine and slowly combined. The mixture was allowed to stir for 48 hours. The solution was diluted with ether (300 ml) resulting in precipitation of a white solid. This was filtered, dissolved in D_2O and the ^1H NMR recorded. Comparison with the ^1H NMR of an authentic sample showed the existence of $((CH_3)_2CH)_2NH_2^+ Cl^-$ (CH_3, doublet, δ = +1.38 ppm, J = 6 Hz; CH, septet, δ = +3.60, J = 6.5 Hz). The ether soluble red oil was chromatographed as in section V-1g-i, again with poor results.

(iii) $\underline{S_7NH + S_2Cl_2 + ((CH_3)_2CH)_2NH}$

S_7NH (1.1 g, 4.6 m moles) in 20 ml tetrahydrofuran was stirred with 50 ml S_2Cl_2 for 30 minutes. The excess S_2Cl_2 was then distilled off using the vacuum line leaving a red oil. This was dissolved in 150 ml of ether and to this was slowly added 1.30 ml (9.2 m moles) of $(CH_3)_2CH)_2NH$ in ether (50 ml). The white precipitate formed ($(((CH_3)_2CH)_2NH_2^+ Cl^-)$, was filtered leaving a yellow orange solution.

Upon removal of solvent a red oil developed. This was chromatographed as in section V-1g-i. The ^1H NMR of the fractions showed some separation of the products but again no $S_7NSSN(CH(CH_3)_2)_2$ was isolated.

(h) Reaction of Triphenylphosphine, Phenylphosphorus Chlorides and Phosphorus Trichloride with N,N'-Thiobisdimethylamine

(i) $(C_6H_5)P$ and $((CH_3)_2N)_2S$

Triphenylphosphine (0.38 m moles, 0.1 g) and $((CH_3)_2N)_2S$ (0.38 m moles, 50 µl) were dissolved in 0.5 ml CD_2Cl_2 in a 5 mm NMR tube. Five drops of tetramethylsilane (TMS) were added and the ^1H NMR spectrum recorded showing no reaction. The capped NMR tube was then held at 50°C in a water bath for 3 days and the ^1H NMR spectrum recorded, again showing no reaction.

(ii) (C_6H_5) PCl and $((CH_3)_2N)_2S$

Special precautions should be taken in the handling of some of the compounds prepared in this section due to their poisonous nature.

$((CH_3)_2N)_2S$ (0.38 m moles, 50 µl) was syringed into a 5 mm NMR tube containing 0.5 ml $CDCl_3$ and 5 drops TMS under a nitrogen atmosphere. The NMR tube was then cooled to -60°C and the NMR recorded of the solution. The sample was then removed from the NMR probe and quickly cooled to -78°C for addition of $(C_6H_5)_2PCl$. The ϕ_2PCl was slowly added using a 50 µl syringe into

the cold solution through a serum cap on the NMR tube. The sample was thoroughly mixed after the addition of each 10 µl. A series of ^1H NMR spectra were recorded as the mole ratio $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S$ was brought to 1:1 and then the sample warmed to room temperature. This corresponded to 68 µl of halophosphine. Spectra were recorded until no change in the spectra could be observed at room temperature after a period of a few hours. Other series of spectra in which the mole ratio $(C_6H_5)_2PCl$: $((CH_3)_2N)_2S$ was brought to 2:1, 3:1 and 4:1 were also recorded. Between 10 and 30 spectra were recorded in each series.

This reaction was also monitored using ^{31}P NMR spectroscopy. In this case, 5 times all volumes used in the ^1H NMR experiment were added to a 10 mm NMR tube with the exception that TMS was not added. Two series of ^{31}P spectra (paralleling the 2:1 and 1:1 mole ratio reactions discussed above) were recorded. Approximately 5 spectra were recorded in each series.

Conductivity measurements were performed as a function of addition of $(C_6H_5)_2PCl$ to a 0.4 M solution of $((CH_3)_2N)_2S$ in CH_2Cl_2 at room temperature. The apparatus used is described in section V-2h. The concentration range studied was 0.0 M to 0.8 M $\left[(C_6H_5)_2PCl\right]$.

A sample of $(C_6H_5)_2P(S)N(CH_3)_2$, XXXVI, was prepared by addition of $(C_6H_5)_2PCl$ (15.2 m moles, 2.72 ml) to $((CH_3)_2N)_2S$ (7.6 m moles, 1.0 ml) in 10 ml CH_2Cl_2. The reaction mixture was allowed to stand at room temperature for 6 hours. The solvent

was removed and the brown oil passed through a silica gel column (75 cm x 2.5 cm of 80 to 200 mesh) using benzene-chloroform as eluent. The compound, XXXVI, came off as a distinct band and upon evaporation of solvent gave white crystals (~1.0 g, melting point 91 to 92°C). A sample was removed for mass spectral analysis as discussed in section III-3iii (Figure III-2).

(iii) $(C_6H_5)PCl_2$ and $((CH_3)_2N)_2S$

The compounds prepared in this section are also quite poisonous and appropriate precautions should be taken.

$(C_6H_5)_2PCl_2$ and $((CH_3)_2N)_2S$ (0.38 m moles, 50 µl) were reacted in CD_2Cl_2 (0.5 ml) using the method just described in section V-leii. Series of ^1H and ^{31}P NMR spectra were recorded for the mole ratios $(C_6H_5)PCl_2$: $((CH_3)_2N)_2S$ = 1:1 and 3:2 (0.38 m moles, 51 µl, 0.57 m moles, 76 µl, respectfully). In this reaction, products formed more quickly than in section V-leii. As a result, initial spectra were recorded at -60°C and subsequent spectra were recorded more frequently as addition of $(C_6H_5)PCl_2$ and increase in temperature occurred.

Conductivity measurements were performed as a function of addition of $(C_6H_5)PCl_2$ to a 0.4 M solution of $((CH_3)_2N)_2S$ in CH_2Cl_2 at -78°C. The apparatus used is described in section V-2h, The concentration range studied was $\left[(C_6H_5)PCl_2\right]$ = 0.0 M to 0.8 M.

(iv) PCl_3 and $((CH_3)_2N)_2S$

The compounds prepared in this section are also quite

poisonous and appropriate precautions should be taken.

Again this reaction proceeded very quickly, necessitating initial NMR spectra to be recorded at -60°C and the frequent recording of subsequent spectra. Initial concentration of $((CH_3)_2N)_2S$ was the same as in the other cases (0.38 m moles = 0.5 ml CD_2Cl_2 plus 5 drops TMS). Three series of ^1H and ^{31}P spectra were recorded in this case, the mole ratios of the reactants being PCl_3 : $((CH_3)_2N)_2S$ = 1:2, 1:1, and 3:2 (0.19 m moles, 16.5 µl; 0.38, 33 µl and 0.57 m moles, 46.5 µl of PCl , respectfully) at the end of each series.

This reaction was also followed by conductivity measurements. The experimental conditions were exactly as described in section V-leiii for the $(C_6H_5)PCl_2$: $((CH_3)_2N)_2S$ reaction.

A sample of $\left[P(Cl_2)(N(CH_3)_2)_2\right]^+ PCl_6^-$, LI , was prepared by distillation of PCl_3 (11.4 m moles, 0.93 ml) onto $((CH_3)_2N)_2S$ (7.6 m moles, 1.0 ml) at -196°C in $CHCl_3$ (20 ml) in an evacuated double ampoule. The mixture was allowed to warm to 0°C and allowed to stand for one hour at which time a white precipitate formed. The mixture was washed through a medium frit leaving behind white platelets. The solvent and excess PCl_3 were distilled off and fresh $CHCl_3$ added. This was distilled into the ampoule arm containing the crystals and used to wash them. After several washings the ampoule was pumped dry and the arm containing the crystals sealed. The Raman spectrum was recorded and the sample then sent for analysis. Yield was approximately 0.5 gram of white air-sensitive

platelets. The Raman and analytical data are presented in section III-5.

(i) Reaction of Triphenylphosphine, Phenylphosphorus Chlorides and Phosphorus Trichloride with N,N'-Dithiobisdimethylamine

(i) $(C_6H_5)_3P$ and $((CH_3)_2N)_2S_2$

Triphenylphosphine (0.33 m moles, 76 mg) was added to a room temperature solution of $((CH_3)_2N)_2S_2$ (0.33 m moles, 50 µl) in CD_2Cl_2 (0.5 ml plus 5 drops TMS) in a 5 mm NMR tube. The ^1H NMR spectrum was recorded at regular intervals over a period of four hours. ^{31}P NMR spectra were also recorded on an equivalently prepared sample using five times the amounts shown above.

(ii) $(C_6H_5)_2PCl$, $(C_6H_5)PCl_2$ and PCl_3 Reacting with $((CH_3)_2N)_2S_2$

Many of the compounds prepared in this section are quite poisonous and appropriate precautions should be taken in their handling.

The phosphorus compound ($(C_6H_5)_2PCl$ 0.33 m moles, 61 µl; $(C_6H_5PCl_2$ 0.33 m moles, 45 µl; PCl_3 0.33 m moles, 29 µl) was added in increments to a cooled (-50°C) solution of $((CH_3)_2N)_2S$ (0.33 m moles, 50 µl) in CD_2Cl_2 (0.5 ml plus 5 drops TMS). After each increment the ^1H NMR spectrum was recorded. Once the mole ratio had reached P compound: $((CH_3)_2N)_2S_2$ = 1:1 , the sample was slowly brought to room temperature again being monitored by ^1H NMR. ^{31}P NMR spectra were then taken on equivalently prepared samples (containing 5 times the amounts in the ^1H NMR spectra) and the reaction monitored

in the same way. A similar series of ^{1}H and ^{31}P NMR spectra were then recorded for each reaction on samples in which the more ratio was brought to P compounds: $((CH_3)_2N)_2S_2$ = 2:1 and 3:1 before it was raised in temperature.

Conductivity measurements were also performed on a 0.4 M solution of $((CH_3)_2N)_2S_2$ in CH_2Cl_2 as a function of amount of phosphorus compound added. The method is described in section V-2h and the results given in sections IV-2, IV-3, IV-4 for $(C_6H_5)_2PCl$, $(C_6H_5)PCl_2$ and PCl_3 respectfully.

A sample of $(C_6H_5)P(S)Cl(N(CH_3)_2)$, XLV, was prepared by the addition of $(C_6H_5)PCl_2$ (13.2 m moles, 1.8 ml) to a solution of $((CH_3)_2N)_2S$ (6.6 m moles, 1.0 ml) in CH_2Cl_2 (10 ml). After reaction for one hour at room temperature, a sample was removed for mass spectral analysis, the results of which are discussed in section IV-3. The compound was not purified through recrystallization so a melting point cannot be given.

(j) Reaction of PX_3 (X = Cl, Br) with $S_7NSN(CH_3)_2$

$S_7NSN(CH_3)_2$ (2.0 g, 6.4 m moles) was dissolved in 4 ml of $CHCl_3$. PX_3 (X = Cl, 0.56 ml, X = Br, 0.61 ml (6.4 m moles)) was added to 1 ml $CHCl_3$ and slowly added to the other solution (at room temperature when X = Cl, at 0°C when X = Br). After two hours in the PCl_3 case or a few seconds in the PBr_3 case, the solution turned reddish-brown. After another 3 hours a red oil separates from the solution which was now green. The green solution was

decanted and the red oil dissolved in 1.5 ml of CS_2. CCl_4 (4 ml) was then added to the solution to cause the oil to come out of solution. In this manner, most of the compound $((CH_3)_2N)P(S)X_2$ was removed from the oil. The oil was then chromatographed on silica gel (1.5 cm x 75 cm of 80 to 200 mesh, hexane). A red band quickly moves through the column and upon collection and removal of solvent a clear red oil results. Raman (Table III-3) and infra-red measurements (Figure III-14) were performed. The red oil had no ^1H or ^{31}P NMR spectrum.

V-2 INSTRUMENTAL

(a) ^{31}P NMR Spectra

Phosphorus NMR spectra were recorded on a Bruker WH90 NMR spectrometer fitted with a probe and radio frequency attachment designed to observe the ^{31}P nucleus at 36.43 MHz. This machine was equipped with a proton decoupler and a Bruker B-ST 100/700 temperature controller. The machine was internally locked to the deuterium signal in CD_2Cl_2 in the samples. All chemical shifts are reported in reference to 85% phosphoric acid, negative chemical shifts being at low field strength. For ^1H coupled spectra, 500 to 3000 scans were necessary for adequate resolution of 0.2 M samples.

(b) ^{13}C NMR Spectra

^{13}C NMR spectra were recorded on the same instrument as the

^{31}P NMR spectra using a probe and radio frequency attachment designed for the observation of the ^{13}C nucleus at 22.62 MHz. The machine was internally locked to the deuterium signal in $CDCl_3$. The proton decoupler was used while observing the ^{13}C spectra as well. Chemical shifts are recorded relative to TMS, negative shifts being to high field.

(c) ^{1}H NMR Spectra

Preliminary ^{1}H NMR spectra were recorded on a Varian T-60 for room temperature samples. Low temperature preliminary spectra were recorded on a Varian A-60 equipped with a variable temperature controller. All final spectra were recorded using the Varian HA-100 spectrometer while it was internally locked to TMS. A frequency counter was used to obtain accurate chemical shifts. Chemical shifts are reported relative to TMS.

(d) Raman Spectra

The Raman spectra were recorded on a Spex Industries Model 1400 3/4 meter Czerny-Turner double monochromator using the green beam (5145 Å) of Spectra Physics Model 164 ion laser for white samples $\left[((CH_3)_2N)_2PCl_2)^+ PCl_6^-\right]$ and the 6328 Å line of a Spectra Physics Model 125 helium-neon laser for red coloured samples (reaction of $S_7NSN(CH_3)_2$ with PCl_3 and PBr_3).

(e) Infra-red Spectra

Infra-red spectra were recorded on a Beckman IR 10, Beckman IR 5 and Perkin-Elmer 321. Oils and liquids were run as thin films between KBr discs. Solutions were run using NaCl solution cells. All spectra were recorded relative to the 1601 cm^{-1} and 1025 cm^{-1} peaks in polystyrene.

(f) Mass Spectra

Mass spectra were recorded on a Consolidated Electrodynamics Corporation Model No. 21-110B double focusing mass spectrometer. The normal energy of the bombarding electrons is about 80 eV. The spectra were referenced to perfluorokerosene.

(g) Melting Points

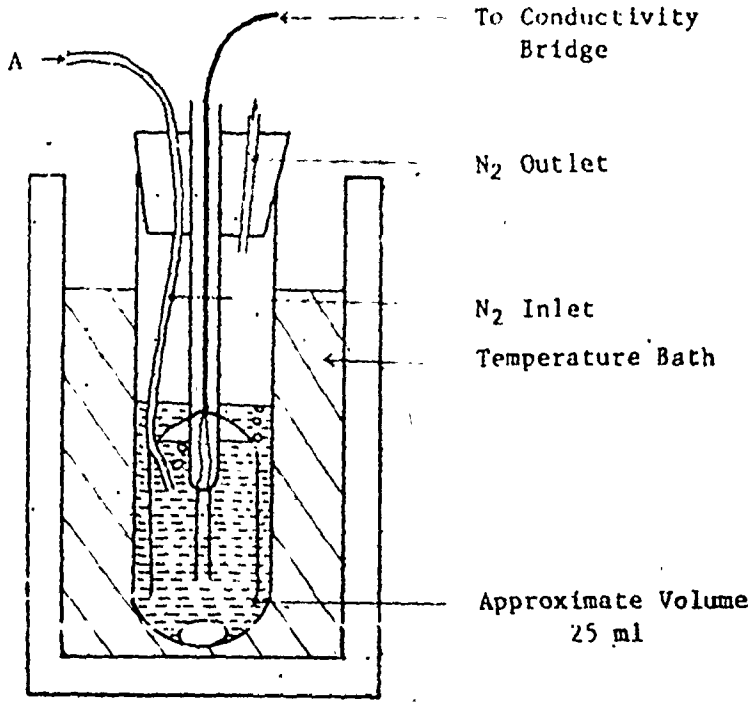
All melting points were recorded using a Thomas-Hoover melting point apparatus and are uncorrected.

(h) Conductivity

Conductivity measurements were performed using a Industrial Instruments Inc., Model RC 16B2 conductivity bridge in conjunction with the cell shown in Figure V-5. With this cell it was possible to syringe the phosphorus compounds into the solution without exposing the solution to the air or warming it up. The phosphorus compounds were injected into the nitrogen inlet tube at A (Figure V-6). Then about 1 ml of solution was syringed back into the tube to

Figure V-6

Conductivity Cell



wash down traces of reactant. The nitrogen flow was then continued. All measurements were taken one minute after addition of phosphorus chloride with the magnetic stirrer turned off. All conductivities reported are specific conductivities, the cell used having a constant of 0.104 cm^{-1} (resistance of 7.4191 g of KCl in 1ℓ H_2O at 21°C = 8.80 ohms).

V-3 SOLVENTS AND CHEMICALS

All solvents used were reagent grade and were used without further purification. The amines were also reagent grade and used

without purification. The sulfur chlorides were purified by the method outlined in Brauer[129]. Sulfur dichloride after purification was stored at 0°C after being diluted 10 times with pentane to inhibit decomposition. Triphenylphosphine, diphenylphosphinous chloride and phenylphosphonous dichloride were reagent grade and not purified. These compounds were stored under a nitrogen atmosphere. Phosphorus trichloride was purified by vacuum distillation at room temperature and stored under nitrogen.

V-4 CHROMATOGRAPHY

All chromatography was performed using 60 to 200 mesh Baker Analysed Reagent Grade silica gel powder. The best method of preparing the columns was as follows. Glass wool was pushed to the bottom of an exactly vertically held column the top of which was fitted with a ground glass joint. The column was then filled with eluent and the bubbles removed from the glass wool. Two centimeters of sand was allowed to settle through the solvent giving a uniform layer. A slurry of the silica gel in the eluent solvent was then prepared in a large separatory funnel fitted with a ground glass joint. This was then placed on top of the column and the stopper opened. The stopper at the bottom of the column was then opened slightly and the column gradually filled in a uniform manner. When enough silica gel had been added the stoppers were closed and another centimeter of sand was allowed to settle on the top of the silica gel.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The sulfur-nitrogen bond in N,N'-thiobisdialkylamines and N,N'-dithiobisdialkylamines has been shown to undergo new reactions. The former compounds have been found to react with the weak protic acid heptasulfurimide (S_7NH) to give the new series of compounds, N,N-dialkyl-N',N'-cycloheptathiosulfoxylic diamides (S_7NSNR_2, R = CH_3, C_2H_5, $CH(CH_3)_2$, C_6H_{11}) in good yield. Structural data has been presented which, when coupled with NMR spectroscopic data, suggests that pπ-dπ bonding is very important in this molecule. The pπ-dπ bonding in the sulfur-nitrogen side chain allows only slow rotation about one of the N-S bonds. This causes groups β to the nitrogen in the side chain to become diastereotopic. The ^1H NMR spectrum of the methylene protons in the ethyl derivative and the methyl groups in the isopropyl compound show this effect. The ^{13}C NMR spectrum of the cyclohexyl derivative also shows diastereotopic groups, in this case carbon atoms in the rings. The pπ-dπ bonding has produced very short N-S "single" bonds and greatly influenced the structure of the whole molecule.

All attempts to prepare the similar compounds R_2NSSNS_7 proved unsuccessful.

N,N'-monothiobisdimethylamine and N,N'-dithiobisdimethylamine were also found to react with chlorinated phosphines. The reactions of the former compounds involved a very facile insertion

of phosphorus into the sulfur-nitrogen bond. A mechanism involving electrophilic attack of phosphorus on sulfur appears to be the initial stage of the reaction. Group migration then occurs similar to that observed in transition metal insertion reactions. The species subsequently undergo further reactions as summarized in Figure VI-I.

Figure VI-1

Reactions of N,N'-Thiobisdimethylamine with Chlorine Substituted Phosphines

(a) $((CH_3)_2N)_2S + (C_6H_5)_3P \longrightarrow$ no reaction

(b) $((CH_3)_2N)_2S + (C_6H_5)_2PCl \longrightarrow \left[(C_6H_5)_2P(N(CH_3)_2)(SN(CH_3)_2)\right]^{\oplus *}Cl^{\ominus}$

$\xrightarrow{(C_6H_5)_2PCl} (C_6H_5)_2P(S)(N(CH_3)_2) + \left[(C_6H_5)_2P(N(CH_3)_2)Cl\right]^{\oplus} Cl^{\ominus}$

(c) $2((CH_3)_2N)_2S + 2(C_6H_5)PCl_2 \longrightarrow 2\ (C_6H_5)P(N(CH_3)_2)(SN(CH_3)_2)Cl\Big]^{\oplus} Cl^{\ominus}$

$\longrightarrow \left[(C_6H_5)P(N(CH_3)_2)Cl_2\right]^{\oplus} Cl^{\ominus} + (CH_3)_2NSCl + (C_6H_5)P(S)(N(CH_3)_2)_2$

$\xrightarrow{(C_6H_5)PCl_2} \left[(C_6H_5)P(N(CH_3)_2)Cl_2\right]^{\oplus} Cl^{\ominus} + (C_6H_5)P(S)(N(CH_3)_2)_2 +$

$(C_6H_5)P(S)(N(CH_3)_2)Cl + Cl_2$

(d) $((CH_3)_2N)_2S + PCl_3 \longrightarrow \left[((CH_3)_2N)P(SN(CH_3)_2)Cl_2\right]^{+} Cl^{-} \longrightarrow$

$(CH_3)_2NSCl + ((CH_3)_2N)PCl_2 \xrightarrow{((CH_3)_2N)_2S}$

$\left[((CH_3)_2N)_2P(SN(CH_3)_2)Cl\right]^{+} Cl^{-} + (CH_3)_2NSCl \longrightarrow$

$2(CH_3)_2NSCl + ((CH_3)_2N)_2PCl \xrightarrow{PCl_3} 2(CH_3)_2NSCl +$

$2((CH_3)_2N)PCl_2 \xrightarrow{PCl_3} ((CH_3)_2N)_2P(S)Cl + ((CH_3)_2N)P(S)Cl_2 +$

$\tfrac{1}{2}\left[((CH_3)_2N)_2PCl_2\right]^{+} PCl_6^{-} + Cl_2$

There is a definite difference in stability of the insertion products. With $(C_6H_5)PCl_2$ and PCl_3, the insertion product is unstable with the usual reaction being loss of N,N-dimethylamine-N-sulfenyl chloride. The diphenyl derivative is most likely more stable due to delocalization of the positive charge into the phenyl groups. The sulfur atom α to the phosphorus atom would then be less susceptible to attack by chloride ion. The insertion product of the diphenylphosphinous chloride was found to be attacked by a second mole of $(C_6H_5)_2PCl$ to give further products.

The reactions of the N,N'-dithiobisdimethylamine with $(C_6H_5)_3P$, $(C_6H_5)_2PCl$, $(C_6H_5)PCl_2$ and PCl_3 were also investigated. The reactions are summarized in Figure VI-2.

When there are three or two phenyl groups attached to phosphorus, the P-compound acts as a desulfurizing agent. As the phenyl groups are replaced by chlorides, the principle reaction is the oxidation of the phosphorus compound and formation of N,N-dimethylamine-N-sulphenyl chloride. Further reaction offers a convenient method of synthesizing these phosphorus V compounds.

Since the area of sulfur-nitrogen chemistry still has many unexplored fields there are always ideas which should be followed up after any investigation. This is the case here. In the reaction of heptasulfurimide with N,N'-dithiobisdimethylamine, perhaps preparation of S_7NSSNR_2 could be effected with the utilization of molecular exclusion chromatography. It would be interesting to study the bonding

Figure VI-2

Reactions of N,N'-Dithiobisdimethylamine with Chlorine Substituted Phosphines and Triphenylphosphine

(a) $(C_6H_5)_3P + ((CH_3)_2N)_2S_2 \longrightarrow (C_6H_5)_3PS + ((CH_3)_2N)_2S$

(b) $(C_6H_5)_2PCl + ((CH_3)_2N)_2S_2 \longrightarrow (C_6H_5)_2P(S)Cl + ((CH_3)_2N)_2S$

$$\xrightarrow{(C_6H_5)_2PCl} (C_6H_5)_2P(S)Cl + \left[(C_6H_5)_2P(N(CH_3)_2)(SN(CH_3)_2)\right]^{\oplus} Cl^{\ominus}$$

$$\xrightarrow{(C_6H_5)_2PCl} (C_6H_5)_2P(S)Cl + (C_6H_5)_2P(S)(N(CH_3)_2) + \left[(C_6H_5)_2P(N(CH_3)_2)Cl\right]^{+} Cl^{-}$$

also

$$(C_6H_5)_2PCl + ((CH_3)_2N)_2S_2 \longrightarrow (C_6H_5)_2P(S)(N(CH_3)_2) +$$

$$(CH_3)_2NSCl \xrightarrow{(C_6H_5)_2PCl} 2(C_6H_5)_2P(S)(N(CH_3)_2) + Cl_2$$

(c) $(C_6H_5)PCl_2 + ((CH_3)_2N)_2S_2 \longrightarrow (C_6H_5)P(S)(N(CH_3)_2)Cl + (CH_3)_2NSCl$

$$\xrightarrow{(C_6H_5)PCl_2} 2(C_6H_5)P(S)(N(CH_3)_2)Cl + Cl_2$$

(d) $(PCl_3) + ((CH_3)_2N)_2S_2 \longrightarrow ((CH_3)_2N)P(S)Cl_2 + (CH_3)_2NSCl$

$$\xrightarrow{PCl_3} 2((CH_3)_2N)P(S)Cl_2 + Cl_2$$

in this molecule. The reaction of the chlorine substituted phosphorus compounds with $(R_2N)_2S$ also could undergo further study. Not only could other halides be investigated but also similar compounds of the other group V elements. The reaction of PX_3(X = Cl, Br) with $S_7NSN(CH_3)_2$ should also be further studied by variation of the substituents on phosphorus. Preparation of S_7NX (X = halogen) would not only be very interesting in itself, but would offer a preparative route to other compounds. The cation S_7N^+, for example, could be easily prepared by this method and should be quite stable, it being isoelectronic with the stable cation S_8^{2+}.

Sulfur-nitrogen chemistry is a field which needs much work to fully understand the principles involved. The bonding is not necessarily straightforward and often necessitates the proposition of an extra π-system. Many sulfur-nitrogen compounds undergo reactions with simple reagents which are as yet unreported in the literature but provide valuable information concerning the overall chemistry of these compounds. Further studies of these systems are desirable as the importance of sulfur-nitrogen compounds is constantly growing in the chemical industry today.

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APPENDIX I

NAMES OF PHOSPHORUS COMPOUNDS

$(C_6H_5)_3P$		Triphenylphosphine
$(C_6H_5)_2PCl$		Diphenylphosphinous Chloride
$(C_6H_5)PCl_2$		Phenylphosphonous Chloride
PCl_3		Phosphorus Chloride
$PCl_2(N(CH_3)_2)$	XLIX	Dimethylphosphoramidous Dichloride
$PCl(N(CH_3)_2)_2$	XLVIII	Tetramethylphosphorodiamidous Chloride
$(C_6H_5)_3PS$	LXIII	Triphenylphosphine Sulfide
$(C_6H_5)_2P(S)Cl$	LXIV	Diphenylphosphinothioic Chloride
$(C_6H_5)_2P(S)(N(CH_3)_2)$	XXXVI	N,N-Dimethyl-P,P-diphenylphosphinothioic Amide
$(C_6H_5)P(S)(Cl)(N(CH_3)_2)$	XLV	N,N-Dimethyl-P-phenylphosphonothioic Chloride
$P(S)(Cl)_2(N(CH_3)_2)$	XXXVIII	Dimethylphosphoramidothioic Dichloride
$(C_6H_5)P(S)(N(CH_3)_2)_2$	XLIII	Tetramethyl-P-phenylphosphonothioic Diamide
$P(S)Cl(N(CH_3)_2)_2$	L	Tetramethylphosphorodiamidothioic Chloride
$(C_6H_5)_2P(Cl)N(CH_3)_2)^+ Cl^-$	XLI	Chlorodimethylaminatodiphenylphosphorus Chloride

$(C_6H_5)_2P(N(CH_3)_2)(SN(CH_3)_2)^+ Cl^-$	XXXV	Dimethylamidosulfenyldimethylaminatodiphenylphosphorus Chloride
$((C_6H_5)_2P(N(CH_3)_2)_2)^+ Cl^-$	XXXIX	Bisdimethylaminatodiphenylphosphorus Chloride
$((C_6H_5)P(N(CH_3)_2)Cl_2)^+ Cl^-$	XLIV	Dichlorodimethylaminatophenylphosphorus Chloride
$((C_6H_5)P(N(CH_3)_2)_2Cl)^+ Cl$	XLVI	Chlorobisdimethylaminatophenylphosphorus Chloride
$((C_6H_5)P(N(CH_3)_2)(SN(CH_3)_2)Cl)^+ Cl^-$	XLII	Chlorodimethylamidosulfenyldimethylaminatophenylphosphorus Chloride
$(P(N(CH_3)_2)_2(SN(CH_3)_2)Cl)^+ Cl^-$	XLVII	Chlorodimethylamidosulfenyldimethylaminato phosphorus Chloride
$(P(N(CH_3)_2)_2Cl_2)^+ PCl_6^-$	LI	Dichlorobisdimethylaminatophosphorus Hexachlorophosphate