Thiodithiazyl compounds

J. R. House

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THIODITHIAZYL COMPOUNDS

by

J. R. HOUSE

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Memorandum

The work described in this thesis was carried out in the University of Durham between October, 1965 and October, 1966. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Summary

The preparations of thiodithiazyldichloride, $S_3N_2Cl_2$, and thiodithiazyldiphenyl, $S_3N_2Ph_2$ are discussed. Reactions of the type $S_3N_2Cl_2 + 2MX \longrightarrow S_3N_2X_2 + 2MCl$, and the formation of metal complexes with $S_3N_2Ph_2$ were attempted. Both thiodithiazyl compounds could be purified by sublimation. The I.R. spectra of the compounds $S_3N_2Cl_2$, S_3N_2Cl and $S_3N_2Ph_2$ were recorded and compared with that of $S_3N_2O_2$. The 'sulphur-nitrogen' bond lengths in $S_3N_2Cl_2$, S_3N_2Cl and $S_3N_2Ph_2$ are predicted. The mass spectra of $S_3N_2Cl_2$, $S_3N_2Ph_2$ and S_4N_4 were recorded and discussed. A possible structure for $S_3N_2Ph_2$ is given.

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INTRODUCTION

INTRODUCTION

Thiodithiazyl derivatives form one class of 'sulphur-nitrogen' compounds. The term 'sulphur-nitrogen' implies that such compounds contain single and/or double bonds between sulphur and nitrogen atoms. Sulphur-nitrogen compounds can be subdivided into three main types:-

1. Polycyclic and cage molecules e.g. S_4N_4;
2. Monocyclic systems e.g. $S_3N_3Cl_3$, $S_3N_3O_3Cl_3$, $S_4N_4H_4$, $S_4N_4F_4$, S_4N_3Cl;
3. Compounds containing sulphur-nitrogen chains e.g. $S_3N_2F_2$, $S_3N_2Cl_2$, $S_3N_2(\text{Aryl})_2$, $S_3N_2O_2$

Several reviews cover these compounds generally[1,2,3,4] while many papers refer to individual compounds. See Table 1.

The references given by no means cover the whole of sulphur-nitrogen chemistry, but certainly give a detailed study of this subject, and inevitably lead to other references of equal interest.

Thiodithiazyl compounds, contain, as the title suggests, an S_3N_2 unit and consequently could be generally designated as $S_3N_2X_2$. There are few compounds of this type known, but the available information is given below under the individual compounds. These are:-

(1) <u>Thiodithiazyldifluoride</u>, $S_3N_2F_2$[1,18,19,45]

$S_3N_2F_2$ is formed by the decomposition of NSF in a glass flask, forming green-yellow crystals. Glemser[1,45] reported that sublimation yielded two fractions, at 40°C and 65°C, both of which gave identical

Table 1.

COMPOUNDS or CLASS	REACTIONS or PREPARATIONS	SPECTROSCOPIC
S_4N_4	Prep. 14, 67 Reaction with NH_3 11; H_2O 12; RMgBr 13.	I.R. 5: Raman 5: U.V. 7: Vis. 7: M.O. calcs. 6, 7. Assignments 5.
$S_4N_4H_4$	Prep. 8 Reaction with S_7NH 10; Oxidation 9; RSO_2Cl 31	I.R. 5, 8 Tentative assignments 5.
NSF SNF and SNF_3	Review 19 Prep. 15, 16. Adducts with BF_3 27	I.R. 15, 16, 20 N.M.R. 20.
$S_3N_3F_3$ $S_4N_4F_4$	Prep. 1	N.M.R. 20
$S_3N_2F_2$	Prep. 18	
S_4N_3F	Prep. 17	I.R. 17
NSCl NSCl and $S_3N_3Cl_3$	Prep. 21, 24, 28	

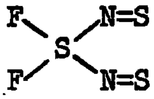
Table 1 (cont.)

COMPOUNDS or CLASS	REACTIONS or PREPARATIONS	SPECTROSCOPIC
$S_3N_2Cl_2$	Prep. 21, 22, 23, 25, 26	
S_4N_3Cl	Prep. 21, 22, 23, 25, 26, 29	I.R. 17, 30: Raman 30: N.M.R. 29
$S_3N_3O_3Cl_3$	Prep. 98	Structure 99, 100
S_3N_2O	Prep. 33, 34	
$S_3N_2O_2$	Prep. 14, 33, 34	X-ray structure 54
$S_3N_2O_5$	Prep. 52, 53	
$S_3N_2R_2$ R = Alkyl = Aryl	 Prep. 21 Prep. 13, 31, 32	
Metal Thio-nitrosyls	Prep. 35-39	
S-N polymers	Prep. 41-44	I.R. 40

A Brief Background Survey of 'Sulphur-Nitrogen' Chemistry

Reference Numbers are given on Page 125

visible spectra (in carbon tetrachloride). Furthermore determination of the molecular weights, oxidation number of the sulphur, and elemental analysis gave the same values for both fractions. This led Glemser to postulate two possible structures (1a) and (1b) of which (1a) was preferred because of the different canonical forms possible, which would account for the intense colour of $S_3N_2F_2$.

$F{-}S{-}N{=}S{=}N{-}S{-}F$ and 

(1a) (1b)

(11) <u>Thiodithiazyldichloride</u>, $S_3N_2Cl_2$

$S_3N_2Cl_2$ was reported as early as 1881[46] when it was prepared by gently heating $N_3S_3Cl_3$ in S_2Cl_2[46,27]. In the presence of excess chlorine it reverts to $N_3S_3Cl_3$ - probably in the following manner:

$$3S_3N_2Cl_2 + 3Cl_2 \longrightarrow (6NSCl + 3SCl_2) \longrightarrow 2N_3S_3Cl_3$$

while further heating in S_2Cl_2[21] or S_2Cl_2 in CCl_4[1] or in CCl_4[25,26] gives S_4N_3Cl probably via S_3N_2Cl[25].

Jolly et. al.[23,25,26] improved the preparation of $S_3N_2Cl_2$ by heating ammonium chloride and S_2Cl_2 under an air condenser for several hours. Crystals of $S_3N_2Cl_2$ formed in the air condenser and the product, freed of S_2Cl_2 on the vacuum line, could be stored under nitrogen or in vacuo for several days.

The mechanism proposed for this reaction:

$$NH_4Cl + 2S_2Cl_2 \longrightarrow NSCl + 3S + 4HCl$$

$$2NSCl + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + SCl_2$$

is based on the fact that with S_2Cl_2 in excess, NSCl is formed in solution[24,25] and it is assumed that the delay time in the formation of $S_3N_2Cl_2$ is caused by the need for an optimum concentration of sulphur, since by adding sulphur to the reaction mixture the induction period can be reduced. Furthermore, the presence of sulphur should cause the equilibria

$$S_2Cl_2 \rightleftharpoons S_2 + Cl_2$$
$$S_2Cl_2 \rightleftharpoons S + SCl_2$$

to shift in favour of S_2Cl_2, thereby reducing the concentration of chlorine and hence lowering the chance of the formation of NSCl or $N_3S_3Cl_3$ by the reaction of chlorine with $S_3N_2Cl_2$.

According to Jolly et. al.[25] sublimation of $S_3N_2Cl_2$ in vacuo at 80-95°C gave dark green S_3N_2Cl.

No structural or spectroscopic data on $S_3N_2Cl_2$ is as yet available although it would seem reasonable to assume that its structure should be similar to $S_3N_2F_2$.

(III) <u>Thiodithiazylmonochloride</u>, S_3N_2Cl

S_3N_2Cl is a green crystalline compound, which can be obtained from S_4N_4 + S_2Cl_2 in the cold[47], or by vacuum sublimation of $S_3N_2Cl_2$ at 80-95°C[25]. Becke-Goehring[48] suggested that the reaction S_4N_4 + S_2Cl_2 was complex and proceeded via some unknown intermediate, and found that S_3N_2Cl was formed by reacting NOCl with S_4N_4, or when $N_3S_3Cl_3$ reacted with NO in nitromethane as solvent. Again structural and spectroscopic data are unavailable. S_3N_2Cl hydrolyses rapidly; its insolubility in organic solvents and low volatility indicate some degree of polymerisation.

(IV) Thiodithiazylmonobromide, S_3N_2Br[49]

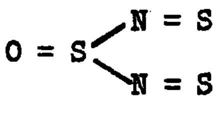
Both Glemser[1] and Goehring[50] mention this compound, both authors commenting on its probable degree of similarity to S_3N_2Cl. Beyond this, nothing is known unless further information is available in the original experimental work[49].

(V) Diisothiazylsulphoxide, $OS(NS)_2$[33,34]

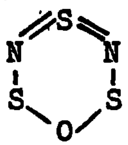
Meuwsen et. al.[33] reported the formation of S_3N_2O by the reactions

1. $S_4N_4H_4 + SOCl_2 \longrightarrow OS(SN)_2$
2. $S_4N_4 + C_2H_5SOCl \longrightarrow OS(SN)_2 + (C_2H_5O)_2SO$
3. $Hg_5(NS)_8 + SOCl_2 \longrightarrow OS(SN)_2$

$OS(NS)_2$ is soluble in many organic solvents - benzene, alcohols, acetic acid, acetone, pyridine, fumes in air, but is insoluble in water[34]. It is decomposed by 5M.NaOH to give $S_2O_3^{2-}$, SO_3^{2-}, and NH_3, and hence the probable structure is (2a) although Goehring preferred the cyclic structure (2b)[3,50] because of its analogy to the sulphur-nitrogen compound S_4N_2 and because of its red colour.



(2a)



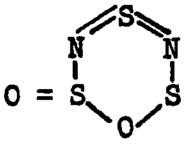
(2b)

Its colour in organic solvents is yellow, and with nitric acid it forms a green liquid.

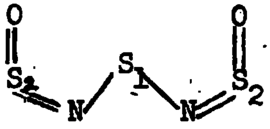
(VI) Thiodithiazyldioxide, $S_3N_2O_2$

$S_3N_2O_2$ can be prepared from S_4N_4 or S_4N_3Cl with SO_2 and $SOCl_2$[50,51] or from sulphur and ammonium chloride with $SOCl_2$[14].

Study of a series of hydrolysis reactions[50], labelling of the sulphur in SO_2 and $SOCl_2$[51], and also of the reaction of $S_3N_2O_2$ with SO_3[52,53] led Goehring to suggest the ring structure (3a) for $S_3N_2O_2$.



(3a)



(3b)

This however was shown to be incorrect by Weiss[54] who proved by X-ray techniques that the structure was a planar chain (3b) where:-

$a = 6.84 Å$ $b = 4.36 Å$ $c = 16.52 Å$

$S_1-N = 1.69 Å$ $S_2-N = 1.58 Å$ $S_2-O = 1.37 Å$ $S_1-S = 2.83 Å$

$S_1 = 95.3^\circ$ $S_2 = 115.3^\circ$ $N = 120^\circ$

$S_3N_2O_2$ is pale yellow, crystalline, with a m.p. 100.7°, and it dissolves in alcohol or benzol. It reacts with water as shown,

$$S_3N_2O_2 + 4H_2O \longrightarrow (NH_4)_2S_3O_6$$

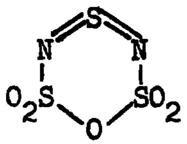
or with damp nitrogen as follows,

$$2S_3N_2O_2 \xrightarrow{\text{damp } N_2} S_4N_4 + 2SO_2$$

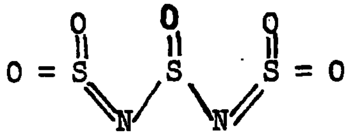
(VII) Thiodithiazylpentoxide, $S_3N_2O_5$

$S_3N_2O_5$ can be prepared, either by the reaction of $S_3N_2O_2$ and SO_3[52], or by the reaction of SO_3 on S_4N_4[53]. The compound is colourless, crystalline, sublimes easily and dissolves in benzene and benzene homologues.

Goehring et. al.[2,3,48,52,53] suggest that the structure of $S_3N_2O_5$ is (4a), but by analogy to Weiss structure of $S_3N_2O_2$[54], structure (4b) would appear to be more probable.



(4a)



(4b)

(VIII) Alkyl and Aryl Substituted Thiodithiazyl Derivatives, $S_3N_2R_2$

Several compounds of this type are known and have been prepared by two main methods:

a) $S_4N_4 + RMgBr \longrightarrow S_3N_2R_2$ [13,21,32]

b) $S_4N_4H_4 + RSO_2Cl \longrightarrow S_3N_2R_2$ [31]

Little progress has been made with aliphatic derivatives since the products tend to be oils or difficult to crystallize[21].

Using $RC_6H_4MgBr + S_4N_4$ Weiss et. al.[13] synthesised a series of derivatives with R=H, Cl, Br, OCH_3. See Table 2.

No analysis figures were given, and the experimental details were very brief. The procedure was to add the Grignard reagent to a benzene solution of S_4N_4, and to this was added 5% acetic acid/ice. The mixture was allowed to stand for a period, after which the benzene layer was separated, dried, evaporated to a viscous oil at the water pump, and finally the product was obtained by recrystallisation of the residual oil in alcohol. An alternative was to use hydrochloric acid instead of acetic acid[32]. Details of compounds prepared using this

Table 2

COMPOUND R in $R_2S_3N_2$	COLOUR	m.p.°C
C_6H_5	brown-gold	105
$pClC_6H_4$	red-brown	160
$pBrC_6H_4$	dark-brown	?
$pCH_3OC_6H_4$	orange-brown	125-126

Products of the Reaction RMgBr + S_4N_4[13.]

Table 3

COMPOUND R in $R_2S_3N_2$	COLOUR	m.p.°C
C_6H_5	orange leaflets	105
$pClC_6H_4$	red-brown needles	160
$pBrC_6H_4$	red-brown leaflets	135
$pCH_3O.C_6H_4$	gold shining leaflets	125

Products of the Reaction RMgBr + S_4N_4 in the Alternative Preparation[32] alternative method are given in Table 3. All these compounds are insensitive to water, and dissolve readily in alcohol but are less soluble in acetone, benzene and dioxane.

Using substituted benzene sulphonyl halides, Farrar[31] obtained a series of products by method (b). The method was to dissolve $S_4N_4H_4$ in dry pyridine and to this was added the sulphonyl halide. After a period of an hour the solid was filtered, washed with cold pyridine and then recrystallised from trichloroethylene and dried. In this manner 12 gm. of 2.4.5. trichlorobenzene sulphonyl chloride and 2gm. $S_4N_4H_4$ gave 0.8gm. of thiodithiazyldi(2.4.5.trichlorobenzene).

The reagents tried, with appropriate melting points and comments are listed in Table 4.

Farrar also notes that the alkaline hydrolysis of $R_2S_3N_2$ gave $R{-}S{-}S{-}R + SO_2 + S_2O_3^{2-} + NH_3$, and makes an interesting note with regard to the use of solvents. Thus it is recommended that solvents such as acetone, ethanol and methanol should not be used in working up these compounds, since the products while similar in m.p. and appearance are analytically different. The reason for this difference is unknown, but apparently it is not due to solvation.

Table 4

R	Product	m.p.°C
Phenyl	no product	-
3.4.dichlorobenzene	no product	-
2.4.5.trichlorobenzene	red crystals of $(2.4.5.Cl_3C_6H_2)_2S_3N_2$	209°C
2.5.dichlorobenzene	$(2.5.Cl_2C_6H_3)_2S_3N_2$	200°C
2.4.5.tribromobenzene	orange $(2.4.5.Br_3C_6H_2)_2S_3N_2$	214°C

Summary of the Reaction of $S_4N_4H_4$ with RSO_2Cl[31].

OBJECTIVES

Objectives

The study of thiodithiazyl compounds arose from a project concerned with the formation of sulphur-nitrogen polymers and sulphur-nitrogen metal polymers.

The use of polymers containing $(S-S)_n$ bonding has been established in the large field of thiokol chemistry. Such polymers find uses as surface coatings, water repellents, vulcanisers, fuel and concrete tank liners etc.[55,57]. Furthermore, studies on dropwise condensation, showed that compounds containing sulphur acted as good water repellents on copper or copper containing surfaces,[58,68-71], while compounds containing nitrogen had a similar, though not always as permanent effect, on stainless steel[58,72].

To quote Poninski and Krysewski[59], "A growing interest in aromatic polymers with a system of continuous conjugated bonds in the chain, is observed in the last decade. Polymeric substances of this type show some interesting features, viz; high thermostabality, relatively high electrical conductivity, (often in semi-conductivity range) distinct paramagnetic properties and strong U.V. and visible light absorption." Consequently it was felt that some sulphur-nitrogen polymers may be of practical use.

Sulphur-nitrogen polymers have been made by the reaction of SCl_2,[41,42] or S_2Cl_2 with small monomers such as methylamine, but the products were difficult to isolate from the resulting mixture of products. Thus it appeared reasonable to attempt the polymerisation using larger monomers already containing sulphur-nitrogen bonds. The requirements for such monomers are satisfied by thiodithiazyl derivatives.

To add further interest to the subject, it was hoped that the thiodithiazyl compounds would complex with metal ions, and that from these it would be possible to form sulphur-nitrogen-metal polymers, which could be selected for maximum hydrolytic and thermal stability. The thinking[73], which led to the selection of thiodithiazyldiaryl compounds for special study can be summarised as follows:

Both sulphur and nitrogen can act as donor atoms. If a sulphur-nitrogen donor compound, which shows appreciable hydrolytic and thermal stability, can be synthesised, then it may be possible to choose the acceptor molecule so that this stability is retained in the product. The aryl derivatives $S_3N_2R_2$ fulfil these requirements to some extent. The attractive features of the known aryl derivatives are:

(1) heating to the m.p. causes little if any decomposition

(11) dilute hydrochloric and acetic acids have no effect

(111) the donor capacity of N^{111}, S^{11}, and S^{1V} is not likely to be impaired by steric crowding when R is Ph or C_6H_4R' (so long as R' is small or in the meta or para position.)

(1V) the probability of π-delocalisation in some of the possible complex compounds is likely to result in further stabilisation

(V) if initial experiments with Grignard reagents proved successful, then bifunctional Grignard reagents could lead to polymeric complexing agents

(VI) polymeric materials can alternatively be made from sulphur-nitrogen metal monomers by partial rupturing of the sulphur-nitrogen π-bonds. The partial rupturing of these bonds could be affected by heating, or by condensation with unsaturated organic compounds[78]. Evidence for the polymerisation of $S\overset{\mathrm{IV}}{\overset{\pi}{=\!=}}N-$ compounds is given in the polymerisation of thionylimine[9,74,75] thionylimines, RNSO[76] which is analogous to the RNSeO system[92] which polymerises very easily at room temperature, and also with compounds of the type $S(=NR)_2$ particularly when R = Bu^t [42,77]. This speculation is of course based on the assumption that $S_3N_2R_2$ has a structure similar to $S_3N_2F_2$ as proposed by Glemser,[1,18,45] that is R-S-N=S=N-S-R. The ease with which the π-bond will break is determined by the energetics of the system, which in turn is governed by the nature of the orbitals involved. Thus the π-bond strength diminishes as the principal quantum number increases and also with increasing d-character, unless the latter is associated with back donation. Further factors to be considered are[90]:

1. electron deficiency in both the bonding sulphur and nitrogen partners
2. the sum of the Pauling electronegativities must be 5
3. the difference between the Pauling electronegativities must be small.

> According to Goubeau[91] the sum of the electronegativities in a sulphur-nitrogen π-bond system is 5.5, and the electronegativities of $N\equiv N$, $HC\equiv N$, and $HB{=}NH$ are 6, 5.5 and 5 respectively. The nitrogen molecule is of course very stable and shows no tendency to polymerisation, whereas HCN can be either monomeric or polymeric, while HBNH exists solely in polymeric form. This would indicate that the sulphur-nitrogen π-bond system is on the borderline between compounds showing no tendency to polymerisation and those which polymerise readily. Consequently, it would seem justifiable to assume that given the correct physical conditions the sulphur-nitrogen π-bond would polymerise.

Since, of compounds of the type $S_3N_2X_2$, only the structure of $S_3N_2O_2$[54] is known, speculation as to the possible structures of thiodithiazyldiaryl metal complexes is of little value. It would seem doubtful that the thiodithiazyl group should contain S^{VI}, and is more likely to contain S^{II} and S^{IV}. Many complexes are known containing donor S^{II} (e.g. R_2S[79,80,97]), donor S^{IV} (e.g. ~~SO_3~~[illegible], the many SO_2 solvates[81]) or donor N^{III} (e.g. metal ammines[82-84], and amines[80]), while many complexes are known in which both S^{II} and N^{III} are present as donors, either when separated from one another (e.g. β-mercaptoethylamine[85,86]) or when bonded together (e.g. Thionitrosyl complexes[60,87,88]). As had already been implied the thiodithiazyl group could be a multidentate ligand, and therefore, it would seem advisable, initially, to select an acceptor molecule or ion which has an affinity preferable to either sulphur or nitrogen. In their review, Ahrland, Chatt and Davies[89], divide the acceptors into three classes:

(a) those acceptors which form the most stable complexes with the first row elements of Groups V, Vl and Vll, i.e. nitrogen, oxygen and fluorine,

(b) those which form most stable complexes with the second row or subsequent row elements of these groups, i.e. phosphorous, sulphur, chlorine etc.,

(c) a class not defined by the authors, but which can be obtained from the text: those elements which are on the border region of classes (a) and (b).

Class (a) is large and includes all the elements, excluding the rare gases, oxygen, fluorine and those mentioned in classes (b) and (c).

Class (b) includes Rh,Pd,Ag,Ir,Pt,Au and Hg.

Class (c) includes Mn,Fe,Co,Ni,Cu,Mo,Tc,Ru,Cd,W,Re,Os,Tl,Pb,Bi and Po.

The immediate objectives were to determine the method or methods of approach and to familiarize the operator with various techniques. Since many of the sulphur-nitrogen compounds are easily hydrolysed, techniques for working with vacuum lines; under nitrogen and inside glove boxes were essential. Furthermore, while the elemental analysis is the ultimate answer to synthesis, familiarity with Infra Red, Ultra Violet and Mass Spectrometry had to be obtained, in order to distinguish probable new compounds and also to keep a complete record of data of vibrational frequencies etc. to add to literature surveys.

The possible lines of approach are listed below:

a) $S_4N_4 + RMgBr \longrightarrow R{-}S{-}N{=}S{=}N{-}S{-}R$[13]

b) $RSO_2Cl + S_4N_4H_4 \longrightarrow R{-}S{-}N{=}S{=}N{-}S{-}R$[31]

c) $Cl{-}S{-}N{=}S{=}N{-}S{-}Cl + PhLi \longrightarrow Ph{-}S{-}N{=}S{=}N{-}S{-}Ph$?

d) $SOCl_2 + S_4N_4H_4 \longrightarrow OS(NS)_2$

e) (c.f. (d)) $MoO_2Cl_2 + S_4N_4H_4 \longrightarrow MoO_2(NS)_2 \longrightarrow$ polymer?
(for prep. MoO_2Cl_2 see[61-66].)

f) $S_4N_4 + NH_3 \longrightarrow HN{-}S{=}N{-}S{-}NH_2 \xrightarrow{10,11} RN{-}S{=}N{-}S{-}NR_2$?

Advantages and disadvantages exist for most of these lines of approach. All of the methods other than c) depend on there being a supply of S_4N_4, which while it can be made is not readily available in that the preparation takes several days[69,14]. Nonetheless, the properties and solubilities of S_4N_4 are known and methods a), b), d) and f) have been shown to work.

Method c) has one major advantage in that $S_3N_2Cl_2$ is readily available in the space of a few hours[25,22,29] and should $S_3N_2Cl_2$ prove a useful intermediate, the starting materials, i.e. sulphur, ammonium chloride and disulphur dichloride, are very cheap. This is a big advantage from an industrial point of view. However, other than the reactions

$$S_3N_2Cl_2 \xrightarrow{CCl_4\ 80^\circ C} S_4N_3Cl^{22,29}$$

$$S_3N_2Cl_2 \xrightarrow[\text{vacuum}]{80\text{-}95^\circ C} S_3N_2Cl^{25}$$

and its property of being easily hydrolysed, very little else is known for certain. Thus the structure is almost certainly similar to $S_3N_2F_2$, but this has not been absolutely proved[27]. Nonetheless, the products of reactions a) and b) are air stable, and should the products of reaction c) prove to be the same, this would be an obvious aid to determining the structure of $S_3N_2Cl_2$.

Futhermore, working with $S_3N_2Cl_2$ would enable the operator to become familiar with inert atmosphere techniques. Since little is known about this compound greater scope is probable in using $S_3N_2Cl_2$ and finally the bifunctional nature of $S_3N_2Cl_2$ may be useful for polymerisation, while its apparent reactivity could be of great value in dry solvents.

For the above reasons it was finally decided to approach the project via method c) i.e. using $S_3N_2Cl_2$, and in the event of no success to try method a), the reaction of S_4N_4 with Grignard reagents.

The discussion on the experimental work which follows is divided into two main sections:

(1) practical details on the preparation, properties and reactions of
    (a) thiodithiazyldichloride and
    (b) thiodithiazyldiphenyl
(2) spectroscopic studies of
    (a) thiodithiazyldichloride and any reaction products
    (b) thiodithiazyldiphenyl and any reaction products as indicated in the text.

EXPERIMENTAL WORK

Preparation of Thiodithiazyldichloride

Thiodithiazyldichloride - $S_3N_2Cl_2$ was prepared as described by Jolly et. al.[25] The main important differences were that the total reaction time reported is 16 hours, whereas the operator found that after 7-8 hours excess sulphur began to sublime, and that the overall yield reported (14gms.) could not be obtained (at best approx. 5gms.). Less drastic heating increased the reaction time but $S_3N_2Cl_2$ formed on the walls of the flask as well as on the condenser. A variety of physical changes were made in an attempt to improve the yield. Heating was tried using flat isomantles, oil baths and isomantles covering almost the whole of the flask. The oil baths prevented charring, while if the flask was totally enclosed sulphur sublimed very easily. By and large, what appeared to be the purest product was obtained using a flat isomantle or an oil bath, such that the oil was about 5-8mm. above the level of the contents of the flask. The best yield of good product appeared to form using a flask of 150-250 cc. capacity and a 15mm. diameter air condenser. The reactants could be heated less vigorously and still allow the S_2Cl_2 to reflux just above the neck of the flask.

The best results were obtained using the following system.

Dry Ammonium Chloride (50gms.) and disulphurdichloride (25ml.) and Sulphur (6.4gms.) were placed in a 250 cc. two necked round bottom flask. One neck contained a high vacuum tap; the other an air condenser made of two small air condensers each 30-35 cm. long and approximately 15 mm. diameter. At the top of the condensers was a vacuum tap and then

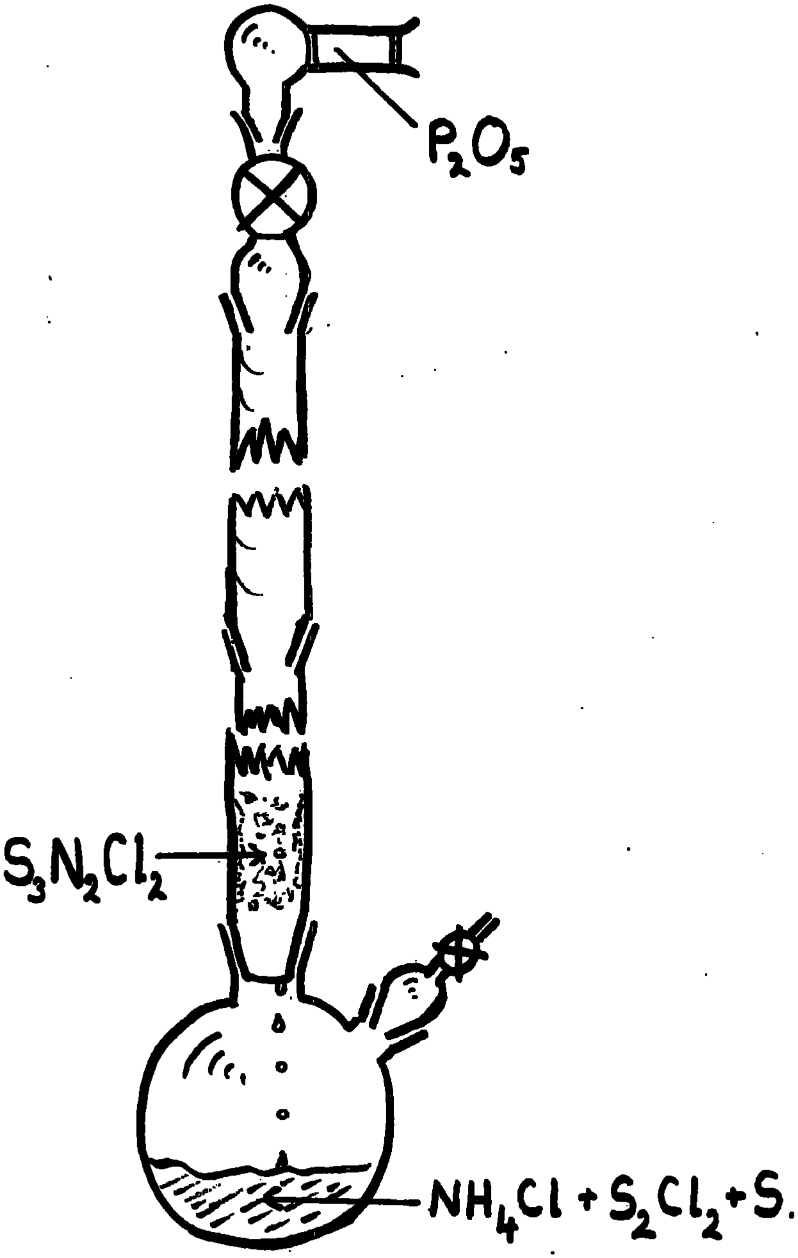


FIG.1.

APPARATUS FOR THE PREPARATION OF

$S_3N_2Cl_2$.

a P_2O_5 tube. See fig. 1.

Heat was gradually applied from a small flat isomantle until the S_2Cl_2 refluxed just above the neck of the flask, inside the condenser. The reaction was continued until sulphur began to sublime on the walls of the flask. Immediately the isomantle was removed and the flask was allowed to stand for at least an hour. The reaction vessel was replaced by a small two necked flask flushed with dry nitrogen, and the whole apparatus was connected to a vacuum line via the tap in the second neck of the flask. The system was evacuated for at least 30 minutes - although for analytical purposes longer evacuation would be necessary. (N.B. the vacuum tap fitted in the reaction flask was to enable a counter current of nitrogen to be passed down the condenser to eliminate any possibility of moisture entering the condenser during the transfer of the flasks. Initially this technique was used, but practice showed that it could be eliminated, provided the new flask was thoroughly flushed out.)

After evacuation the apparatus was let down to dry nitrogen, the condenser disconnected at its mid-point and the crystals of $S_3N_2Cl_2$ were scraped with a rod into the flask below, against a current of dry nitrogen. The product was an orange/brown mixture of needle and leaf type crystals. If slight hydrolysis occurred the crystals had a metallic lustre. Before evacuating the apparatus the crystals appeared orange/red in the lower parts of the condenser (presumably due to trapped S_2Cl_2) and orange to orange/brown in the higher regions. Grinding the crystals in an inert atmosphere gave a yellow powder. The crystals could be preserved for over a week in a dry inert atmosphere. A chlorine analysis of one sample gave Cl 39.5% (theoretically 36.41%).

The reaction between $S_3N_2Cl_2$ and water was vigorous and strongly exothermic. It formed a black/red mixture which probably contained S_4N_4. In damp air it formed a dark brown layer on the crystal surface which hindered further reaction and appeared to be a contributing factor to poor dissolution. Hence dry solvents must be used.

Ammonium Sulphate is a cheap and readily available biproduct of the chemical industry. For this reason and because of an interest in the role played by ammonium chloride in the preparation of $S_3N_2Cl_2$, an equivalent amount of dry ammonium sulphate was substituted for ammonium chloride. The overall yield was about the same, but for some reason the induction period was shorter. The exact differences in the induction periods were difficult to estimate since no two heating programmes could be said to be identical. A chlorine analysis on one sample gave Cl 36.7% calc. 36.41%. The infra red and mass spectroscopic data of $S_3N_2Cl_2$ are discussed in the spectroscopic section.

In his paper[25] Jolly appears to regard the $S_3N_2Cl_2$ as being 'pure'. The reasons for this are not given, although presumably elemental analysis backs this use of the word 'pure'. Nonetheless it was felt that recrystallisation from a suitable solvent would be ideal if one could be found.

To this end the following solvents were used, Carbon Tetrachloride;

Ether; Methylene Chloride; Tetrahydrofuran; Benzene, Monoglyme; Thionyl Chloride; Pyridine; Carbon Disulphide; Formic Acid and Dimethyl Sulphoxide. Any observations made are reported under each solvent.

Carbon Tetrachloride:- $S_3N_2Cl_2$ dissolved slightly and the solution turned green and finally yellow on warming[25]. - Jolly

Ether:- Partially dissolved but left a black deposit. On total evaporation, small orange deposit left. The black deposit was thought to be $S_3N_2Cl_2$ with a surface layer of hydrolysis product.

Methylene Chloride:- Dissolved partially. Gave an orange/red solution. Evaporation of solvent and cooling gave a deep yellow precipitate in small yield. Evaporation of all CH_2Cl_2 left a dark-brown solid which on standing turned orange/brown. On initial dissolution and filtration small green crystals were left on the side of the flask. This may have been S_3N_2Cl[25]. S_3N_2Cl

Tetrahydrofuran:- $S_3N_2Cl_2$ dissolved partially to give a deep red solution and left a black solid. Evaporation of the T.H.F. to half volume and cooling gave a fairly large precipitate, which unfortunately ppt. was very soluble and on warming to room temperature had dissolved again. Further evaporation and cooling formed a yellow solution which gave a mixed yellow and brown precipitate. On standing the filtered solution turned dark green, and when cooled a dark orange/brown precipitate formed. The Infra red spectrum of this product showed it to be a possible sulphur-nitrogen compound. All details of this spectrum are given in the spectroscopic section.

Benzene:- Partial dissolution occurred, but on warming to the boiling point of benzene some decomposition occurred. However, dry benzene has proved to be of some use up to about 60°C.

Monoglyme:- $S_3N_2Cl_2$ dissolved partially in fresh dry monoglyme to give a green/yellow solution. In order to filter the solution, the receiving vessel was immersed in liquid nitrogen. On liquifying the filtrate it was found to be a red/brown colour. Evaporation, cooling and filtration left a small quantity of dark-brown solid.

Thionyl Chloride:- Slight dissolution occurred to form an orange/red solution. Filtration and immediate evaporation left an orange solid which either liquified at room temperature or dissolved in absorbed thionyl chloride. If the solution were allowed to stand an orange precipitate formed. This proved to be S_4N_3Cl[93]. S_4N_3Cl

Pyridine:- $S_3N_2Cl_2$ appeared to react with pyridine and formed a dark brown solution. On evaporation and consequent cooling, needle crystals formed. However, these were very soluble and on reaching room temperature, had dissolved once more. Total evaporation left a dark brown solid the I.R. of which showed the possibility of the formation of a pyridine complex.

Carbon Disulphide:- Partial dissolution occurred. On filtration the solution was red. Total evaporation left a rust coloured solid. The I.R. of this solid indicated almost certainly that it was impure S_4N_4. S_4N_4

Formic Acid:- $S_3N_2Cl_2$ dissolved in dry formic acid (distilled over copper sulphate)[94] with evolution of a gas. The reaction proceeded at a steady rate, and S_4N_4 was identified as one product. S_4N ←

Dimethyl Sulphoxide:- When D.M.S. was added to $S_3N_2Cl_2$ a violent exothermic reaction occurred to form a red solution, which gradually turned yellow and formed a yellow colloidal substance. Vapours of methyl thiol were given off. The I.R. of both the impure liquid and colloid showed the presence of possible S-N and S=N bonds.

Since recrystallisation had proved of no help in purifying $S_3N_2Cl_2$, an attempt was made to sublime the compound. An initial attempt was made at approximately 10^{-2} mm. and at room temperature subliming onto a liquid nitrogen cold finger. The sublimate was of low yield and of a yellow colour. This was thought to be sulphur, but on exposure to air the sublimate became brown. A second attempt was made under similar conditions but at 50-60°C; an orange/yellow sublimate formed in low yield, insufficient for an I.R. nujol mull spectrum.

Under high vacuum and at room temperature over a period of 4 hours, a small yield of a white/yellow sublimate formed. Jolly[25] has reported that at 80-95°C under vacuum $S_3N_2Cl_2$ forms S_3N_2Cl which apparently is a green/black colour. However, when $S_3N_2Cl_2$ was heated at 80-95°C under high vacuum, subliming onto a liquid nitrogen cold finger, the initial deposit was a green/yellow colour but on increasing in volume this appeared as a dark orange/brown. An identical experiment, using a water cooled cold finger, left a green deposit and deeper red to brown sublimate. Spectral data on the sublimates are given in the spectroscopic section.

Reactions of Thiodithiazyldichloride

The chlorine atoms of $S_3N_2Cl_2$ appeared to be particularly labile and so an attempt was made to form compounds of the following types:

(i) $S_3N_2X_2$ where X is some group substituted for the chlorine atoms in a condensation reaction with subsequent elimination of a small molecule such as HCl, LiCl or MgBrCl.

(ii) complexes with probably an $S_3N_2^{2+}$ cation.

Experimental observations in the attempts to form compounds of these classes are given under the headings of the reagents used.

Class (i)

Diphenylamine:- (D.P.A.) $S_3N_2Cl_2$ was dissolved in benzene and the solution was filtered. To this solution was added a solution of D.P.A. in benzene. The orange solution turned initially purple and then dark brown. The solvent was evaporated, and a mixture of small green and black particles formed. The I.R. spectrum was somewhat obscure but indicated a monosubstituted aromatic compound with peaks which could be assigned to S-N and S=N vibrational frequencies.

Trichlorophenol:- (T.C.P.) A small quantity of T.C.P. was melted (67°C) and to this was added $S_3N_2Cl_2$. The colourless liquid turned deep red and then black. An acidic gas was given off.

The reaction was repeated with recrystallised T.C.P. dissolved in ether. The solution of T.C.P. and dissolved $S_3N_2Cl_2$ in ether was refluxed for four hours, until there was no further evolution of acidic vapours. The solution was partially evaporated, cooled in an acetone/Cardice bath and then filtered. Orange crystals formed mixed with a yellow deposit. I.R. spectra were done on crystals, yellow deposit, and pure T.C.P. The orange crystals proved to be impure T.C.P., but the yellow deposit had absorptions corresponding to T.C.P. plus others which were in suitable regions for S-N and S=N vibrational modes. However, these extra absorptions correspond exactly to those in S_4N_4. Hence it would appear that the yellow deposit may have been S_4N_4 contaminated with T.C.P.

<u>Phenyl Lithium</u>:- Phenyl Lithium was prepared as directed by Adams and Raynor[95]. An ether solution of $S_3N_2Cl_2$ under nitrogen was stirred gently while PhLi was added slowly. A vigorous reaction ensued, and only sufficient PhLi was added such that $S_3N_2Cl_2$ was in slight excess. The brown solution was filtered and the ether evaporated to leave an orange brown oil, with finely divided particles throughout. When no more ether could be removed, dry absolute Ethanol was added to the liquid. (This was an attempt to separate $S_3N_2Ph_2$[13]). An exothermic reaction ensued and the solution turned a purple colour, with a brown deposit, now as a solid. Filtration, evaporation and cooling of the solution gave an orange/brown solid, the I.R. spectrum of which indicated an O-H bond, but no other features of ethanol, and a monosubstituted aromatic system, plus several small peaks. A portion of the alcoholic solution was taken to which was added a few drops of water. A grey precipitate formed, the I.R. spectrum of which was singularly uninformative, but was very similar to that just mentioned only with a much weaker O-H bond. The remaining solution was yellow and had a dark oil dispersed throughout. On standing

the oil collected below the aqueous alcoholic layer, which was removed. The spectrum of the dry oil showed that O-H bonds were absent, and that the system contained phenyl groups and possibly sulphur-nitrogen bonds.

The alcoholic solution above was centrifuged and the alcoholic layer was removed, leaving (on further evaporation of residual alcohol) an orange viscous liquid. The I.R. of this liquid indicated that alcohol was present with some aromatic system, but it was doubtful if any sulphur-nitrogen bonds were in evidence. Since the orange liquid contained alcohol, it was subjected to a vacuum of 10^{-2}mm. and gently heated. This gave two products - a colourless oil and a white solid. The I.R. spectrum of the oil proved to be virtually identical to that of the oil from the aqueous extract, except that the slight indications of sulphur-nitrogen bonds were absent. On the other hand, the I.R. spectrum of the white solid indicated the presence of an O-H bond, an aromatic system and a definite possibility of sulphur-nitrogen bonds. This was later shown to be false by comparison with $Ph_2S_3N_2$ from S_4N_4. Evaporation of the remaining alcoholic solution gave a viscous suspension of an orange and dark purple solid. The contact liquid I.R. spectrum of this suspension was the same as the spectrum for the orange liquid mentioned above.

In an attempt to clarify the above jumble of facts a series of small experiments were carried out. The various operations and observations are given on the following page. It should be understood that PhLi is a solution of phenyl lithium in ether.

(Dry)EtOH + $S_3N_2Cl_2 \xrightarrow{\text{Room Temp.}}$ Yellow solution

EtOH + $S_3N_2Cl_2 \xrightarrow{\text{Warmed}}$ Orange solution (A)

Excess EtOH + PhLi $\xrightarrow[\text{Reaction}]{\text{Vicious}}$ LiOEt + C_6H_6 (B)

Solution (A) + Solution (B) $\longrightarrow$ purple solution

Solution (A) + (Dry) Benzene $\longrightarrow$ white precipitate (C)

+ orange/yellow solution (D)

Solution (B) + solid (C) $\longrightarrow$ no reaction and solution colourless

Excess PhLi + solid (C) $\longrightarrow$ no reaction

Solution (D) + PhLi $\longrightarrow$ purple solution

Solution (A) + Ether $\longrightarrow$ no change

Solution (A) + LiOEt $\longrightarrow$ purple solution (G) + white solid (E)

+ dark solid (F)

The I.R. spectrum of solid (C) indicated the possibility of sulphur-nitrogen bonds and sulphur-oxygen bonds. Solid (E) and solid (C) are different according to the I.R. spectrum of each substance, and both are different from LiOEt. In fact (C), (E) and (F) are all different and each one has characteristic absorptions which could be assigned to sulphur-nitrogen bonds.

A further attempt was made and it was noticed that with very little PhLi (i.e. a few drops) the solution was green, but on adding more PhLi it became the familiar brown colour. The ethereal solution was refluxed for several hours and PhLi was added until no further reaction took place. The solution was then evaporated to dryness and the solid mess remaining was placed in the thimble of a soxlet extractor. Ether was used as the solvent, and when no further extraction seemed likely the solution was allowed to cool, whereupon a light brown precipitate formed. An attempt was made to recrystallise this product from ether. The I.R. spectrum showed that the compound was almost certainly S_4N_4, although the mass spectrum of the compound did not have an identical pattern to that of S_4N_4. There are differences in the I.R. spectra, namely in the shape of the peaks in the $18\text{-}20\,\mu$ region, but originally this was put down to the specimen being impure S_4N_4. Hence there is a possibility that the light brown precipitate may be S_3N_2 formed as shown

$$2PhLi + S_3N_2Cl_2 \longrightarrow Ph\text{-}Ph + 2LiCl +$$

<u>Isopropanol</u>:- Isopropanol was added to $S_3N_2Cl_2$ and the solution was refluxed until the evolution of HCl ceased. On cooling a buff coloured solid was precipitated. Warming the solution and filtering gave two precipitates, one fine yellow needle-like crystals, the other the buff coloured solid already mentioned. The yellow crystals proved to be almost certainly S_4N_4 with isopropanol trapped inside the crystals; while an analysis on the recrystallised buff coloured solid gave C 7.82%, H 6.18% and Cl 45.8%. Furthermore, a qualitative analysis showed nitrogen to be absent and sulphur to be present in the compound. A mass spectrum of the compound confirmed this fact.

In a second attempt at this reaction the $S_3N_2Cl_2$ isopropanol mixture was constantly stirred for an hour under nitrogen, while the reaction vessel was immersed in an ice bath. The $S_3N_2Cl_2$ did not dissolve immediately, although a precipitate of apparently different composition formed continuously. The solution was an opaque orange colour. At the end of one hour the ice bath was removed and the solution was stirred for several hours until no further evolution of HCl was evident. By this time a dark brown deposit had formed and the solution was a transparent pale orange colour. The solid was tested for stability to air, but the I.R. spectrum indicated an ammonium salt. It was found that the brown solid eventually (2-3 days) turned orange. Evaporation of the solution precipitated a yellow solid which gave an I.R. spectrum indicating the possibility of sulphur-nitrogen bonds. However, the yellow solid was air sensitive and turned orange on standing, to give the same 'ammonium' spectrum mentioned above.

Benzyl Alcohol:- $S_3N_2Cl_2$ under N_2 was stirred in benzyl alcohol. Hydrogen chloride was liberated, and the solution was red in colour. No heat was applied although the reaction was reasonably spontaneous and exothermic. On cooling an orange/yellow deposit formed and was filtered off. There were also some crystals but these were too small to separate. The I.R. spectrum of the yellow deposit showed no peaks due to an aromatic system and at no place did it bear any resemblance to benzyl alcohol. However, it did contain peaks characteristic of S_4N_4 plus some broad peaks at 7.15μ, 8.55μ, 10.50μ and 16.40μ. Shaking the yellow solid with benzene gave a white plastic pliable material and an orange solution. The spectrum of this material showed that the S_4N_4 peaks had now disappeared and the only ones remaining were those indicated above.

Hydrogen Sulphide:- $S_3N_2Cl_2$ was added to ether saturated with dry H_2S. Initially the solution was yellow but after refluxing and further bubbling of H_2S through the solution it gradually changed to orange. HCl was given off during the reaction. A small quantity of dark solid remained in the flask at the end of the reaction, and this proved to be S_3N_2Cl. The solid was filtered off and the solution was then partially evaporated until an orange precipitate began to form. The I.R. spectrum of this precipitate was very obscure, but it definitely was not S_4N_4. Small peaks at 7.92 μ, 8.65 μ, 9.22 μ, 9.82 μ, 10.28 μ, 11.20 μ, 12.50 μ and 13.88 μ were present in the spectrum. Whether these frequencies have any significance remains in doubt.

Chloroform:- Finely ground $S_3N_2Cl_2$ was refluxed for several hours with dry chloroform until the evolution of acidic gases had ceased. The solution was deep orange. Evaporation to dryness left a semi solid, the contact liquid I.R. spectrum of which showed the presence of possible sulphur-nitrogen bonds. Addition of pure dry chloroform to the semi solid, and cooling gave orange crystals of m.p. 187°d. The I.R. spectrum of these crystals showed them to be S_4N_4. Benzene was then added to the solid left after total evaporation of the chloroform. The solution became S_4N_4 orange but left a white solid. I.R. spectroscopy of this solid showed that there was still some S_4N_4 present, and that the remaining vibrational frequencies were between 5-10 μ.

S_4N_4 was obtained as a relatively pure product from the chloroform reaction, and it was this that prompted the examination of spectra of earlier products, for peaks characteristic of S_4N_4. As has been seen evidence for this fact in several reactions. S_4N_4 may have been a hydrolysis product, but on the other hand, the conditions of the reaction may have been too drastic and could have broken up the intermediate molecule to form S_4N_4. The fact that lower temperatures of reaction produced healthier coloured solutions, rather than the usual dark brown solution, supported this reasoning. The slow evolution of HCl in the reactions would suggest that $S_3N_2Cl_2$ was not as reactive as one might expect. This immediately raised queries with regard to the structure of $S_3N_2Cl_2$. In a further experiment $S_3N_2Cl_2$ was ground to a fine powder in chloroform under nitrogen. The solution turned yellow and on refluxing gradually became deep brown. HCl gas was evolved and an orange/brown solid formed. This proved to be largely S_4N_3Cl. When $S_3N_2Cl_2$ was ground in chloroform under nitrogen and allowed to stand for 2-3 days, at room temperature, the colour of the solution turned gradually from pale yellow to orange/red. The solid remaining and the residue from the solution were shown to be identical. Infra red spectra showed that the principal product was S_3N_2Cl, but that some $S_3N_2Cl_2$ and S_4N_3Cl were also present.

Dimethylformamide:- (D.M.F.) $S_3N_2Cl_2$ was ground, under nitrogen, in D.M.F. and the solution was allowed to stand for several days. The solution was filtered, partially evaporated (without heating) and then cooled. Irregular crystals formed, and these proved to be a mixture of S_4N_3Cl and S_3N_2Cl.

Phenyl Magnesium Bromide:- prepared as in Mann & Saunders[96].

The reaction of PhMgBr with $S_3N_2Cl_2$ was done in conjunction with the reaction of S_4N_4 and Grignard reagents. No attempt was made to isolate any products, only observations were made with regard to colour changes.

On adding PhMgBr in ether to a benzene solution of $S_3N_2Cl_2$ the solution turned dark red (c.f. S_4N_4 reaction). If excess of PhMgBr were added, the red colour disappeared to leave a pale yellow/khaki solution. When this solution was poured into an ice/dilute acetic acid mixture[13], the benzene layer turned dark brown. As will be seen later these observations are on a parallel with those in the analogous S_4N_4 reaction. There are obviously two separate reactions taking place. These are:

1. the formation of some 'complex' which has a deep red colour in benzene
2. a reaction between this 'complex' and further PhMgBr forming some product which is pale yellow to colourless in benzene.

Class (ii)

Stannic Chloride:- The reactants were dissolved in toluene, and the two solutions mixed. A black solution formed and it was refluxed for some four hours. Partial evaporation and cooling gave a black precipitate. The I.R. spectrum of this solid showed no toluene, no S_4N_4, but peaks which could be assigned to S=N, S-N and S-S vibrational frequencies. These showed a marked similarity to frequencies found in S_4N_3Cl, although there was not an exact correspondence.

On further evaporation to dryness, a black oil remained. A contact liquid spectrum of this oil showed toluene peaks but the aromatic ring modes of vibration (13 μ-15 μ) were not those of a monosubstituted aromatic system.

Preparation of Thiodithiazyldiphenyl

The procedure adopted for this preparation was that given by Weiss[13], and the authors of reference 32. Since these reports were very brief, certain facts had to be ascertained. These were:

1. the manner in which the reagents should be mixed
2. the optimum temperature of the reaction
3. the ratio of the Grignard reagent to S_4N_4
4. the length of time which should be allowed before adding the acid solution to the benzene.

Several attempts were made to prepare $S_3N_2Ph_2$, and in order to clarify the spectroscopic data recorded in the later section, the experiments are numbered in the order in which they were carried out. Initially a few small scale reactions were done as observational exercises, rather than preparative ones.

Phenyl Magnesium Bromide was prepared as directed by Mann and Saunders[96].

Experiment 1.

PhMgBr in ether was added to a solution of S_4N_4 in benzene. The solution turned deep red, but with excess PhMgBr, a khaki colour developed (c.f. PhMgBr/$S_3N_2Cl_2$). When the process was repeated using PhMgBr:S_4N_4 = 2:1, an orange precipitate came out of the red solution. This solid proved to be air sensitive turning dark brown on exposure to air. The red solution was shaken with dilute hydrochloric acid[32], and the dark red benzene layer was then removed, dried, and evaporated to dryness. The I.R.

spectrum of this residue indicated that it was diphenyl disulphide.

Experiment 2.

S_4N_4 (0.3gm.) was dissolved in a litre of hot benzene. This solution was added to an equivalent amount of PhMgBr in ether to form $Ph_2S_3N_2$. The solution turned red/orange and a fine deposit formed as above. Immediately ice/dilute acetic acid mixture was added and shaken with the bulk solution. The benzene layer was removed and dried over anhydrous sodium sulphate. Having filtered off the drying agent the benzene was evaporated at the water pump to approximately 10-20mls. Crystals formed on standing, were filtered and had a melting point of 179°C. As was suspected, the I.R. spectrum showed the crystals to be S_4N_4.

Experiment 3.

In a repeat of the above experiment 1gm. of recrystallised S_4N_4 was dissolved in 150mls. of benzene at approximately 60°C. The equivalent amount of PhMgBr in ether was added to the solution and the mixture was allowed to stand for 30 minutes. An orange precipitate formed immediately. After 30 minutes the solution was poured onto an ice/dilute acetic acid slurry and the benzene layer turned black instantly. The aqueous layer was removed and the benzene then dried over sodium sulphate and evaporated to about quarter volume at the water pump. From this solution golden needle crystals formed. A second fraction was obtained on evaporating the solution still further. The overall impure yield was 0.7gms. but the I.R. spectrum of both samples showed the crystals to be unreacted S_4N_4.

The black solution was evaporated to dryness, and dry absolute alcohol was added to the residue. Not all the residue dissolved, but on warming the alcoholic solution, filtering and evaporating, some golden brown crystals formed. The crude yield was 0.3gm. and the substance had a melting point of 87°C-91°C. Recrystallisation from absolute alcohol gave a m.p. of 97°C. I.R. spectroscopy showed that this product could well be that reported by Weiss[13] and the authors of 32.

The fact that only a small yield had been obtained suggested that

a) the reaction time may have been too short

and/or

b) the temperature of reaction may have been too high.

Experiment 4.

S_4N_4 (0.8gm.) in 160mls. dry benzene at room temperature, was reacted with an equivalent amount of Grignard reagent in ether. On syringing the Grignard into the S_4N_4 solution the latter turned deep red, but by the time all the Grignard had been added the solution was orange with the precipitate formed as before. The mixture was allowed to stand some twenty hours, and was then poured onto the ice/acetic acid slurry. The benzene layer was now a deep ruby red and was treated in an analogous manner to that in earlier experiments. Partial evaporation and cooling gave no S_4N_4 deposit, so eventually the solution was evaporated to dryness and absolute alcohol was added to the residue. Warming and then cooling the alcoholic solution gave a rust coloured precipitate in 0.5gm. yield and m.p. 47-50°C. Recrystallisation from alcohol gave a melting point of 86-87°C with decomposition and charring. The alcohol was totally evaporated to leave a deep red semi solid, which contained mainly diphenyl disulphide. Analysis figures for the crystalline product m.p. 86-87°C were C=59.7% and H=4.42%. (Theor. C=51.8%, H=3.60%). Further recrystallisation gave a product m.p. 99°C, the analysis figures of which were C=50.4% and H=3.47%. The I.R. spectrum of the rust coloured precipitate showed that it contained no S_4N_4 and that it possessed many of the characteristics of the spectrum of the golden brown specimen obtained in the previous experiment. The few differences in the spectra indicated that (a) neither sample contained the other as impurity or (b) neither were pure samples and thus not all of the absorption frequencies were characteristic of the major components.

Experiment 5.

S_4N_4 (0.5gm.) was dissolved in 80ml. of dry benzene and an equivalent amount of PhMgBr was syringed into this solution against a current of dry nitrogen. A precipitate formed immediately. The solution was allowed to stand for 30 minutes and then poured into dilute cold acetic acid. Removal of the black benzene layer, drying the benzene and gradually evaporating the solution, showed no sign of any precipitation of S_4N_4. When only a semi solid residue remained, dry absolute alcohol was added, warmed and then cooled. Golden brown crystals formed m.p. 89-91°C, and were recrystallised from alcohol to give a product m.p. 102°C ± 0.5°C. There was also a product in the first precipitation which was insoluble in alcohol.

Weiss et. al.[13] reported that the $Ph_2S_3N_2$ was golden brown and had a melting point of 105°C. Nonetheless the specimen was taken for a carbon hydrogen analysis which gave C=51.9%, H=3.99%, whereas the calculated values for $(C_6H_5)_2S_3N_2$ are C=51.8% and H=3.60%.

<u>Experiment 6.</u>

S_4N_4 (4.2gms.) in dry benzene and excess PhMgBr, (greater than ratio PhMgBr:S_4N_4 = 2:1) was added to the solution. Precipitate formed in the normal manner, but on addition of excess Grignard reagent, the precipitate dissolved back into the solution. The latter was then poured into a 5% acetic acid/Ice mixture, shaken until the ice had melted, and then allowed to stand. The dark red benzene layer was separated from the aqueous layer, dried with Na_2SO_4, and then evaporated to dryness. Alcohol was added to the remaining brown semi solid, and caused a dark brown solid to be precipitated. This was filtered and divided into two fractions (a) and (b).

(a) was dissolved in petrol ether, forming a brown solution. Cooling caused the precipitation of an orange product, the I.R. spectrum of which showed it to be $S_3N_2Ph_2$ with some diphenyl disulphide.

(b) was sublimed onto a liquid nitrogen cold finger, to form an orange/yellow sublimate. This was shown to be diphenyl disulphide.

Evidence from all these experiments suggested that the main impurities were diphenyl disulphide and S_4N_4. It therefore seemed desirable to remove both of these constituents before attempting to recrystallise the $S_3N_2Ph_2$. The techniques employed to affect this separation were (1) chromatographic and (2) fractional sublimation.

(1) Studies on the chromatographic purification of $S_3N_2Ph_2$ were done initially by dissolving the brown residue, from the alcoholic solution, in benzene, and then eluting this solution down an alumina acid Woelm Grade I column. The initial brown layer separated almost immediately into several separate bands. After a period of half an hour the colour of each band, descending the column was, light brown, black, green, rust, purple and pale yellow. Unfortunately the retention time for this system was too long to be of practical use, and it was felt that the presence of the various coloured bands was due to decomposition on the column. Consequently the next column tried was one of neutral alumina, Woelm Grade IV. The eluent in this case was petrol ether, and separation occurred into five bands, the colours of which in descending order were, rust, light brown, yellow/green, orange and pink. Twenty two separate fractions were taken and the U.V. absorption spectra for each fraction recorded. Those fractions which showed different absorption spectra were evaporated to dryness and the I.R. spectra of the residues recorded. No evidence of $S_3N_2Ph_2$ was found, and thus it was concluded that $S_3N_2Ph_2$ must dissociate into smaller fragments while passing down the column. In a further experiment the brown residue from the alcoholic solution was dissolved in benzene and eluted with the same solvent down a neutral alumina, Woelm Grade III column. In this case two main bands were obtained; the first a

dark brown colour which remained stationary (probably containing polymeric materials), and the second an orange band which was shown from the I.R. spectrum, on eluting and evaporating, to be largely diphenyl disulphide.

(2) A small sample of the residue from the alcoholic solution was sublimed at 80°C onto a water cooled cold finger. The I.R. spectrum of the sublimate and of the residue showed that both of the samples were diphenyl disulphide.

Experiment 7.

Providing that the ratio of S_4N_4:PhMgBr was less than or equal to 1:2, an orange/brown precipitate formed on adding the Grignard reagent to the benzene solution of S_4N_4. In an attempt to find the importance of the role played by this precipitate, it was decided to separate the solid from the mother liquor, and then to add the acid solution to the benzene and the precipitate separately, extracting any soluble products from the decomposed solid in fresh benzene.

The above procedure was carried out in a three armed schlenk (fig. 2) under an atmosphere of nitrogen. The Grignard reagent was syringed into the S_4N_4 benzene solution contained in (A) and the fine precipitate which formed was filtered on the sinter into (B), and finally filtered again into (C). The benzene solution was then poured into a 5% acid solution, shaken, separated, dried over magnesium sulphate and evaporated to leave an orange solid. This proved to be S_4N_4.

The solid in arms (A) and (B) of the schlenk was shaken with benzene and then washed into a 5% acid solution. The thin deposit left on the side

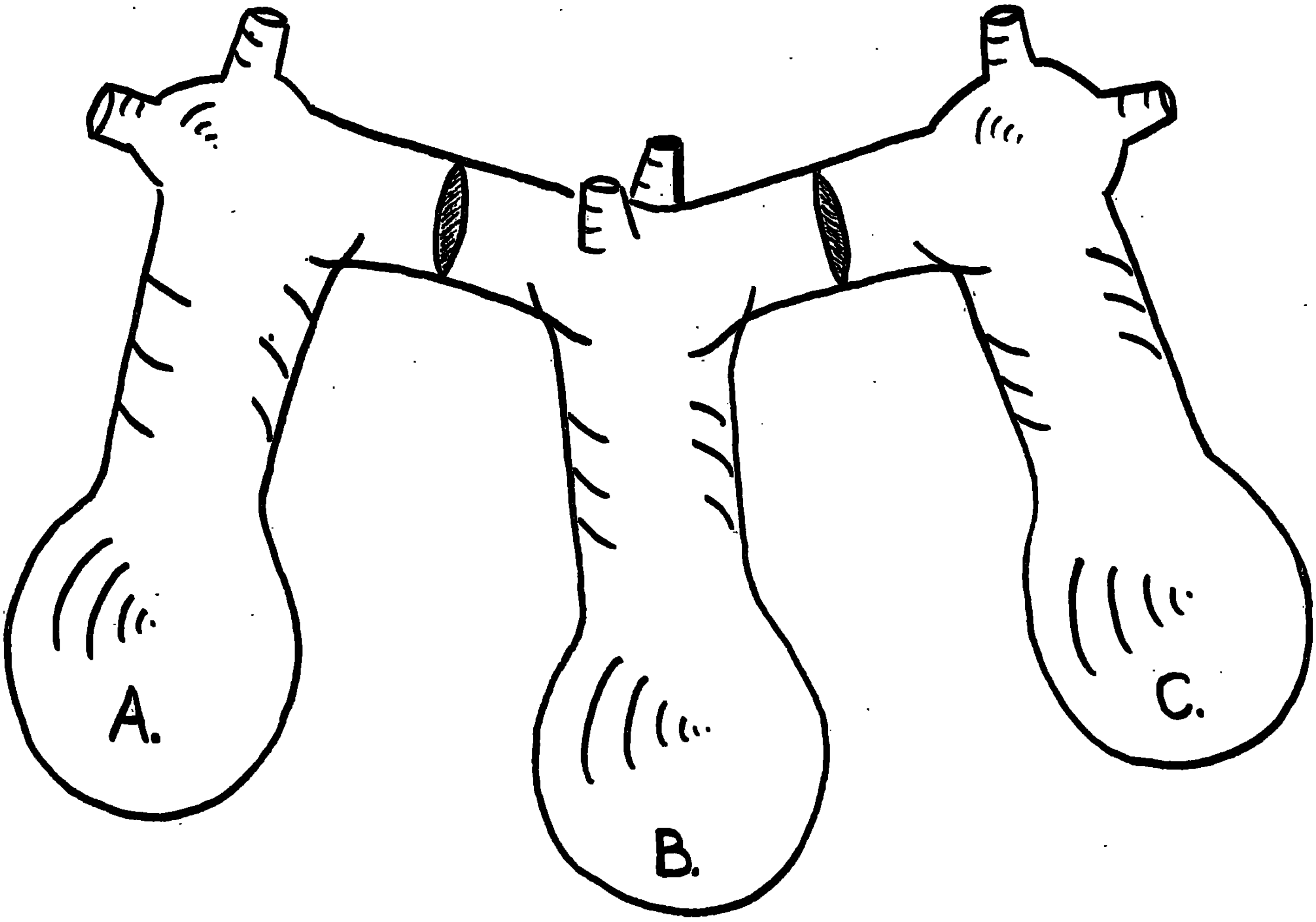


FIG.2.

A THREE ARMED SCHLENK.

of the flask turned green/yellow. Treatment of the benzene layer in the usual manner, adding alcohol to the residue left on evaporation of the benzene, and cooling the resulting solution, gave some dark brown crystals. By the I.R. spectrum these were shown to be a mixture of S_4N_4 and $S_3N_2Ph_2$. Sublimation of this sample at 100°C onto a water cooled cold finger, gave a brown sublimate which had a similar I.R. spectrum to the original crystals. There were, however, some differences in the relative intensities of the absorption peaks. Furthermore, it was noted that on exposure to air the sublimate turned orange/yellow, and the I.R. spectrum of this sample, though similar to the original sublimate, showed differences once more in the relative intensities of the absorption bands. Sublimation of a further sample at 84°C ± 0.5°C gave a yellow sublimate of principally S_4N_4 with a little $S_3N_2Ph_2$. The I.R. spectrum of the residue showed no sign of S_4N_4, and had all the characteristics of $S_3N_2Ph_2$. The sample had a melting point of 101°C ± 1°C.

Experiment 8.

S_4N_4 (10gm.) was dissolved in a litre of benzene. 64.3mls. of 1.68M Grignard reagent (standardised with 0.1M HCl, using bromocresol green as an indicator) were syringed into the benzene solution. The solution was allowed to stand for an hour before an ice cold solution of 5% acetic acid was added. The benzene layer turned black, and was separated from the aqueous layer, dried and then evaporated to a black oil. Petrol ether (40°-60°) was then added to the oil, warmed, filtered and cooled. The remaining insoluble solid was shown to contain some S_4N_4. The petrol ether solution was cooled to give crystals which were shown to be $S_3N_2Ph_2$ with some S_4N_4. Evaporation and cooling of the same solution gave two products: one, crystalline and almost colourless, the other dark brown. The I.R. spectrum of the colourless leaflet crystals showed similarities to Ph_2S_2 and $S_3N_2Ph_2$, but did not contain S_4N_4. Since the crystals were colourless, it was thought that they may have been $Ph_4S_4N_4$ and/or $Ph_3S_5N_3$[101]. The dark deposit was shown to contain characteristics of the colourless crystals and $S_3N_2Ph_2$. Evaporation of the petrol ether to dryness left a black semi solid, the contact spectrum of which indicated that it contained the same constituents as the dark brown deposit. Since $Ph_4S_4N_4$ and $Ph_3S_5N_3$ had been separated by chromatographic techniques[101], an attempt was made to repeat this procedure by dissolving the black semi solid in petrol ether and eluting the solution down a neutral alumina, Woelm Grade III-IV column. The spectrum of the bonds in descending order was; green/yellow, colourless, mauve, colourless, orange, colourless and mauve. Extraction of the coloured fractions gave three solutions coloured orange, mauve and green/yellow. On standing the mauve solution became colourless. I.R. spectra on the residues from these solutions showed that the deposit from the orange and yellow solutions were identical, while that from the colourless solution was Ph_2S_2.

Experiment 9.

Experiment 8 was repeated, the only variation being that absolute alcohol was used as the recrystallising solvent. Recrystallisation in alcohol for four times gave a 2.8gm. yield of golden brown leaves m.p. 95°C (analysis figures C=20.4%, H=1.57%). This product was dissolved in hot alcohol, filtered and recrystallised twice more, to give a golden brown product m.p. 101°C (analysis figures C=44.9%, H=3.16%). A further recrystallisation from hot alcohol gave a similar product m.p. 101°C (analysis figures C=45.8%, H=3.35%). On each occasion the deposit left on filtration of the hot alcohol was S_4N_4, and therefore it was thought probable that on heating in alcohol $Ph_2S_3N_2$ may have decomposed to give some S_4N_4. Consequently some of the latest recrystallisation product was dissolved in alcohol at room temperature, filtered and then cooled in an acetone/ice bath. Golden leaflet crystals formed m.p. 97°-98°C (analysis figures C=51.9%, H=3.59%). A further sample of the same recrystallisation product was dissolved in alcohol at room temperature, filtered and then allowed to stand in the refrigerator for several days. Brown/rust needle crystals formed.

Experiment 10.

In further preparations of $S_3N_2Ph_2$ either or both of the following techniques were used. Each preparation was done starting with 10gm. of S_4N_4, and the initial impure product was obtained in an average yield of 5gm. From this about 3gm. of pure product was obtained.

The procedure adopted was to dissolve S_4N_4 (10gm.) in sodium dried benzene (approx. 650ml.) to form an almost saturated solution at room temperature. Preparation of the Grignard reagent was done in the usual manner[96], and the standardisation carried out as indicated in Experiment 8. Both reagents were kept under an atmosphere of dry nitrogen, and a counter current of the latter was employed during the transfer of the Grignard reagent to the S_4N_4 solution. The quantities used were such that the ratio PhMgBr:S_4N_4 = 2:1. On addition of the Grignard reagent, and subsequent formation of the brown solid, a period of at least an hour was allowed to lapse, before adding the 5% ice cold acetic acid solution (about 250ml.). The mixture was thoroughly shaken and then allowed to stand so that the separation of the aqueous and benzene layers could occur. Removal of the benzene layer, and the evaporation of the benzene (usually done on a rotary evaporator) left a black oil. Addition of absolute alcohol to this oil often caused the immediate precipitation of a golden brown leaflet crystalline solid. In the event of this not occurring, cooling of the alcoholic solution was sufficient to cause the precipitation. The solid was filtered, dissolved in fresh alcohol at room temperature, and then either:

a) chilled in an acetone slush bath, or

b) allowed to stand in the refrigerator at about -10°C for a few days.

Using method (a) the gold product formed rapidly, and if on the initial precipitation of the product, the solution was filtered, any remaining S_4N_4 could be removed, and the pure product obtained by chilling the solution again.

If method (b) had been employed, a rust/brown product in the form of crystalline needles was obtained. Analysis of one such product gave S=34.02%, N=10.59%, C=52.3%, H=3.59% and a m.p. of 103.5°C.

Theoretical S=34.55%, N=10.06%, C=51.76%, H.3.62%.

C : 51.469
H : 3.620
S : 34.549
N : 10.062

Reactions of Thiodithiazyldiphenyl

Sulphur and nitrogen donor complexes are well known[79-89]. It has been pointed out in the introduction, that Ahrland, Chatt and Davies[89], divide the acceptor elements into three categories. Elements within class (a) should have a preference for nitrogen donors; those in class (b) a preference for sulphur donors; while class (c) elements should form complexes through either or both of these donor atoms. Several attempts were made to form complexes, and the experimental details are given under each reagent, within the class as defined by Ahrland, Chatt and Davies.

Class (a)

Titanium Tetrachloride:- Initial tests with this reagent showed a rather strange phenomenon. At the time the experiment was carried out, a solution of $S_3N_2Ph_2$ in benzene was available. To this was added a saturated solution of $TiCl_4$ in carbon tetrachloride, and immediately a blood red solution formed. However, when the solvent was benzene or cyclohexane for both reagents, no colour change was observed. Furthermore, if $S_3N_2Ph_2$ was dissolved in cyclohexane and to this was added some of the carbon tetrachloride solution of $TiCl_4$, no colour change was observed again. In the event of carbon tetrachloride being used as the common solvent the blood red solution formed. It was decided to try to study this reaction by recording the visible absorption spectrum of several solutions of $S_3N_2Ph_2$ and $TiCl_4$, each solution having a different ratio of one reagent to the other[102]. In this way it was hoped to determine the ratio of $S_3N_2Ph_2$ to $TiCl_4$ in the complex. The solvent used was carbon tetrachloride (dried over P_2O_5), in which even dilute solutions of $S_3N_2Ph_2$ gave fairly intense colours. Consequently the concentrations of reagents used were in the region 2 x 10^{-2} molar. On mixing the two solutions no colour change occurred. The I.R. spectrum of the sample of $S_3N_2Ph_2$ being used showed the presence of a small amount of Ph_2S_2. Thus, when using larger concentrations of reagent, the blood red colour may have been due to a complex with the Ph_2S_2 impurity. Tests with pure Ph_2S_2 showed that a red colour was formed, but that the intensity of the colour was by no means the same as the blood red colour observed previously, irrespective of the ratio of Ph_2S_2 to $TiCl_4$. Assuming that some hydrolysis of the $TiCl_4$ occurred, there was a chance that $S_3N_2Ph_2$ could have been protonated. Bubbling HCl gas into a carbon tetrachloride solution of $S_3N_2Ph_2$ showed that the red/orange colour was bleached.

As has already been seen, three different coloured forms of $S_3N_2Ph_2$ have been shown to exist; namely gold leaflets, orange leaflets and rust brown needles. It will be noted later in the reaction of $S_3N_2Ph_2$ (gold) with $Fe(CO)_5$, that the orange form was obtained once more. This sample and a gold sample of $S_3N_2Ph_2$ m.p. 103°C were used as 2 x 10^{-2} molar solutions in benzene and carbon tetrachloride to react with a 2 x 10^{-2} molar solution of $TiCl_4$ in carbon tetrachloride. Details of these experiments are summarised in Table 5. The yellow precipitate mentioned formed immediately with the $S_3N_2Ph_2$ m.p. 103°C, whereas its formation was much slower with the sample m.p. 95°C.

Table 5

Solvent	Colour of solution $S_3N_2Ph_2$ m.p. 95°C	Colour of solution $S_3N_2Ph_2$ m.p. 103°C	Addition of $TiCl_4$ in CCl_4 Observation for sample	
			m.p. 95°C	m.p. 103°C
Benzene	orange/red	pale orange	clear green	pale yellow
CCl_4	orange/red	orange	green/yellow solution + yellow solid	green/yellow solution + yellow solid

Details of the Reaction $S_3N_2Ph_2$ + $TiCl_4$ in Benzene and Carbon tetrachloride

Class (b)

Palladium Dibromide:- $PdBr_2$ was found to be virtually insoluble in all common solvents. However, it did dissolve a little in alcohol. To this solution was added another of $S_3N_2Ph_2$ in alcohol, and the mixture was kept heated to about 60°C. On cooling, an orange/yellow precipitate formed, m.p. 175°C. The I.R. spectrum of this product showed some similarity to S_4N_4, although the 18.08 μ and 18.92 μ peaks were absent.

Sodium Chloropalladite:- Na_2PdCl_4 was dissolved in alcohol, and to this was added an alcoholic solution of $S_3N_2Ph_2$. The mixture was allowed to stand at room temperature. A fine white precipitate, which was assumed to be sodium chloride, formed gradually over a period of 3-4 hours. The white precipitate was filtered, and the solution was then evaporated. The product was extremely soluble in alcohol, but its solubility was depressed by adding chloroform. From the alcohol/chloroform solution a brown solid was obtained, but the I.R. spectrum of this sample showed that phenyl groups were absent.

Class (c)

Iron Pentacarbonyl:- $S_3N_2Ph_2$ and $Fe(CO)_5$, in the ratio 1:1, were dissolved in chloroform and allowed to stand at room temperature for 4-5 hours. No apparent reaction occurred. Hence, the reaction was repeated but the solution was refluxed for several hours. Cooling the solution gave a black precipitate which was filtered, and on subsequent evaporation and cooling of the solvent, orange leaflet crystals, m.p. 103°C of $S_3N_2Ph_2$ were obtained. The black solid was thought to be iron sulphide, (addition of HCl gave H_2S and thiocyanate gave a positive test for iron), but on exposure to air over several days it gradually turned yellow. It was thought that this may have been an iron thionitrosyl[36].

A repeat of this experiment, but in an atmosphere of dry nitrogen, gave the same black iron compound. When the solution was evaporated and cooled, a precipitate formed but this was shown to be diphenyl disulphide.

Cobalt Chloride:- $CoCl_2$ was refluxed with freshly distilled thionyl-chloride to remove the water of crystallisation. An alcoholic solution of $CoCl_2$ was then added to a similar solution of $Ph_2S_3N_2$ in a ratio of $CoCl_2:Ph_2S_3N_2 = 1:1$. Initially the solution was green/yellow but on refluxing for about four hours, it gradually turned dark green. Cooling and filtration of the solution gave a turquoise solid. The I.R. spectrum of this solid was very obscure and gave no indication of any S-N or phenyl absorption frequencies. Evaporation of the solution to dryness showed the presence of diphenyl disulphide.

Nickel Chloride:- $NiCl_2$ was dried in the same manner as the cobalt chloride. The alcoholic solution of $NiCl_2$ and $S_3N_2Ph_2$ was refluxed, but there was no noticeable colour change of the red/brown solution. Evaporation and cooling gave an orange/brown material which was shown to be impure diphenyl disulphide.

The reactions to form metal complexes with $S_3N_2Ph_2$ were not encouraging, although the results only demonstrated the reluctance of $S_3N_2Ph_2$ to complex under the stipulated conditions, rather than the total inability of $S_3N_2Ph_2$ to form metal complexes.

As will be shown in the Discussion section it was possible that $S_3N_2Ph_2$ formed a complex or complexes with S_4N_4 with the sulphur atoms of $S_3N_2Ph_2$ acting as acceptors. Furthermore, it was known that $S_3N_3O_3Cl_3$ forms complexes with pyridine and isoquinoline[103]. Although the sulphur in $S_3N_3O_3Cl_3$ is in the S^{VI} state as opposed to the S^{IV} and S^{II} states in $S_3N_2Ph_2$, it was thought that $S_3N_2Ph_2$ may undergo complex formation with similar donor molecules. Consequently, the reaction of $S_3N_2Ph_2$ with pyridine was attempted.

<u>Pyridine</u>:- Refluxing $S_3N_2Ph_2$ and dry pyridine in a ratio of 1:3 in benzene, gave an orange solid which was shown to be S_4N_4.

Tetrasulphur Tetranitride (S_4N_4)

S_4N_4 used in the preparation of $S_3N_2Ph_2$ was prepared as directed by Jolly[67]. However, the method is long and tedious unless a supply of dry, pure solvents is readily available. Large quantities (10gm. per experiment) of S_4N_4 were used in later preparations of $S_3N_2Ph_2$ and consequently attempts were made to prepare S_4N_4 on a 30-40gm. scale, i.e. approximately double scale to that described by Jolly[67].

It was shown to be uneconomical to prepare S_4N_4 on this scale, particularly with respect to the ammonia. Thus, the bubbling time for the passage of ammonia was approximately trebled rather than doubled, when S_4N_4 was prepared on twice the scale described by Jolly.

Dioxane dissolves S_4N_4 more readily than benzene. However, the purification of the former can take several days. It was found that pure S_4N_4 could be extracted in benzene using a Soxhlet extraction apparatus for about 10 hours (usually overnight), and that pure S_4N_4 crystallised when the benzene was cooled. S_4N_4 was prepared as described below.

S_2Cl_2 (25ml.) was added to carbon tetrachloride (700ml.), which had been dried over P_2O_5. The solution was contained in a litre three-necked round bottom flask, which was immersed in an ice bath. One neck of the flask was open. The centre neck was also open but through it passed the shaft of an efficient stirrer with a Teflon blade. The third neck held an inlet tube which was connected to a chlorine or ammonia cylinder.

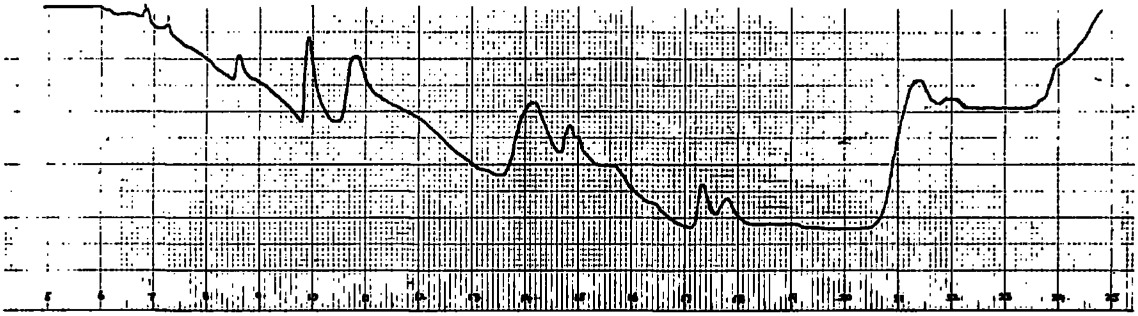
The solution was stirred rapidly and chlorine was bubbled into it until a distinct green layer of chlorine was evident above the liquid level. A line was drawn on the flask, level with the liquid, which was kept topped up as the reaction ensued on addition of ammonia.

Once the solution was saturated with chlorine, ammonia was passed into it. The rate of bubbling the ammonia was fairly fast, but was controlled such that the white fumes just poured from the neck of the flask. The fumes disappeared after about 20 minutes, and the solution gradually became more viscous. Various colour changes occurred during the reaction - purple, green/grey, brown, orange/yellow and finally pink/orange. The last stage occurred after 2½ to 3 hours.

The solid was filtered from the solution, slurried with 600-700 mls. of water for 10 minutes, filtered once more, and then allowed to air-dry for two days, during which time the yellow solid turned yellow/green.

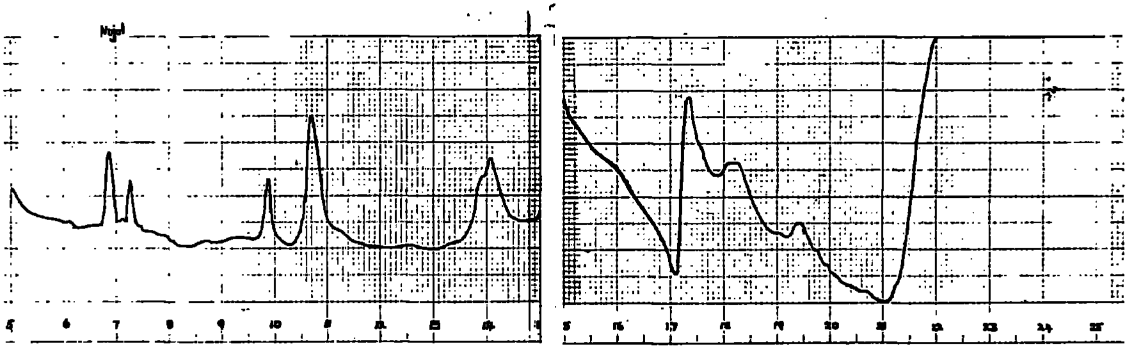
The solid was then shaken with ether, to remove S_7NH, and then placed in a porous thimble, in a Soxhlet extraction apparatus, using sodium dried benzene as the extraction solvent. The extraction took about 10 hours (usually overnight), and on cooling pure S_4N_4 crystallised from the solution.

SPECTROSCOPIC DATA



a

MULL BETWEEN KBr PLATES

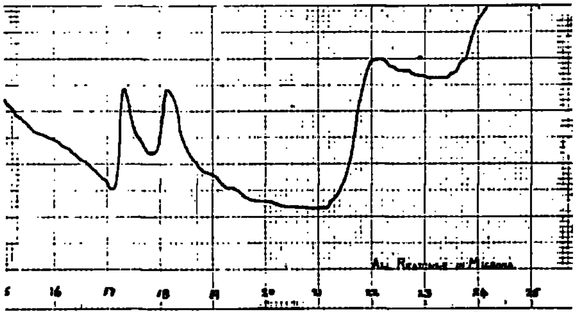


b

MULL BETWEEN NaCl PLATES

c

MULL BETWEEN POLYTHENE SHEETS



d

MULL GROUND WITH KBr

FIG.SP.1.

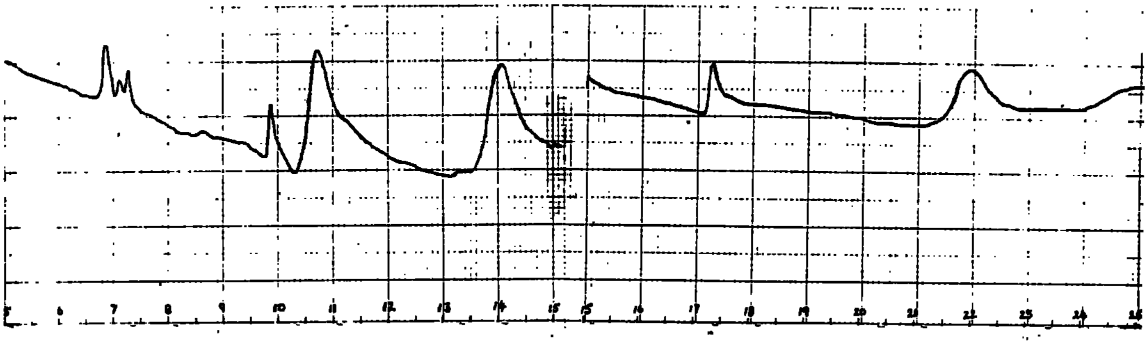
I.R. SPECTRA OF $S_3N_2Cl_2$

Table 6

Tentative Assignments	Microns	Cm^{-1}
S=N	9.86, 10.68	1,014, 936.3
S-N	13.9, 14.07	719.4, 710.7
S=N	17.32, 18.19	577.4, 549.7
S-Cl	19.40	515.4
S-N	21.38, 22.00	467.7, 454.5

I.R. Data $S_3N_2Cl_2$

(see FIG. SP.1)

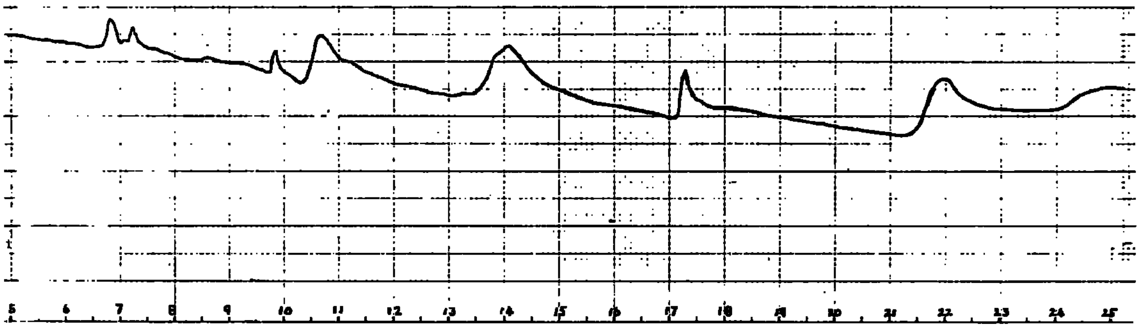


a

PRODUCT FROM $(NH_4)_2SO_4$: MULL BETWEEN NaCl PLATES

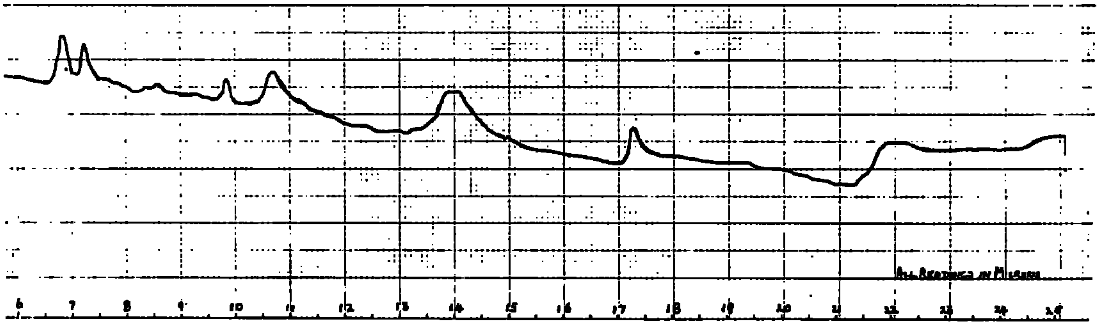
b

PRODUCT FROM $(NH_4)_2SO_4$: MULL BETWEEN POLYTHENE SHEETS



c

PRODUCT FROM $(NH_4)_2SO_4$: MULL GROUND WITH KBr



d

PRODUCT FROM NH_4Cl: MULL GROUND WITH KBr

FIG. SP. 2.

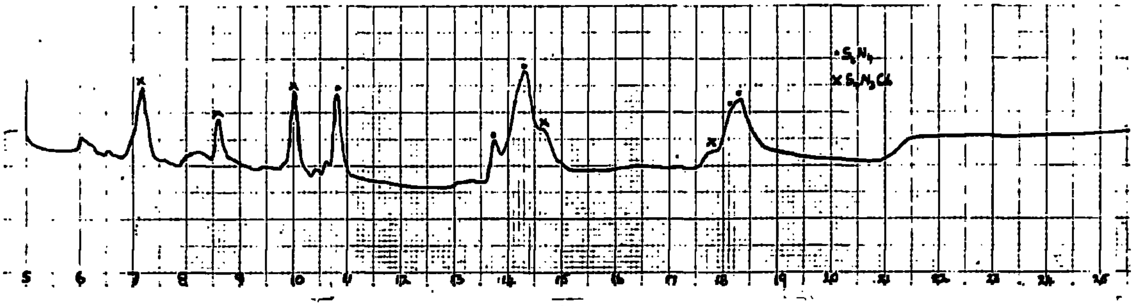
I.R. SPECTRA OF $S_3N_2Cl_2$

Table 7

Tentative Assignment	Microns	Cm^{-1}
S=N	9.87 (m) 10.73 (s) 11.23 (m)	1,013, 932.0 890.5
S-N	13.35 (w) 13.90 (s) 14.07 (s)	749.1, 719.4 710.7
S-Cl	17.32 (s) 17.60 (m)	577.4, 568.2
S=N	21.95 (s)	455.6
S-N	approx. 25.00 (m)	400.0

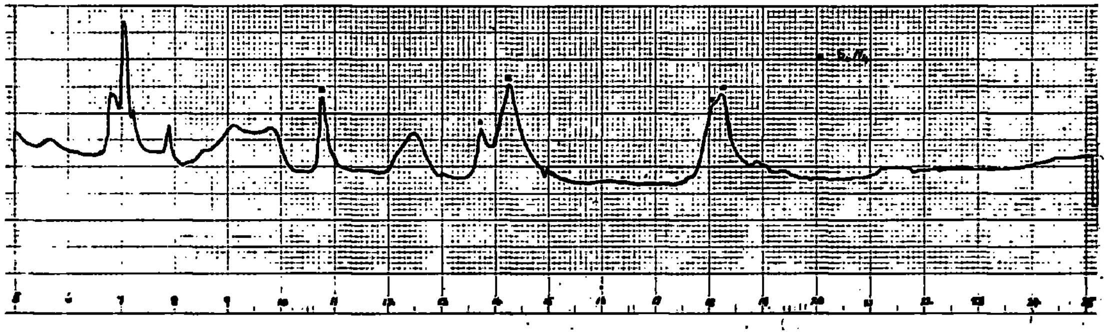
I.R. Spectrum of $S_3N_2Cl_2$

(see FIG. SP.2)



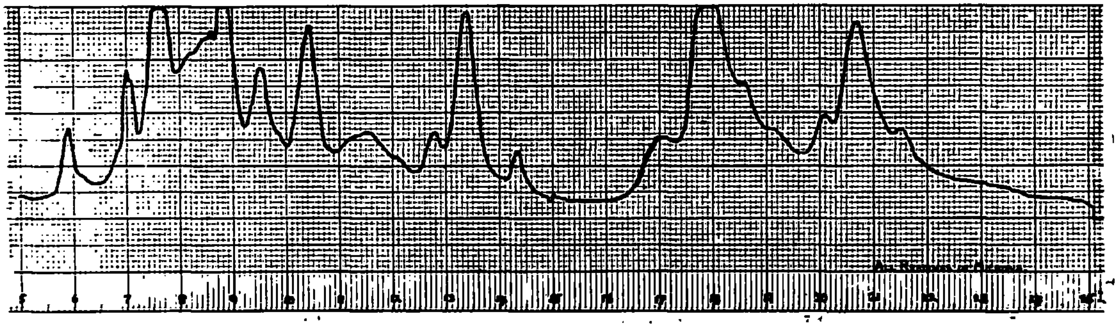
a

PRODUCT FROM TETRAHYDROFURAN



b

PRODUCT FROM CARBON DISULPHIDE

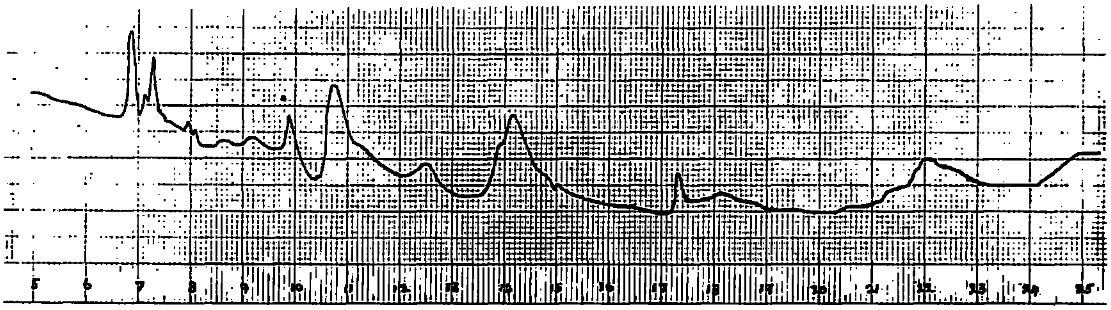


c

PRODUCT FROM DIMETHYLSULPHOXIDE

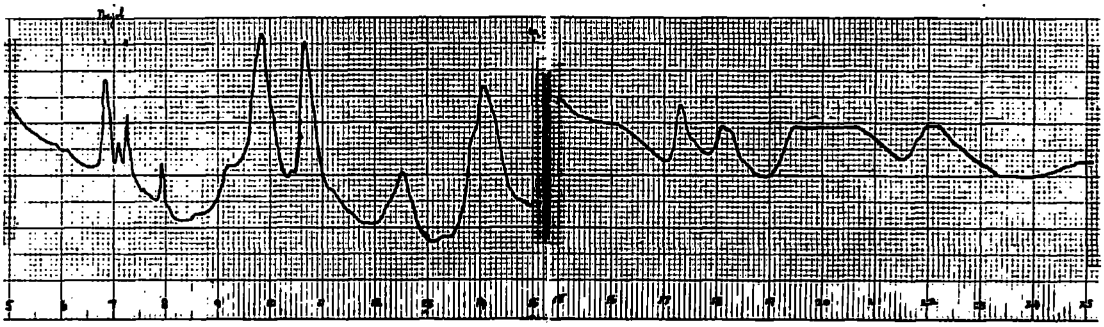
FIG SP.3.

I.R. SPECTRA OF PRODUCTS OBTAINED IN THE SOLVENT EXTRACTION OF $S_3N_2Cl_2$



a

MULL OF SUBLIMATE BETWEEN KBr PLATES

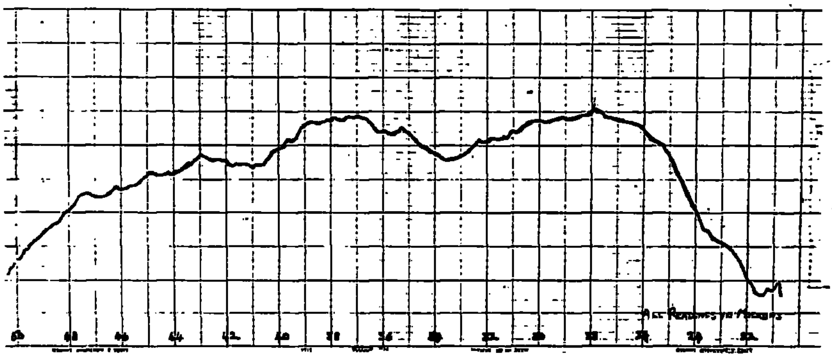


b

MULL OF SUBLIMATE BETWEEN NaCl PLATES

c

MULL OF SUBLIMATE BETWEEN POLYTHENE SHEETS



d

FAR I. R: SUBLIMATE BETWEEN POLYTHENE SHEETS

FIG.SP. 4.

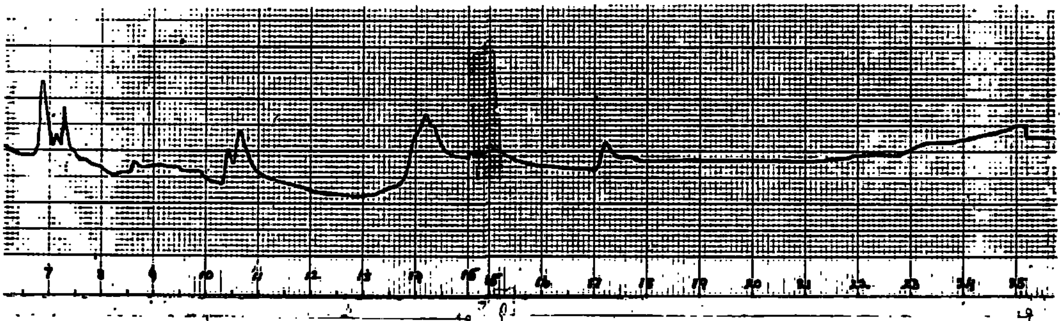
I.R. SPECTRA OF $S_3N_2Cl_2$ SUBLIMATE AT 80° - 95°C ONTO A LIQUID NITROGEN COLD FINGER

Table 8

Tentative Assignment	Microns	Cm^{-1}
?	7.09 (m)	1,410
?	7.92 (m)	1,262
?	9.20 (m)	1,087
S=N	9.83 (s) and 10.76 (s)	1,017, 929.3
?	12.52	798.7
S-N	13.9 (m) and 14.08 (s)	719.4, 710.2
S=N	17.30 and 18.10	578.0, 552.4
S-Cl?	Peak extends as a plateau from 19.45 to 20.70 (extropolation gives 20.0)	514.1-483.0 (500.0)
S-N	22.10	452.5
? ? ?	27.9 36.9 42.9	358.4 271.0 233.1

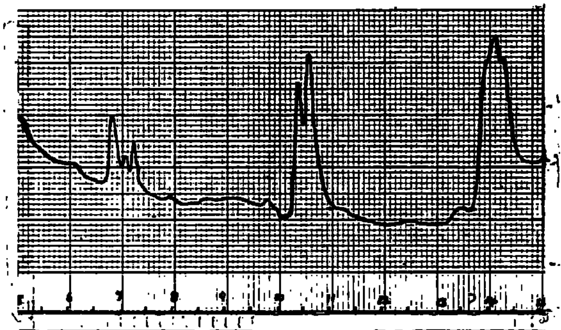
I.R. Data of $S_3N_2Cl_2$ Sublimate

(see FIG. SP.4)

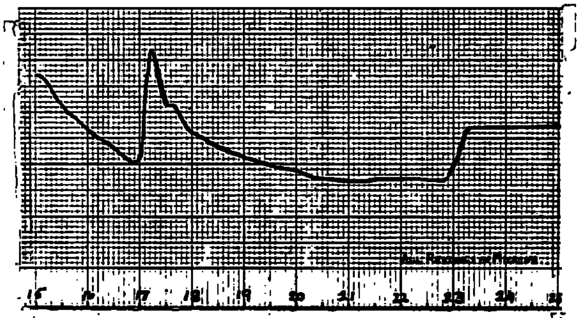


a
GREEN DEPOSIT. MULL BETWEEN NaCl PLATES

b
GREEN DEPOSIT. MULL BETWEEN POLYTHENE SHEETS



c
RED SUBLIMATE. MULL BETWEEN NaCl PLATES



d
RED SUBLIMATE. MULL BETWEEN POLYTHENE SHEETS

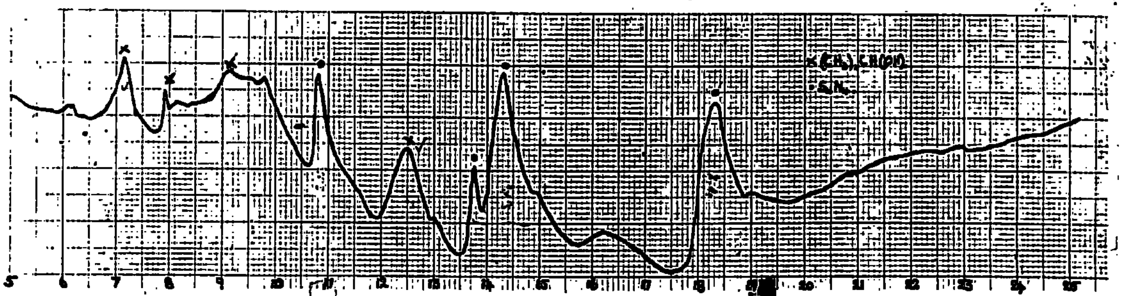
FIG. SP. 5.
I.R. SPECTRA OF THE SUBLIMATION PRODUCTS OF $S_3N_2Cl_2$ AT 80°- 95°C USING A WATER COOLED COLD FINGER

Table 9

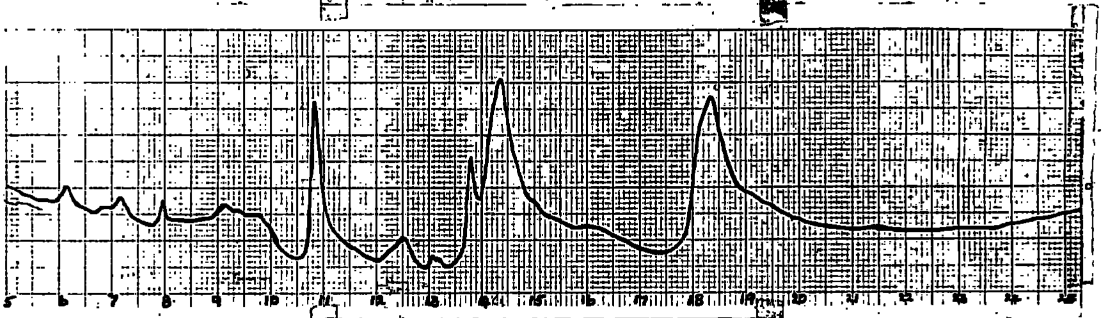
Tentative Assignment	Microns	Cm^{-1}
?	7.95 (w) 8.60 (w) 9.84 (w) 10.00 (w)	1,259, 1,163 1,055, 1,000
S=N	10.40 (m) 10.62 (s)	961.5, 941.6
?	12.50 (w)	800.0
S-N	13.50 (w) 14.00 (s) 14.15 (vs) 14.30 (s)	740.7, 714.3 706.7, 699.3
S-Cl	17.22 (s) 17.60 (m)	580.7, 568.2
S=N	23.30 plateau	429.2

I.R. Data of $S_3N_2Cl_2$ Sublimate

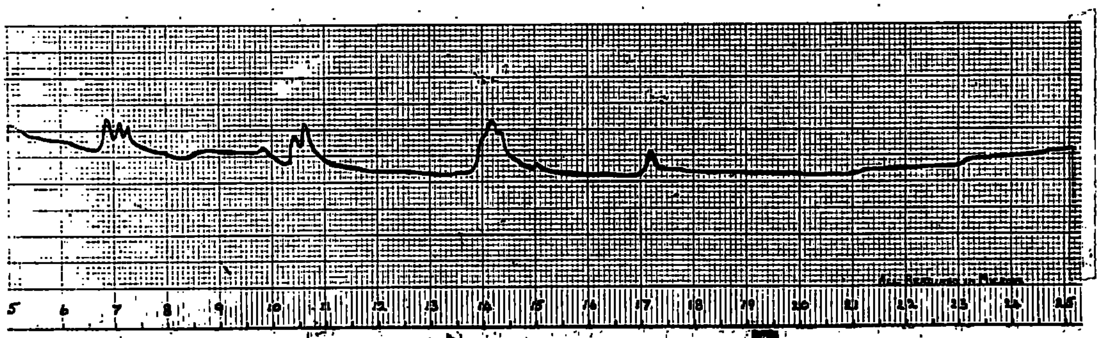
(see FIG. SP.5)



a
REAGENT: ISOPROPANOL



b
REAGENT: PHENYL LITHIUM



c
REAGENT: HYDROGEN SULPHIDE

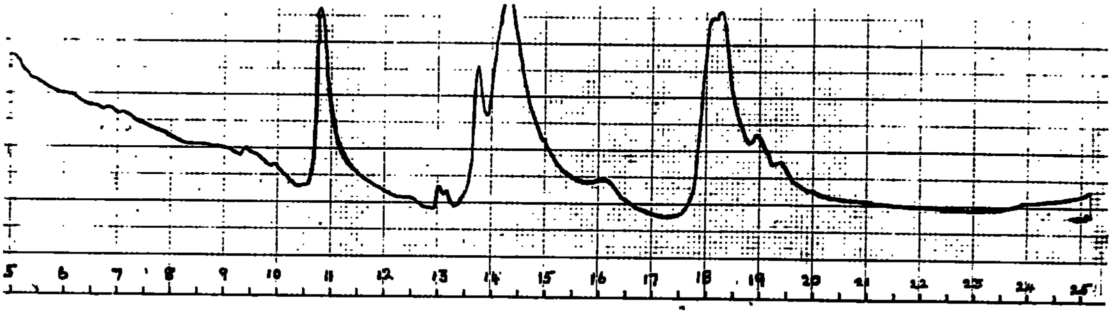
FIG. SP. 6.
I.R. SPECTRA OF REACTION PRODUCTS OF $S_3N_2Cl_2$
AND VARIOUS REAGENTS

Table 10

Tentative Assignment	Microns	Cm^{-1}
?	7.95 (w) 8.60 (w) 9.84 (w) 10.00 (w)	1,259, 1,163 1,055, 1,000
S=N	10.41 (m) 10.61 (s)	960.6, 942.5
S-N	13.50 (w) 14.00 (s) 14.15 (s) 14.30 (s)	740.7, 714.3 706.7, 699.3
S-Cl	17.20 (m) 17.60 (w)	581.4, 568.2
S=N	23.30 plateau	429.2

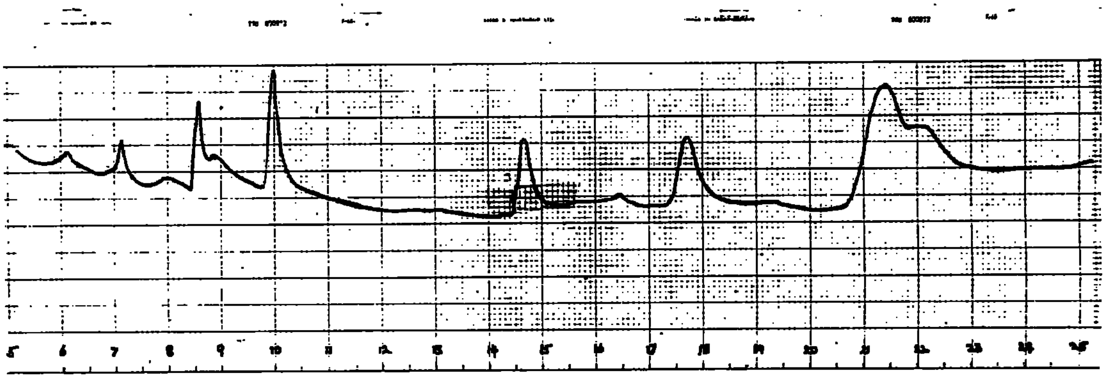
I.R. Data of S_3N_2Cl from $S_3N_2Cl_2$ + H_2S

(see FIG. SP.6c)



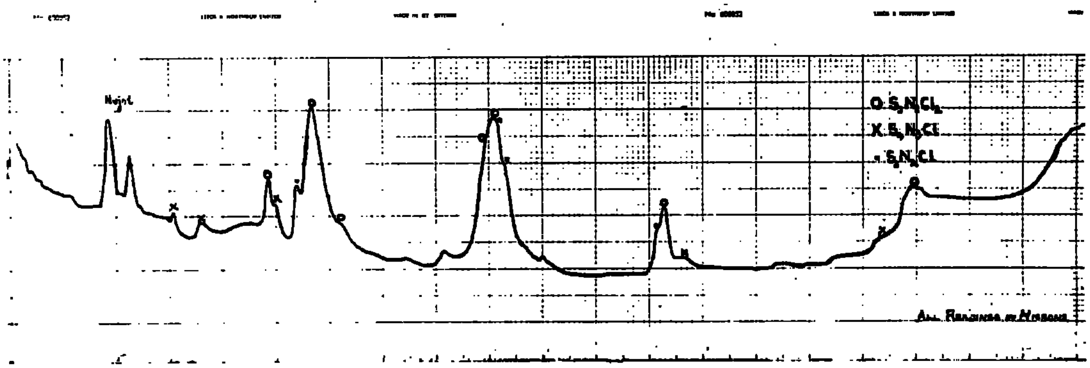
a

PRODUCT: S_4N_4



b

PRODUCT: S_4N_3Cl



c

PRODUCT: $S_3N_2Cl_2 + S_3N_2Cl + S_4N_3Cl$

FIG. SP. 7

I.R. SPECTRA OF PRODUCTS FROM THE REACTION OF S_3N_2Cl WITH CHLOROFORM

Table 11a

Microns	Cm^{-1}
9.40 (w) 9.95 (w) 10.79 (s)	1,064, 1,005, 926.8
13.02 (w) 13.18 (w) 13.75 (m) 14.31 (s) 16.10 (w)	768.0, 758.7, 727.3 698.8, 621.1
18.10 (s) 18.27 (s) 18.93 (m) 19.38 (w)	552.5, 547.3, 528.3 516.0

S_4N_4 from $S_3N_2Cl_2$ + $CHCl_3$

(see FIG. SP.7a)

Table 11b

Microns	Cm^{-1}
6.12 (m) 7.13 (m) 8.00 (w)	1,634, 1,405, 1,250
8.58 (s) 8.85 (m) 9.98 (vs)	1,166, 1,130, 1,002
14.67 (s) 15.62 (w) 16.45 (w)	681.7, 640.2, 607.9
17.70 (s) 19.35 (w)	565.0, 516.8
21.40 (s) 22.00 (s) plateau	467.3, 454.5

S_4N_3Cl from $S_3N_2Cl_2$ + $CHCl_3$

(see FIG. SP.7b)

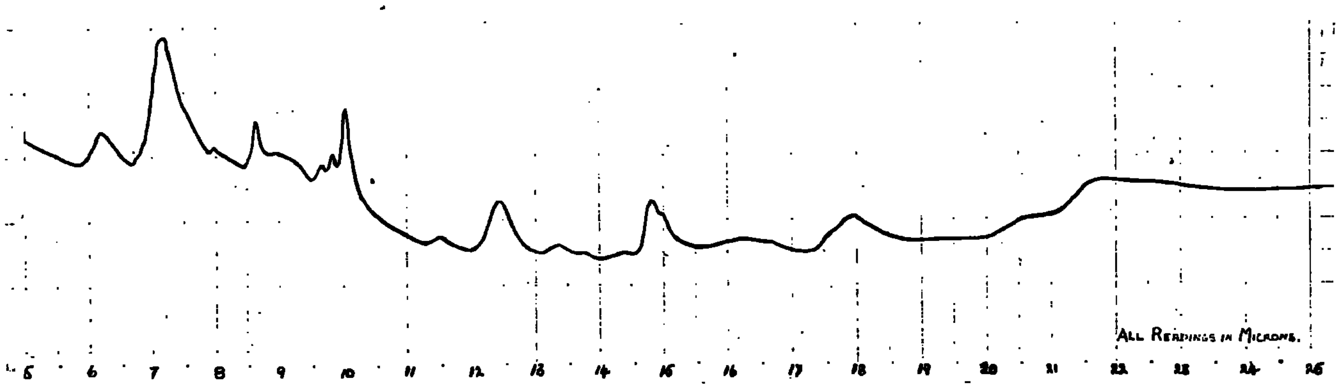
Table 11c

Compound Present	Microns	Cm^{-1}
$S_3N_2Cl_2$	9.82 (m) 10.66 (s) 11.20 (m) 13.95 (s) 14.08 (s) 17.27 (m) 21.93 (m)	1,018, 938.1, 892.9 716.8, 710.2, 579.0 456.0
S_3N_2Cl	10.35 (m) 14.12 (s) 14.28 (m) 17.13 (m)	966.2, 708.2, 700.3 583.7
S_4N_3Cl	8.07 (w) 8.58 (w) 9.98 (m) 17.68 (w) 21.40 (m)	1,239, 1,166, 1,002 565.6, 467.3
?	12.45 (w) 13.12 (w)	803.2, 762.2

Product from $S_3N_2Cl_2$ + $CHCl_3$ at Room Temperature

(see FIG. SP.7c)

a
REAGENT: DIMETHYLFORMAMIDE



b
REAGENT: STANNIC CHLORIDE

FIG. SP. 8.

I.R. SPECTRA OF PRODUCTS FROM THE REACTION OF $S_3N_2Cl_2$ WITH DIMETHYLFORMAMIDE AND STANNIC CHLORIDE

Table 12a

Compound	Microns	Cm^{-1}
S_4N_3Cl	7.13 (s) 8.57 (m) 8.85 (w) 9.82 (m) 9.98 (s) 14.63 (m) 17.72 (m) 21.58 (m) 22.00 (m) plateau	1,403, 1,167, 1,130 1,018, 1,002, 683.5 564.3, 463.4 454.5
S_3N_2Cl	10.38 (m) 10.57 (s) 13.98 (s) 14.13 (s) 14.31 (s) 17.15 (m)	963.4, 946.1, 715.3 707.7, 698.8, 583.1
?	6.07 (w) 7.65 (w) 8.12 (m)	1,647, 1,307, 1,231

Product from Reaction of $S_3N_2Cl_2$ and Dimethylformamide

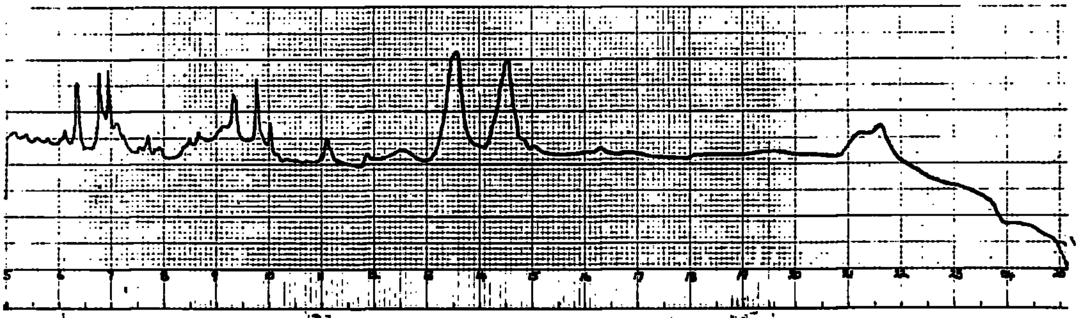
(see FIG. SP.8a)

Table 12b

Microns	Cm^{-1}
6.17 (m) 7.14 (s) 7.94 (w)	1,621, 1,401, 1,259
8.62 (m) 9.63 (w) 9.80 (w)	1,160, 1,038, 1,020
10.00 (m) 11.48 (w) 12.40 (m)	1,000, 871.1, 806.5
13.34 (w) 13.70 (w) 14.35 (w)	749.6, 729.9, 696.9
14.79 (m) 14.92 (m) 16.39 (w)	676.1, 670.2, 613.5
17.92 (m) 20.80 (m) 21.80 (m)	558.0, 480.8, 458.7

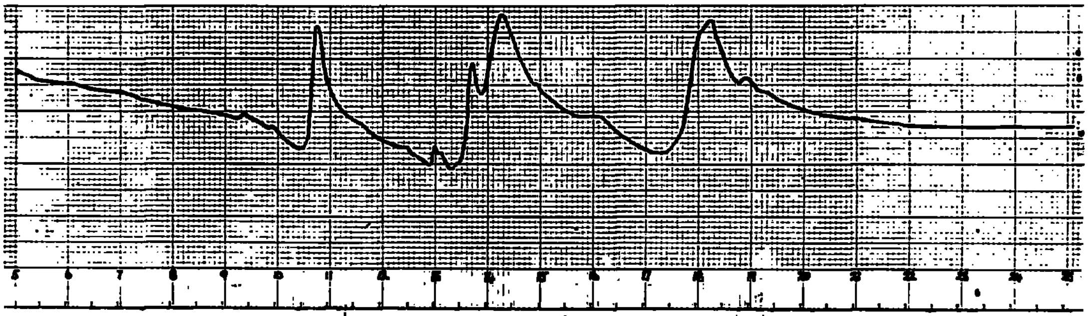
Product from $S_3N_2Cl_2$ + Stannic Chloride

(see FIG. SP.8b)



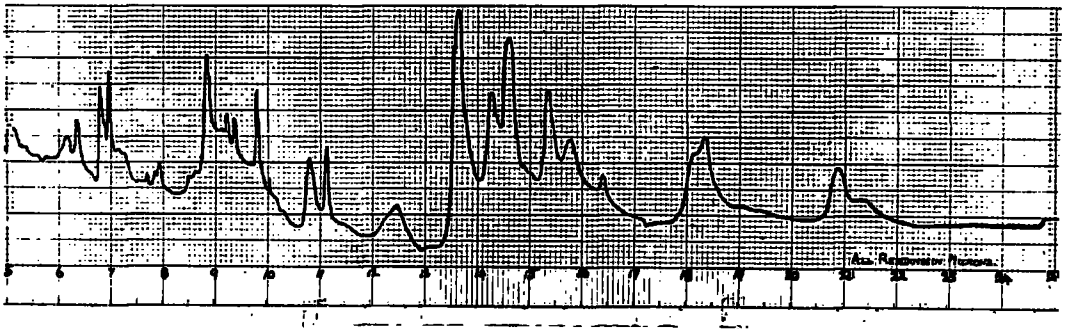
a

EXPERIMENT I. DIPHENYL DISULPHIDE



b

EXPERIMENT 2. S_4N_4



c

EXPERIMENT 3. GOLD PRODUCT m.p. 97°C

FIG. SP. 9.

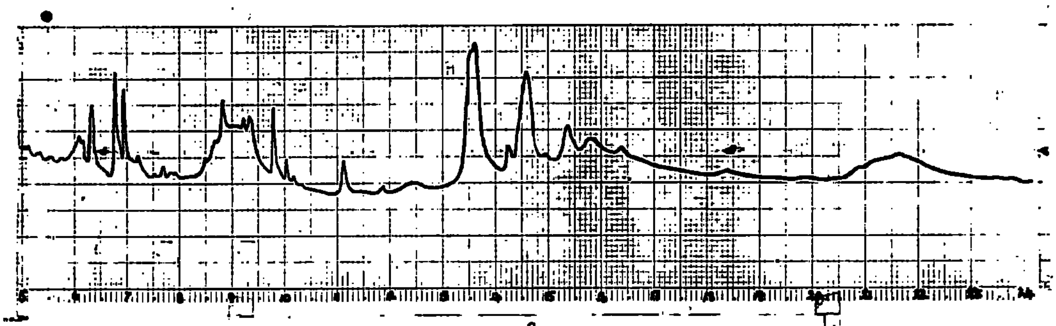
I.R. SPECTRA OF PRODUCTS FROM THE REACTION S_4N_4 + PhMgBr

Table 13

Tentative Assignment	Microns	Cm^{-1}
C-H	3.42 (m) 3.51 (m)	2,924, 2,849
C=C conjugated	6.10 (m) 6.34 (m)	1,639, 1,577
Conjugated substituted	6.78 (s) 6.95 (s) 7.15 (w) 7.28 (w) 7.69 (w)	1,475, 1,439, 1,399 1,374, 1,300
Aromatic C-H deformations + C-C aromatic	7.82 (w) 7.92 (w) 8.48 (w) 8.52 (w) 9.12 (m) 9.36 (m) 9.79 (s) 10.02 (w) 10.15 (w) 10.30 (w) 11.12 (m)	1,279, 1,263, 1,179 1,174, 1,096, 1,068 1,021, 998.0, 985.2 970.9, 899.3
S=N	8.82 (s) 9.22 (m) 10.79 (m)	1,134, 1,085, 926.8
?	12.45 (m)	803.2
Monosub. aromatic	13.63 (vs) 14.60 (vs)	733.7, 684.9
S-N	14.27 (s) 15.35 (s) 15.76 (m) 16.38 (m)	700.8, 651.5 634.5, 610.5
S=N	18.12 (m) 18.32 (s)	551.9, 545.9
S-N	20.88 (m) 21.35 (m)	478.9, 468.4

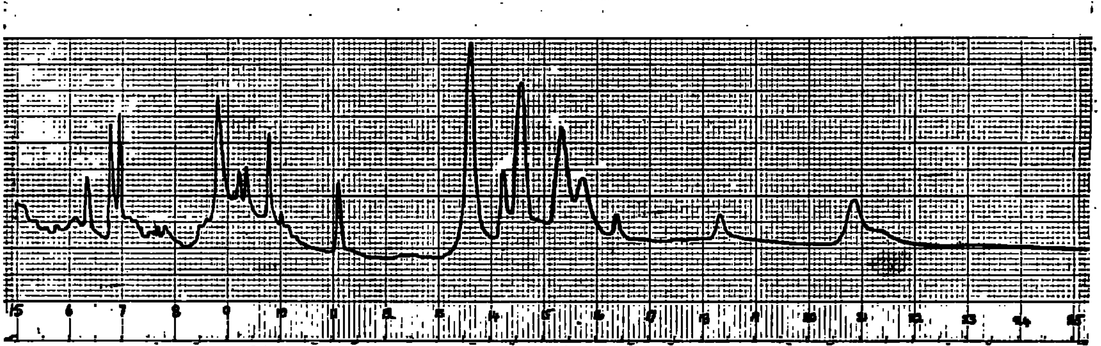
I.R. Spectral Data of Golden Crystals m.p. 97°C

(see FIG. SP.9)



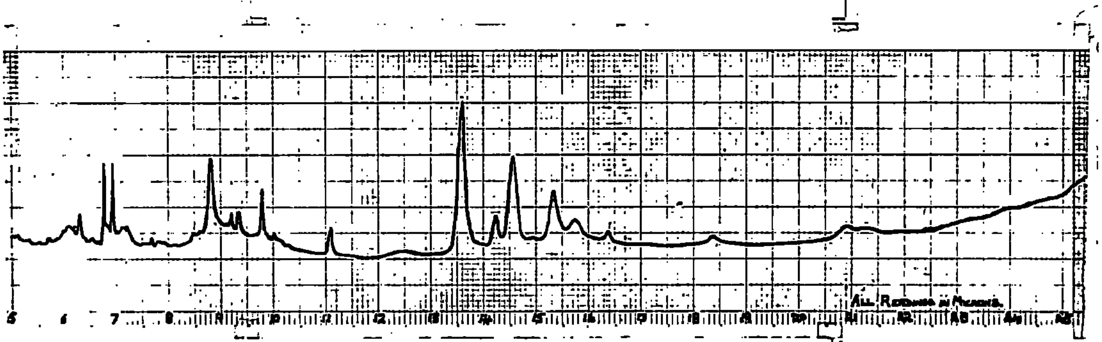
a

EXPERIMENT 4. ORANGE PRODUCT m.p. 86°--87°C.



b

EXPERIMENT 4. ORANGE PRODUCT m.p. 99° ± 0·5°C.



c

EXPERIMENT 5. GOLD PRODUCT m.p. 102° ± 0·5°C.

FIG. SP. 10.

I.R. SPECTRA OF PRODUCTS FROM THE REACTION S_4N_4 + PhMgBr

Table 14a

Tentative Assignment	Microns	Cm^{-1}
C-H aromatic	3.42 (w) 3.51 (w)	2,924, 2,849
C=C aromatic	6.09 (w) 6.18 (w) 6.34 (m)	1,642, 1,618, 1,577
Conjugated substitution	6.79 (s) 6.95 (s) 7.22 (w) 7.52 (w) 7.71 (w)	1,474, 1,439 1,385, 1,330, 1,297
Aromatic C-H and C-C	7.82 (w) 7.92 (w) 8.49 (w) 8.68 (m) 9.34 (m) 9.79 (s) 10.04 (m) 10.18 (w) 10.32 (w) 11.12 (m)	1,279, 1,263, 1,178 1,152, 1,071, 1,021 996.0, 982.3, 969.0 899.3
S=N	8.82 (s) 9.22 (m)	1,134, 1,085
?	11.88 (w) 12.45 (w)	841.8, 803.2
Aromatic substitution	13.53 (vs) 13.62 (vs) 14.59 (s)	739.1, 734.2 685.4
S-N	14.45 (m) 14.25 (m) 15.36 (m) 15.78 (m) 16.38 (w)	692.0, 701.8, 651.0 633.7, 610.1
S=N	18.38 (w)	544.1
S-N	21.68 (m)	461.3

I.R. Data of Rust Precipitate m.p. 86-87°C

(see FIG. SP.10a)

Table 14b

Tentative Assignment	Microns	Cm^{-1}
C=C Aromatic	6.12 (w) 6.34 (m)	1,634, 1,577
Conjugated Substitution	6.79 (s) 6.95 (s) 7.10 (w) 7.22 (w) 7.52 (w) 7.65 (w)	1,472, 1,439, 1,408 1,385, 1,330, 1,307
Aromatic C-H Deformations at C-C Aromatic	7.80 (w) 7.92 (w) 8.49 (w) 8.65 (w) 9.10 (w) 9.38 (m) 9.80 (s) 10.05 (w) 10.18 (w) 10.30 (w) 11.13 (s)	1,282, 1,263, 1,178 1,156, 1,099, 1,066 1,020, 995.0, 982.3 970.9, 898.5
S=N	8.83 (s) 9.23 (m)	1,183, 1,083
Aromatic Substitution	13.63 (vs) 14.59 (vs)	733.7, 685.4
S-N	14.25 (m) 15.35 (s) 15.76 (m) 16.38 (w)	701.7, 651.5, 634.5 610.5
S=N	18.36	544.7
S-N and/or S-S	20.90 21.30 plateau	478.5 469.5

I.R. Data of Orange Product m.p. 99°C

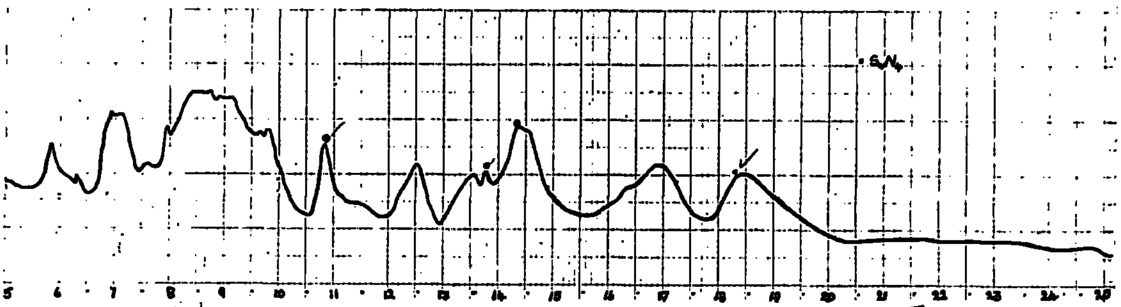
(see FIG. SP.10b)

Table 14c

Tentative Assignment	Microns	Cm^{-1}
C-H	3.42 (m) 3.50 (m)	2,924, 2,857
C=C Aromatic	6.10 (m) 6.32 (m)	1,639, 1,582
Conjugated substitution	6.55 (w) 6.64 (w) 6.78 (s) 6.93 (s) 7.13 (w) 7.22 (w)	1,527, 1,506, 1,475 1,443, 1,403, 1,385
Aromatic C-H deformations at C-C aromatic	7.68 (w) 7.80 (w) 7.92 (w) 8.47 (w) 8.60 (w) 9.10 (m) 9.34 (m) 9.79 (s) 10.02 (w) 10.11 (w) 10.27 (w) 11.10 (m)	1,302, 1,282, 1,263 1,181, 1,163, 1,099 1,071, 1,021, 998.0 989.1, 973.7, 900.9
S=N	8.82 (s) 9.21 (m)	1,134, 1,086
?	12.50 (w)	800.0
Monosubstituted aromatic	13.61 (vs) 14.57 (s)	734.8, 686.3
S-N	14.23 (m) 14.92 (w) 15.34 (m) 15.73 (m) 16.38 (w)	702.7, 670.2, 651.9 635.7, 610.5
S=N	18.35 (w)	545.0
S-N	20.90 (w) 21.23 (w)	478.5, 471.0

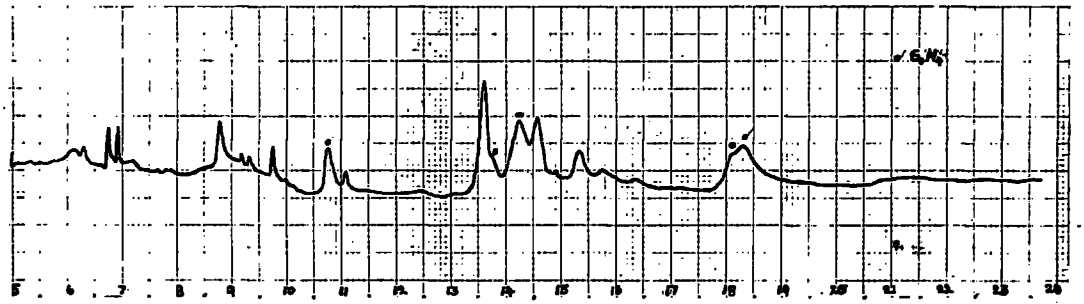
I.R. Data of Golden Crystals m.p. 102°C

(see FIG. SP.10c)



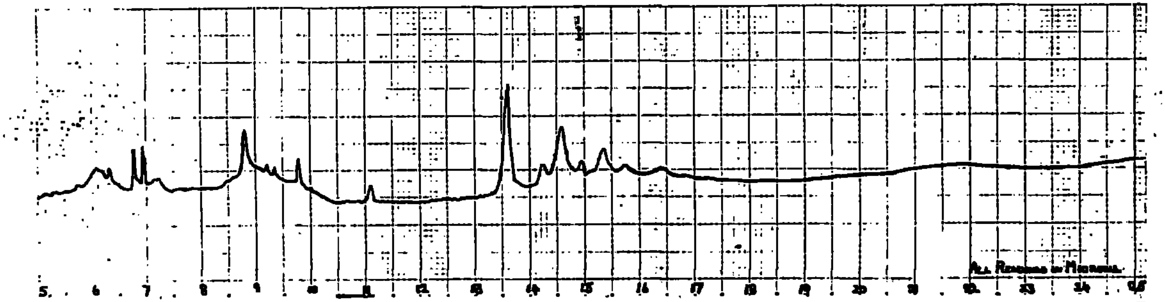
a

EXPERIMENT 7 GREEN-YELLOW DEPOSIT LEFT ON SIDE OF SCHLENK



b

EXPERIMENT 7 BROWN CRYSTALS FROM SOLID EXTRACT



c

EXPERIMENT 7. SUBLIMATION PRODUCT m.p. 101° ± 1°C

FIG. SP. 11.

I.R. SPECTRA OF PRODUCTS FROM THE REACTION S_4N_4 + PhMgBr

Table 15

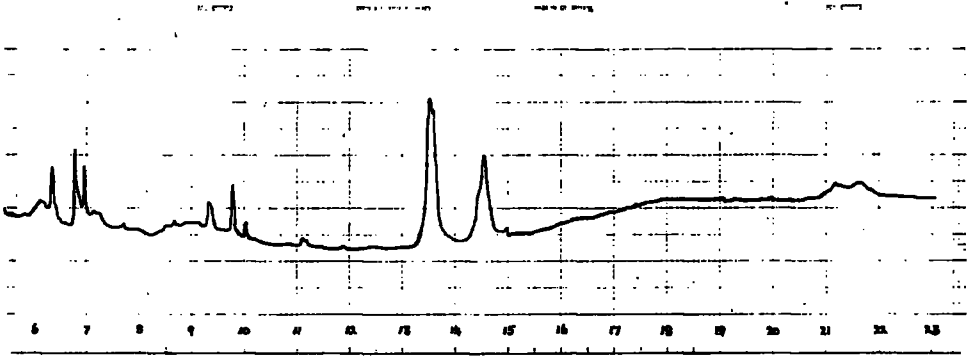
Tentative Assignment	Microns	Cm^{-1}
C=C Conjugated	6.07 (w) 6.17 (w) 6.32 (m)	1,647, 1,621, 1,582
Conjugated Substitution	6.78 (s) 6.95 (s) 7.15 (w) 7.23 (w) 7.62 (w)	1,475, 1,439, 1,399 1,383, 1,312
Aromatic C-H Deformations + C-C Aromatic	7.82 (w) 7.92 (w) 8.65 (w) 8.57 (w) 9.33 (m) 9.78 (s) 10.02 (w) 11.10 (m)	1,279, 1,263, 1,183 1,167, 1,072, 1,022 997.0, 900.9
S=N	8.81 (s) 9.20 (m)	1,135, 1,087
Monosubstituted Aromatic	13.60 (vs) 14.59 (s)	735.3, 685.4
S-N	14.23 (m) 15.35 (m) 15.75 (m) 16.40 (m)	702.7, 651.5, 634.9 609.8

I.R. Data of $S_3N_2Ph_2$ Sublimed m.p. 101°C

(see FIG. SP.11c)

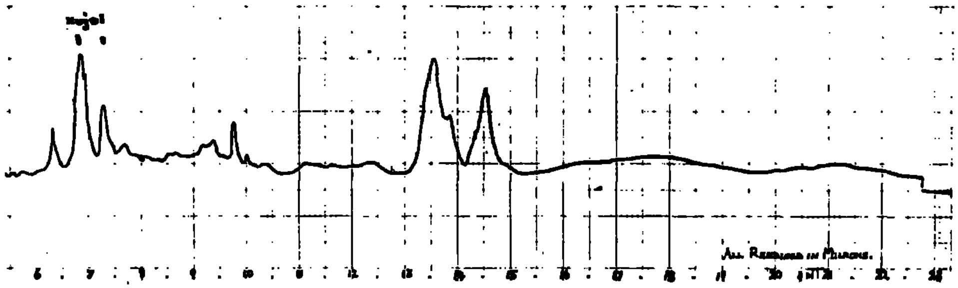
a

EXPERIMENT 8. COLOURLESS LEAFLET CRYSTALS



b

EXPERIMENT 8. Ph_2S_2 FROM COLOURLESS EXTRACT



c

EXPERIMENT 8. RESIDUE FROM ORANGE AND YELLOW EXTRACTS

FIG. SP. 12.

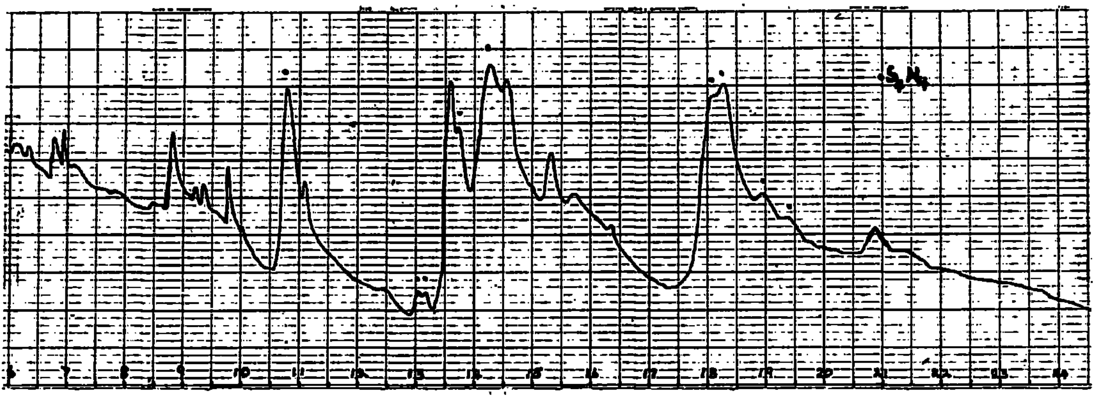
I.R. SPECTRA OF PRODUCTS FROM THE REACTION S_4N_4+PhMgBr.

Table 16

Microns	Cm^{-1}
6.10 (w) 6.33 (m) 6.78 (s)	1,639, 1,580, 1,475
6.95 (m) 7.13 (w) 7.25 (w)	1,439, 1,403, 1,379
7.72 (w) 8.68 (w) 9.32 (m)	1,295, 1,152, 1,073
9.78 (m) 10.03 (w) 11.10 (w)	1,022, 997.0, 900.9
13.50 (vs) 13.59 (vs) 14.45 (m)	740.7, 735.8, 692.0
14.55 (s) 21.17 (m) 21.62 (m)	687.3, 472.4, 462.5

Ph_2S_2 from Chromatographic Extraction of $Ph_2S_3N_2$

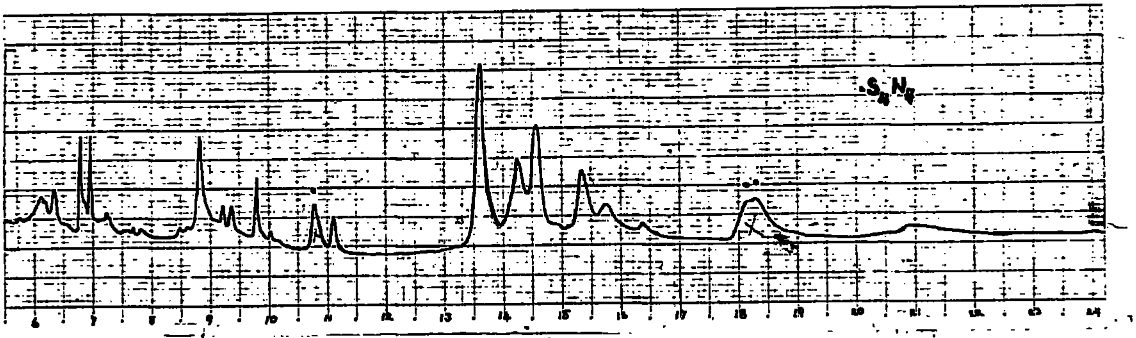
(see FIG. SP.12b)



a

EXPERIMENT 9 PRODUCT AFTER FOUR RECRYSTALLISATIONS

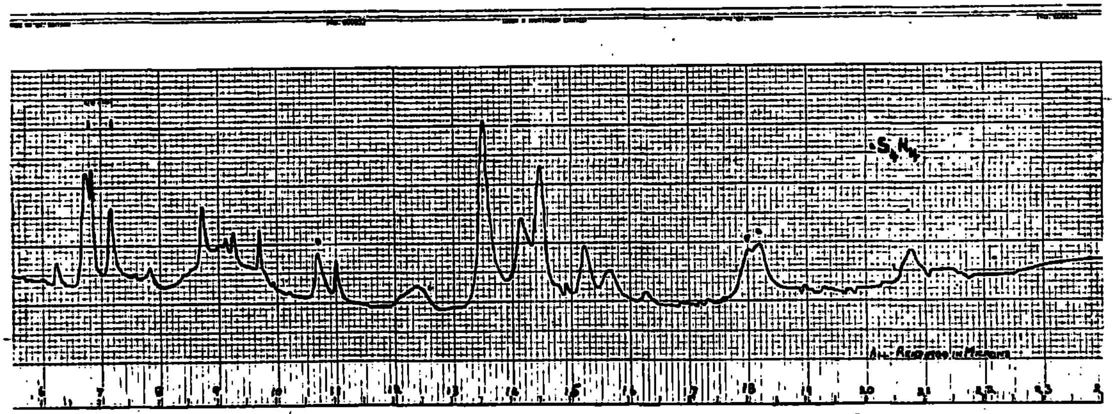
m.p. 95°C



b

EXPERIMENT 9. PRODUCT AFTER SIX RECRYSTALLISATIONS

m.p. 101°C



c

EXPERIMENT 9. PRODUCT m.p. 97°- 98°C.

FIG. SP. 13.

I.R. SPECTRA OF PRODUCTS FROM THE REACTION S_4N_4+PhMgBr.

Table 17a

Tentative Assignment	Microns	Cm^{-1}
C=C Aromatic	6.12 (m) 6.32 (m)	1,634, 1,582
Conjugated Substitution	6.55 (w) 6.80 (s) 6.93 (s) 7.13 (w) 7.22 (w)	1,527, 1,471, 1,443 1,403, 1,385
Aromatic C-H Deformations at C-C Aromatic	7.68 (w) 7.82 (w) 8.49 (w) 8.60 (w) 9.10 (w) 9.36 (m) 9.80 (s) 10.02 (w) 10.11 (w) 10.27 (w) 11.10 (m)	1,302, 1,279, 1,178 1,163, 1,099, 1,068 1,020, 998.0, 989.1 973.7, 900.9
S=N *in S_4N_4	8.82 (s) 9.21 (m) 10.79 (m)*	1,134, 1,086 926.8*
Monosubstituted Aromatic	13.61 (vs) 14.57 (s)	734.8, 686.3
S-N	14.23 (m) 14.92 (w) 15.34 (m) 15.73 (m) 16.38 (w)	702.7, 670.2, 651.9 635.7, 610.5
*in S_4N_4	18.12 (m)* 18.28 (m)*	551.9*, 547.0*
S-N or S-S	20.90 (w)	478.5

I.R. Data of $S_3N_2Ph_2$ Products

(see FIG. SP.13b and SP.16)

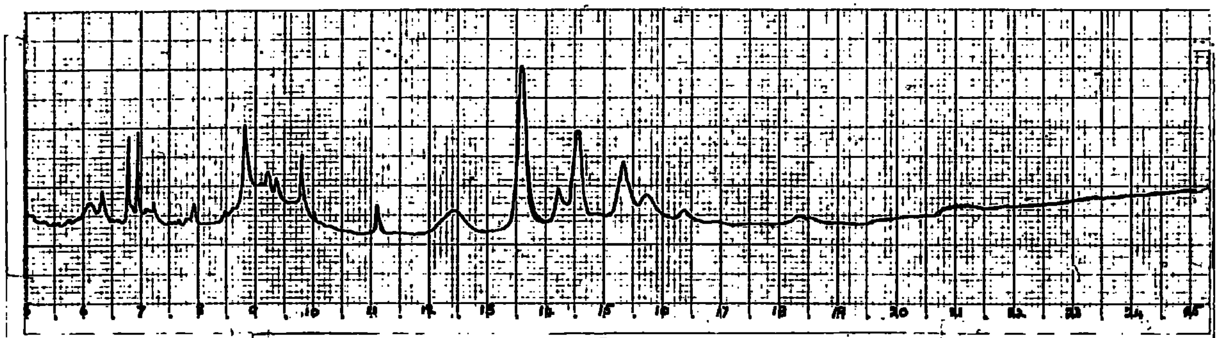
see P. 108 for FIG. SP.16

Table 17b

Tentative Assignment	Microns	Cm^{-1}
C=C Aromatic	6.12 (m) 6.32 (m)	1,634, 1,582
Conjugated Substitution	6.55 (w) 6.80 (s) 6.93 (s) 7.13 (w) 7.22 (w)	1,527, 1,471, 1,443 1,403, 1,385
Aromatic C-H Deformations at C-C Aromatic	7.68 (w) 7.82 (w) 8.49 (w) 8.60 (w) 9.10 (w) 9.36 (m) 9.80 (s) 10.02 (w) 10.11 (w) 10.27 (w) 11.10 (m)	1,302, 1,279, 1,178 1,163, 1,099, 1,068 1,020, 998.0, 989.1 973.7, 900.9
S=N *in S_4N_4	8.82 (s) 9.21 (m) 10.79 (m)*	1,134, 1,086 926.8*
? in SP.13c	12.42	805.2
Monosubstituted Aromatic	13.61 (vs) 14.57 (s)	734.8, 686.3
S-N	14.23 (m) 14.92 (w) 15.34 (m) 15.73 (m) 16.38 (w)	702.7, 670.2, 651.9 635.7, 610.5
*in S_4N_4	18.12 (m)* 18.28 (m)*	551.9*, 547.0*
S-N or S-S	20.65 (w) 20.80 (m) 21.20-21.50	484.3, 480.8 471.7-465.1

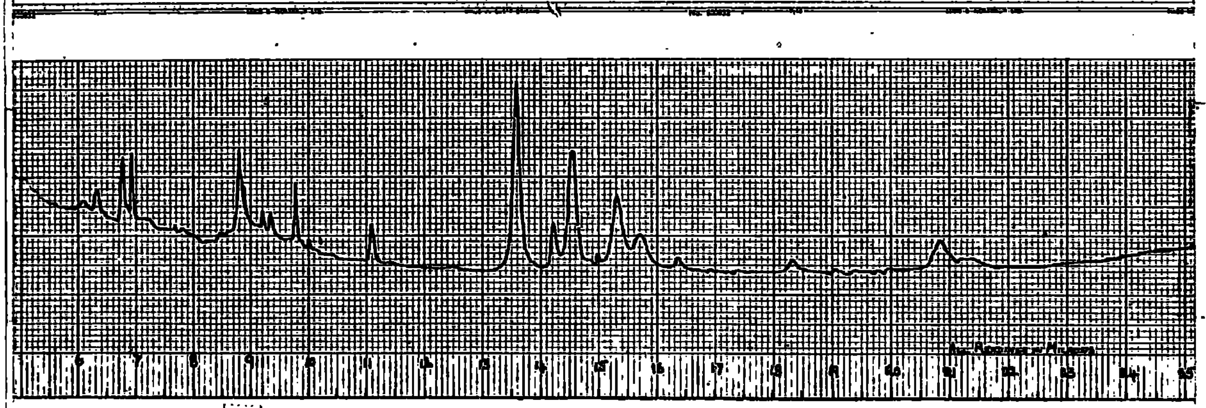
I.R. Data of $S_3N_2Ph_2$ Products

(see FIG. SP.13c and SP.16)



a

EXPERIMENT 9. PRODUCT, BROWN CRYSTALLINE NEEDLES



b

EXPERIMENT 10. PRODUCT, BROWN CRYSTALLINE NEEDLES

FIG. SP 14.

I.R. SPECTRA OF PRODUCTS FROM THE REACTION $S_4N_4 + PhMgBr$

Table 18

Tentative Assignment	Microns	Cm^{-1}
C=C Aromatic	6.10 (w) 6.32 (m)	1,639, 1,582
Conjugated Substitution	6.43 (w) 6.78 (s) 6.93 (s) 7.22 (w)	1,555, 1,475, 1,443 1,385
Aromatic C-N Deformations at C-C Aromatic	7.68 (w) 7.81 (w) 7.92 (w) 8.46 (w) 8.60 (w) 9.10 (w) 9.34 (m) 9.78 (s) 10.01 (w) 10.11 (w) 10.40 (w) 11.10 (m)	1,302, 1,280, 1,263 1,182, 1,163, 1,099 1,071, 1,022, 999.0 989.1, 901.5, 900.9
S=N	8.80 (s) 9.20 (m)	1,136, 1,087
?	12.50 (w)	800.0
Monosubstituted Aromatic	13.59 (vs) 14.55 (s)	735.8, 687.3
S-N	14.22 (m) 14.88 (w) 15.32 (m) 15.72 (m) 16.36 (w)	703.2, 672.0, 652.7 636.1, 611.2
S=N	18.33 (w)	545.5
S-N or S-S	20.85 (m) 21.25 (w)	479.6, 470.6

I.R. Data of Brown Crystalline $S_3N_2Ph_2$

(see FIG. SP.14a and 14b)

Peaks Underlined Stronger in 14a than 14b

DISCUSSION

DISCUSSION

Part 1

Thiodithiazyldichloride

The I.R. spectra recorded in FIGS. SP.1 and SP.2a-2c are of the orange/brown crystals obtained from the reaction of S_2Cl_2 with ammonium chloride or ammonium sulphate respectively. Spectra FIG. SP.2 have common absorption frequencies with spectra FIG. SP.1, but the latter have extra peaks. These could presumably be absorption frequencies of reactants and/or other products. It is interesting to note that the peaks at 8.59, 14.83, 17.80, 21.39 and 22.00 microns (FIG. SP.1a), show some similarity to frequencies of S_4N_3Cl (FIG. SP.7b), and perhaps an even greater similarity to some frequencies in FIG. SP.8b, which is the spectrum of the product from the reaction of $S_3N_2Cl_2$ with stannic chloride.

Chlorine analysis of the sample of $S_3N_2Cl_2$ used for FIG. SP.1 showed that the chlorine content was high (39.5%) compared with the theoretical value (36.41%), whereas a similar analysis on the crystals used for FIG. SP.2a-2c and FIG. SP.2d gave a chlorine content of 36.7% and 36.3% respectively. The excess chlorine in the first case (FIG. SP.1) may have been due to S_2Cl_2 trapped in the crystals.

Initially, it was thought that the absorption at 19.40 microns (FIG. SP.1c) could probably be assigned to an S-Cl stretching frequency in $S_3N_2Cl_2$. Evidence supporting this was obtained on grinding $S_3N_2Cl_2$ with KBr and recording the I.R. spectrum (FIG. SP.1d), which showed that the 19.40 microns peak had been reduced in intensity. A similar explanation of the induction period before the formation of $S_3N_2Cl_2$. However, while the experimental data recorded by the author could be used to substantiate Jolly's mechanism, it does not rule out the possibility of other mechanisms.

The mechanism proposed by Jolly is based on the reactions

$$3S_3N_2Cl_2 + 3Cl_2 \longrightarrow 6NSCl + 3SCl_2$$

$$6NSCl \longrightarrow 2N_3S_3Cl_3$$

As a consequence of these reactions any $S_3N_2Cl_2$ would be decomposed in the presence of chlorine to NSCl and $N_3S_3Cl_3$. Jolly proposed that chlorine was present as a result of the decomposition of S_2Cl_2 to chlorine and sulphur, and that during the induction period equilibria (1) and (2) occurred, thereby increasing the sulphur concentration in the reaction mixture.

$$S_2Cl_2 \rightleftharpoons 2S + Cl_2 \qquad (1)$$

$$S_2Cl_2 \rightleftharpoons S + SCl_2 \qquad (2)$$

Consequently as the concentration of sulphur increased, equilibria (1) and (2) tended to favour the formation of S_2Cl_2, and thus the chlorine concentration was gradually decreased, thereby allowing $S_3N_2Cl_2$ to form without further decomposition with chlorine to NSCl and $S_3N_3Cl_3$.

In Jolly's mechanism[25], NSCl is formed in solution, and being volatile reacts with S_2Cl_2 in the air condenser to give $S_3N_2Cl_2$ and SCl_2. The author has shown that SCl_2 could have been present in one sample of $S_3N_2Cl_2$. However, Jolly based part of his proposed mechanism on the equilibria (1) and (2), without considering any other 'sulphur-chlorine' equilibria. The author suggests that one should examine all the possible 'sulphur-chlorine' equilibria rather than selected ones.

The equilibria concerned are:

$$\left.\begin{array}{ll} S_2Cl_2 \rightleftharpoons \frac{2}{x}S_x + Cl_2 & (3) \\ S_2Cl_2 \rightleftharpoons \frac{1}{x}S_x + SCl_2 & (4) \end{array}\right) \text{c.f. Jolly (1) and (2) above}$$

$$\begin{array}{ll} SCl_2 \rightleftharpoons \frac{1}{x}S_x + Cl_2 & (5) \\ 2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2 & (6) \end{array}$$

where S_x is some molecular species of sulphur.

For Jolly's argument to be valid the reaction $S_2Cl_2 \longrightarrow 2S + Cl_2$ (3) must occur at the reaction temperature (ca. 140°C). According to Gmelin[119] however, this reaction does not occur appreciably below 250°C. The presence of red SCl_2 in yellow S_2Cl_2 demonstrates the probability of equilibrium (4) occurring, even at room temperature. Although the reaction $S + Cl_2 \longrightarrow SCl_2$ requires molten sulphur[120], the decomposition of SCl_2 to sulphur and chlorine (5) occurs to a small extent at room temperature, but principally to S_2Cl_2 and chlorine (6)[121]. The reaction $S_2Cl_2 + Cl_2 \longrightarrow SCl_2$ is a standard preparation of SCl_2 at room temperature, and according to Trautz[122] is the principal 'sulphur-chlorine' equilibrium at 'high temperatures'.

Thus Jolly's proposals that, during the induction period, chlorine is consumed (by $S_3N_2Cl_2$) and the sulphur concentration increases, are still acceptable if one replaces the equilibria (1)-(2) by equilibria (3)-(6), the forward reaction (3) occurring to a minor or negligible extent.

If kinetic factors control the 'sulphur-chlorine' system, it is possible that as the reaction temperature rises the chlorine concentration increases via reactions (4)-(6).

The equilibrium $S_2Cl_2 + Cl_2 \rightleftharpoons 2SCl_2$ is considerably more complicated than is implied by this equation. For example the following equilibria also occur[122].

$$S_2Cl_2 + Cl_2 \rightleftharpoons S_2Cl_4 \text{ (fast)} \qquad (7)$$

$$S_2Cl_4 \rightleftharpoons 2SCl_2 \text{ (slow)} \qquad (8)$$

$$SCl_2 + Cl_2 \rightleftharpoons SCl_4 \text{ (very fast)} \qquad (9)$$

$$S_2Cl_2 + SCl_4 \rightleftharpoons SCl_2 + S_2Cl_4 \text{ (fast)} \qquad (10)$$

As chlorine is produced, reactions (7), (9) and (10) produce S_2Cl_4. Eventually the concentration of sulphur is sufficient to retard the production of chlorine, thereby favouring the formation of S_2Cl_2. At this point the production of SCl_2 via reaction (8) could become important. The SCl_2 could then react with ammonium ions to produce $S_3N_2Cl_2$. Thus, equilibrium (8) could be the controlling reaction, and a contributing factor to the induction period.

In either of the two cases, SCl_2 or S_2Cl_2 could be the reactive species, although the former is perhaps less likely if thermodynamic control of the 'sulphur-chlorine' equilibria is effective.

A possible mechanism for the formation of $S_3N_2Cl_2$ is as follows:

$$NH_4^+ + SCl_2 \rightarrow (NH_4^+SCl_3^-) \rightarrow NH_2SCl + HCl + H^+$$

$$NH_2SCl + S_2Cl_2 \rightarrow NSCl + 2S + 2HCl \text{ (c.f. Jolly)}$$

$$2NSCl + S_2Cl_2 \rightarrow S_3N_2Cl_2 + SCl_2 \text{ (c.f. Jolly)}$$

$$2NH_2SCl + SCl_2 \rightarrow S_3N_2Cl_2 + S + 4HCl$$

It is possible that the following could also occur. (c.f. formation of phosphonitrilic compounds[123].)

$$NH_2SCl \rightarrow (NH{=}S)$$

$$(NH{=}S) + SCl_2 \rightarrow HCl + ClSNS$$

$$ClSNS + NH_4^+ \rightarrow NH_2SNS + HCl + H^+$$

$$NH_2SNS + 2SCl_2 \rightarrow S_3N_2Cl_2 + S + 2HCl$$

or $$2HNS + 2SCl_2 \rightarrow S_3N_2Cl_2 + S + 2HCl$$

The possible formation of a cyclic intermediate may occur via an S_3N_2 unit as shown:

$$2HN{=}S + SCl_2 \rightarrow S_3N_2 + 2HCl$$

$$S_3N_2 + SCl_2 \rightarrow S_3N_2Cl_2 + S$$

One fact that is difficult to explain, is the reduction in the induction period when using ammonium sulphate as a starting reagent. At first it was thought that this may be due to the relative vapour pressures of ammonium chloride and ammonium sulphate. However, thermogravimetric studies on these compounds[106], showed that ammonium chloride starts to decompose at 173°C while ammonium sulphate starts to decompose at 266°C. Perhaps the sulphate dissolved in S_2Cl_2 acts as an oxidising agent or even a catalyst, to form SCl_2 and sulphur, or a compound with the latter in a higher oxidation state.

$S_3N_2Cl_2$ should in all probability have the same structure as $S_3N_2F_2$ which Glemser[1,45] suggests has the structure:

$$F{-}S{-}N{=}S{=}N{-}S{-}F$$

Both Jolly's mechanism for the formation of $S_3N_2Cl_2$ via $N{\equiv}S{-}Cl$, and the alternative proposed mechanism above lead to the same structure.

The only thiodithiazyl compound to have had its structure determined is $S_3N_2O_2$[54]. Details of this structure have been given in the introduction, where it will be seen that, substituting oxygen for fluorine in the $S_3N_2F_2$ structure proposed by Glemser, the sequence of the atoms is identical. The main difference is that in $S_3N_2O_2$ there are two S^{IV} and one S^{II} atoms, whereas in $S_3N_2F_2$ the number of S^{IV} and S^{II} atoms is reversed. Consequently while not expecting exact correlation of the 'sulphur-nitrogen' absorption frequencies in the I.R. spectra of $S_3N_2O_2$[107], (FIG. SP.15) and $S_3N_2Cl_2$, one would expect some degree of similarity in the pattern of the spectrum. This is in fact observed.

Mass spectral data (Table 20) on $S_3N_2Cl_2$ gave little indication as to the possible structure. However, this could have been due to the compound having broken down before reaching the ion source of the mass spectrometer. The fact that an S_3N_2 unit is present in small quantities could suggest its presence in $S_3N_2Cl_2$, although it could be equally a product of ion bombardment. One interesting factor that the spectrum does show is that the S_4N_2 unit should be reasonably stable[48].

In their studies on the characteristic vibrations of the sulphuryl

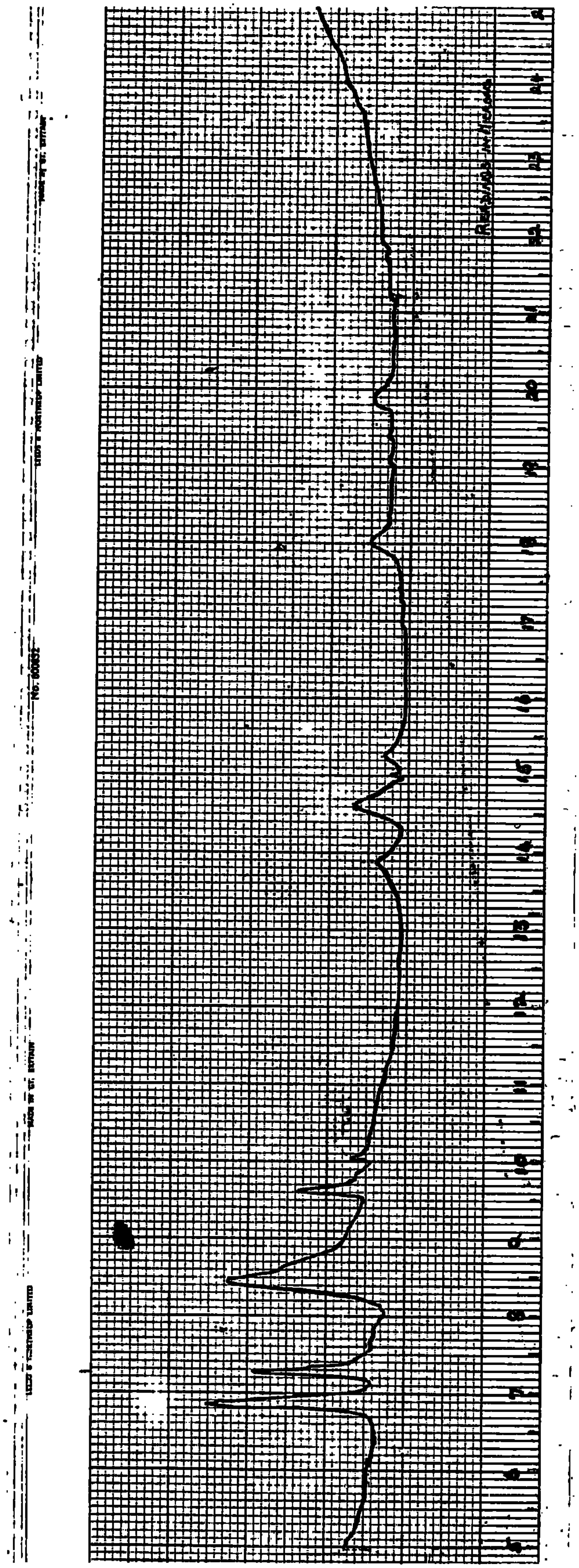


FIG. SP. 15.

I.R. SPECTRUM OF $S_3N_2O_2$[107]

Table 19

Tentative Assignment	Microns	Cm^{-1}
S=O	8.44 (s) 8.60 (m)	1,185, 1,162
S=N	9.61 (m) 9.81 (w) 10.01 (w)	1,041, 1,019 998.0
S-N	13.86 (w) 14.62 (m) 15.23 (w)	721.5 684.0 656.6
either S=O or S=N	18.00 (w) 19.88 (w)	555.6 503.0

I.R. Data of $S_3N_2O_2$

(see FIG. SP.15)

Table 20

Assigned Ion	Mass Number
Cl	35 and 37
S	32
S_2	64
SN	46 and 48
SCl	67 (and others)
S_2N	78
NSCl	81
S_2N_2	92 and 94
SCl_2	102, 104, 106
S_3N_1	110, 112
S_3N_2	124
S_3N_3	140
S_4N_2	156, 158, 160

Mass Spectral Data of $S_3N_2Cl_2$

(Ion Source Temp. 230±10°C)

group, Robinson[108], and Gillespie[109], plotted the stretching frequencies of different sulphuryl species against the known bond lengths, and obtained a relatively smooth curve. Using this plot as a standard, they then were able to predict the bond lengths of compounds, the structural details of which were unknown. Employing the same technique it has been found[110] that a similar smooth curve can be obtained for 'sulphur-nitrogen' stretching frequencies (see fig. 3). Using this plot the predicted 'sulphur-nitrogen' bond lengths for $S_3N_2O_2$ and $S_3N_2Cl_2$ are as shown:

$S_3N_2O_2$	S=N = 1.56 ± .02Å S-N = 1.79 ± .04Å	$S_3N_2Cl_2$	S=N = 1.59 ± .02Å S-N + 1.75 ± .04Å

These values were calculated from an average of the absorption frequencies of S=N and S-N, given in Tables 19 and 7. The corresponding bond lengths for S=N and S-N in $S_3N_2O_2$, as determined by Weiss[54], were S=N = 1.58Å and S-N = 1.69Å, showing poor agreement between the determined and predicted bond length of S-N.

Solvent extraction proved of little value in attempts to recrystallise $S_3N_2Cl_2$. In fact it appeared that either some reaction took place or that $S_3N_2Cl_2$ decomposed to give S_4N_3Cl or S_4N_4 (see FIG. SP.3). This supports the note made by Jolly[25] that S_4N_3Cl can be obtained from $S_3N_2Cl_2$ simply by heating it in some solvent which does not have to be S_2Cl_2 as reported by Meuwsen[21].

In his studies on the sublimation of $S_3N_2Cl_2$, Jolly states that 'when $S_3N_2Cl_2$ is heated to 80-95°C in vacuo, greenish-black S_3N_2Cl is formed:

$$3S_3N_2Cl_2 \longrightarrow 2S_3N_2Cl + 2NSCl + SCl_2'$$

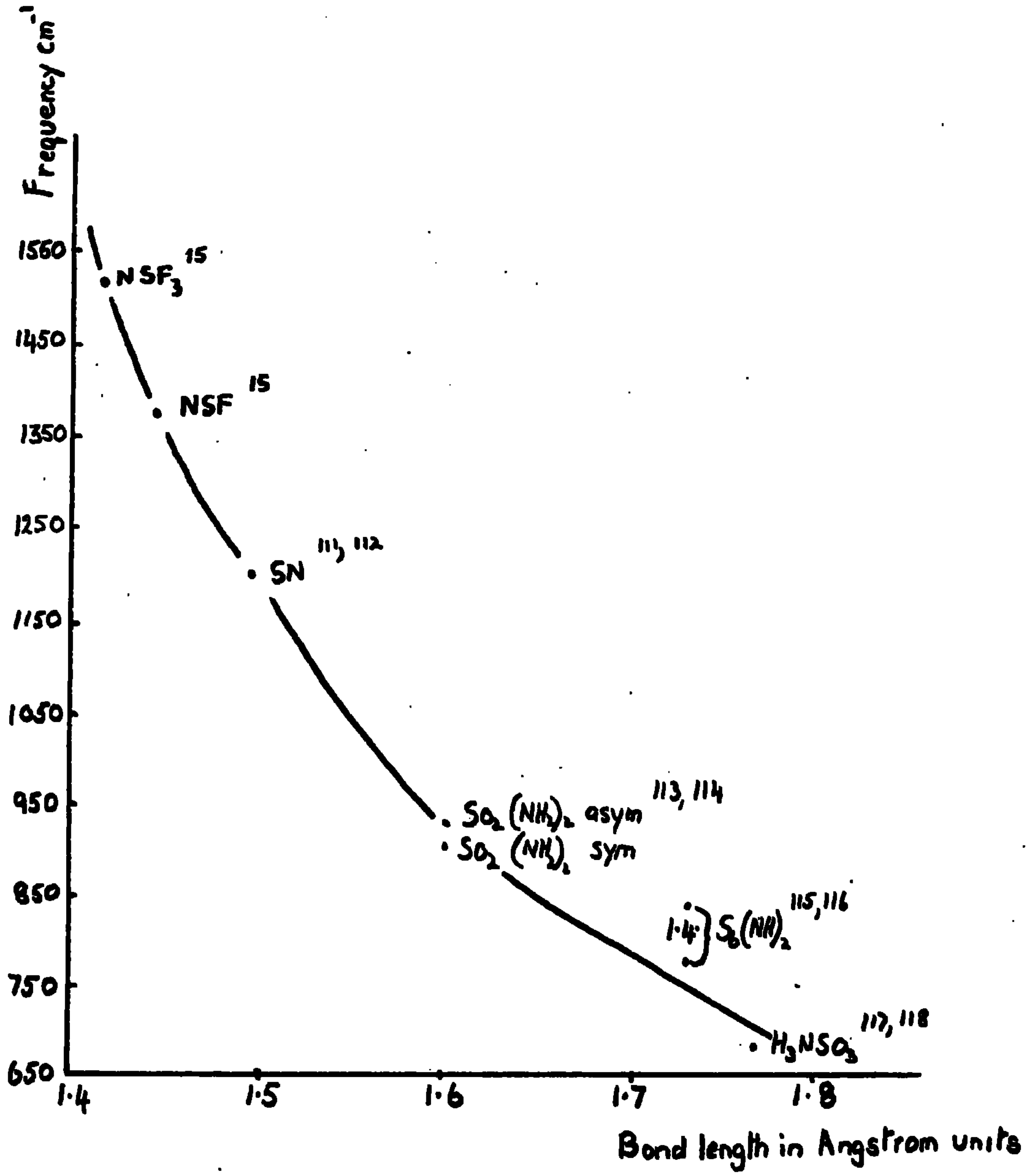


FIG. 3

CORRELATION OF ABSORPTION FREQUENCY AND BOND LENGTH FOR 'SULPHUR-NITROGEN' BONDS

As can been seen no details of the actual experimental conditions are given. When this work was repeated it was found that different sublimates could be obtained depending on the temperature of the cold finger (see FIGS. SP.4 and SP.5). Sublimation of $S_3N_2Cl_2$ at 80-95°C onto a liquid nitrogen cooled finger gave an orange/brown sublimate the I.R. spectrum of which (FIG. SP.4) showed that the principal product was $S_3N_2Cl_2$. Furthermore earlier experiments at room temperature and at 50-60°C, which gave low yields of yellow/orange sublimates would suggest that the pure product could be obtained at a sublimation temperature of about 70°C.

When the sublimation was repeated at 80-95°C, but in this case using a water cooled finger, a deep red sublimate and a green/black deposit were obtained. The I.R. spectra of these products are shown in FIG. SP.5. Close examination of these spectra showed that the two products must be very similar. Comparison of FIG. SP.5a and b, with FIG. SP.6c, (the I.R. spectrum of the product from the reaction of $S_3N_2Cl_2$ with hydrogen sulphide) showed the spectra to be identical. From evidence which will be considered later, it was concluded that the green deposit was the S_3N_2Cl reported by Jolly.

The structure of S_3N_2Cl is unknown although its involatility and insolubility and the fact that no monomeric structure can be formulated, suggests that it is at least a dimer and very probably a polymer $(S_3N_2Cl)_x$ where X must be an even number. Examination of the spectrum of S_3N_2Cl shows two absorption frequencies in the S=N stretching region.

These are closer together than in $S_3N_2Cl_2$.

Using Robinson's and Gillespie's method of plotting absorption frequencies versus bond lengths, the predicted sulphur-nitrogen distances in S_3N_2Cl are:

$$S{=}N = 1.59 \pm .02Å \qquad S{-}N = 1.76 \pm .03Å$$

These bond lengths were calculated from an average of the S=N and S-N absorption frequencies given in Table 9.

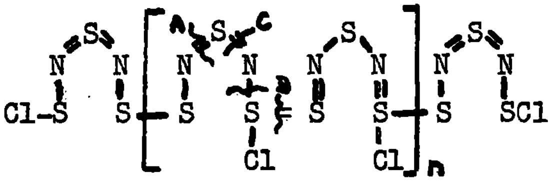
Reactions of $S_3N_2Cl_2$ with various reagents in an attempt to substitute the chlorine atoms for alternative groups, did not prove particularly successful. In general the procedure was $S_3N_2Cl_2 + 2MX = S_3N_2X_2 + 2MCl$. In the reaction with isopropanol the sulphur-nitrogen compound obtained was tetrasulphur-tetranitride. This was undoubtedly the same product as that obtained from the reaction between $S_3N_2Cl_2$ and phenyl lithium. However, as mentioned in the experimental section, the I.R. spectra of these products show great resemblances to S_4N_4, even though there are differences in the 18-19 micron region from a spectrum of pure S_4N_4. It will be recalled that in the phenyl lithium reaction the possibility of the formation of S_3N_2 was mentioned. This was based on a comparison of the mass spectral data of S_4N_4 and the product from this reaction. Both the spectra were practically identical except for a peak at 124 mass units in the mass spectrum of the product from the phenyl lithium reaction. This mass unit corresponds to S_3N_2. The presence of the S_3N_2 unit could have been due to the length of time the product was in the ion source rather than being present in the original compound.

When $S_3N_2Cl_2$ was reacted with hydrogen sulphide, the product formed gave an I.R. spectrum identical to the I.R. spectrum of the deposit from the sublimation of $S_3N_2Cl_2$ (c.f. FIG. SP.6c and FIG. SP.5a and 5b, Tables 9 and 10). It was thought that this product was S_3N_2Cl.

In the reaction of $S_3N_2Cl_2$ with chloroform, three separate products were obtained (FIG. SP.7, Table 12). Refluxing $S_3N_2Cl_2$ with chloroform for several hours gave S_4N_4 (FIG. SP.7a), while when the same reagents were heated for a shorter time the product was S_4N_3Cl (FIG. SP.7b), and when the reagents were allowed to stand at room temperature for 2-3 days the product was shown to be a mixture of $S_3N_2Cl_2$, S_3N_2Cl and S_4N_3Cl (FIG. SP.7c).

Although this reaction did not give the desired products, it is interesting since it almost certainly indicates the pattern of the breakdown of $S_3N_2Cl_2$. Thus it would appear that on heating, $S_3N_2Cl_2$ initially forms S_3N_2Cl which in turn gives S_4N_3Cl, and the latter, under continual reflux, is finally converted to S_4N_4. It was noticed that in this reaction the evolution of HCl was very slow but on the formation of S_4N_3Cl it tended to be faster. Jolly et. al.[25] noted that when S_3N_2Cl was heated to 130-150°C in vacuo a variety of products including NSCl and SCl_2 were evolved and a residue of pure S_4N_3Cl was formed. If one considers that S_3N_2Cl is a polymer $(S_3N_2Cl)_x$ then it is possible that this could decompose to give S_4N_3Cl, SCl_2 and NSCl.

Since S_4N_3Cl is ionic, i.e. $S_4N_3^+Cl^-$, the positions for rupturing $(S_3N_2Cl)_x$ are not determined by the position of any S-Cl bond in S_4N_3Cl.



where n = x-2

Thus it will be seen, that having ruptured $(S_3N_2Cl)_x$ at point A, further decomposition could occur either by the loss of $\frac{1}{2}S_2Cl_2$ (rupturing at B) or by the loss of sulphur and NSCl (by rupturing at C).

In the reaction with dimethylformamide at room temperature, the product obtained was shown to be a mixture of S_4N_3Cl and S_3N_2Cl (FIG. SP.8a). Presumably these products formed in the similar manner to those in the reaction with chloroform. A possible general mechanism is given below:

$$x(S_3N_2Cl_2) + xHX \longrightarrow (S_3N_2Cl)_x + xHCl + \frac{x}{2}X_2$$

$$\text{or} \quad x(S_3N_2Cl_2) \xrightarrow{heat} (S_3N_2Cl_2)_x$$

$$(S_3N_2Cl_2)_x + xHX \longrightarrow (S_3N_2Cl)_x + xHCl + \frac{x}{2}X_2$$

$$(S_3N_2Cl)_x \longrightarrow S_4N_3Cl \qquad \text{as above}$$

The spectrum of the products from the reaction $S_3N_2Cl_2$ with stannic chloride has already been discussed. Examination of FIGS. SP.1a, SP.7b and SP.8b, Tables 6, 12 and 13, will show that several peaks are common to these spectra. There is not an exact correspondence to S_4N_3Cl and therefore it would seem that this product may contain an ion similar to S_4N_3Cl although this is by no means certain.

Part II

Thiodithiazyldiphenyl

Initial reactions between S_4N_4 and phenyl magnesium bromide to form thiodithiazyldiphenyl proved to be unsuccessful. This was partially due to insufficient data on experimental procedure. However, after several experiments the following facts were ascertained:

1. It is essential to have the ratio of PhMgBr:S_4N_4 not greater than 2:1
2. As a consequence of (1) the Grignard reagent must be added to the S_4N_4 solution and not vice versa
3. The reaction should be carried out at room temperature or below, and while this was not done in toluene, it is recommended that it may well prove beneficial to do so rather than in benzene, since the former can be cooled well below room temperature
4. On mixing the reagents they should be allowed to stand for at least an hour before the addition of the 5% acid solution

Diphenyl disulphide (FIG. SP.9a) and S_4N_4 (FIG. SP.9b) were obtained from the first two preparations and the product m.p. 97°C formed in Experiment 3 was shown by Infra Red spectra (FIG. SP.9c) to probably contain some S_4N_4. This was suspected by the existence, in the I.R. spectrum, of absorption frequencies at 10.83, 18.12 and 18.35 microns which are very close to similar absorptions in the S_4N_4 spectrum. (c.f. Table 12 and Table 14). However, the spectrum of the product showed little similarity to that of S_4N_4 in the region 13-15 microns and thus indicated the possibility of adduct formation between S_4N_4 and $S_3N_2Ph_2$. This will be discussed later. The orange product synthesised in Experiment 4, m.p. 86-87°C was shown from the I.R. spectrum (FIG. SP.10a) to contain some diphenyl disulphide and on recrystallisation the similarly coloured product m.p. 99°C was shown (FIG. SP.10b) to be identical spectroscopically to the gold product (FIG. SP.10c) and the brown crystalline product (FIGS. SP.14a and 14b). Analysis figures for the orange sample (FIG. SP.10b) were C=50.4% and H=3.47%. (Theor. C=51.76%, H=3.62%).

The gold product m.p. 102°C from Experiment 5 again showed a slight absorption at 18.30 microns, although the carbon-hydrogen analysis was very close to the theoretical value for $Ph_2S_3N_2$ (Calc. C=51.9%, H=3.99%: Theor. C=51.76%, H=3.62%).

It is of interest to note that when the recrystallising solvent was petrol ether, the product obtained was orange coloured. It has been noted in the introduction that Farrar[31] commented on the use of solvents such as acetone, methanol and ethanol in working up similar thiodithiazyl compounds. Thus while elemental analysis of products recrystallised from trichloroethylene and acetone etc. showed them to be different, no explanation of this was given by Farrar. However, I.R. spectra of the gold and orange samples of $S_3N_2Ph_2$ showed that there was little or no difference between them.

Chromatographic extraction proved of little value in purifying $S_3N_2Ph_2$. Repeated experiments indicated that any $S_3N_2Ph_2$ was broken down to diphenyl disulphide on the extraction column. The evidence is not conclusive since the impure sample would probably contain diphenyl disulphide. Nonetheless, some $S_3N_2Ph_2$ was present in the dissolved sample and was not found in any fraction extracted.

The results from Experiment 7 proved that the solid formed on the addition of PhMgBr to S_4N_4 was an essential intermediate in the formation of $S_3N_2Ph_2$. One factor difficult to explain is that atmospheric hydrolysis of this intermediate compound gave S_4N_4 (FIG. SP.11a) while acid hydrolysis of the same intermediate gave, among other things, the required product again with some S_4N_4 (FIG. SP.11b). Sublimation of the latter product at 84°C left a deposit m.p. 101°C, the I.R. spectrum of which had all the characteristics of $S_3N_2Ph_2$ (FIG. SP.11c), while the sublimate was shown to be S_4N_4. Consequently purification of $S_3N_2Ph_2$ by sublimation is possible.

The nature of the colourless leaflet crystals obtained in Experiment 8 is unknown, and the I.R. spectrum of this sample (FIG. SP.12a) gave little information other than the fact that phenyl, phenyl-sulphur and sulphur-nitrogen bonds were probably present. Purification of this sample by chromatographic extraction[101] proved unsuccessful since the extracts were shown to be diphenyl disulphide (FIG. SP.12b) and some compound with a similar but not identical spectrum to diphenyl disulphide (FIG. SP.12c).

In further purifications of $S_3N_2Ph_2$ repeated recrystallisations from alcohol were attempted (see Experiment 9). Four recrystallisations gave a sample m.p. 95°C (analysis figures C=20.4%, H=1.57%). The I.R.

spectrum of this sample (FIG. SP.13a) showed the presence of S_4N_4, in a ratio $S_3N_2Ph_2$:S_4N_4 equal to 1:2.32 which is approximately 3:7. When this sample was recrystallised twice more it gave a m.p. 101°C (analysis figures C=44.9%, H=3.16%). I.R. data on this sample (FIG. SP.13b) showed that the quantity of S_4N_4 was drastically reduced and that the region 13-15 microns showed no absorptions common to S_4N_4 in the same region, again indicating the possibility of adduct formation. The ratio $Ph_2S_3N_2$:S_4N_4 based on the carbon analysis was 4.33:1 which is approximately 13:4. Recrystallisation of the latter sample once more gave a product m.p. 101°C (analysis figures C=45.8%, H=3.35%) which indicated a ratio of $Ph_2S_3N_2$:S_4N_4 equal to 5.1:1. Each recrystallisation was carried out by dissolving the sample in hot alcohol and filtering any insoluble material. In every case the latter proved to be S_4N_4 and therefore, it was felt that probably $S_3N_2Ph_2$ decomposed on warming to give S_4N_4 and diphenyl sulphide i.e.

$$2S_3N_2Ph_2 \longrightarrow 2Ph_2S + S_4N_4$$

Consequently, the final recrystallisation was executed by dissolving the product in alcohol at room temperature, dividing the solution into two parts: the first was chilled rapidly in an acetone slush bath and gave a gold product m.p. 97°C (FIG. SP.13c) with analysis figures of C=51.9%, H=3.59% which were very close to the theoretical values, even though the I.R. spectrum still showed the possible presence of S_4N_4. The second part was cooled for several days at -10°C and gave rust coloured needle crystals with identical melting point, analysis figures and I.R. spectrum to the product from Experiment 10 (c.f. FIG. SP.14a and 14b). This product, m.p. 103.5°C, formed rust coloured needle crystals with analysis figures C=52.3%, H=3.59%, S=34.02%, N=10.59%. (Theor. C=51.76%, H=3.62%, S=34.55%, N=10.06%). The spectra of this product (FIG. SP.14b) showed no sign of S_4N_4.

It is doubtful whether S_4N_4 and $S_3N_2Ph_2$ form adducts. Certain evidence suggested possible adduct formation. This was:

1. The very slow change in composition of impure $S_3N_2Ph_2$ on repeated recrystallisation from ethyl alcohol (Experiment 9). This is, however, explained by fortuitous solubility similarities for S_4N_4 and $S_3N_2Ph_2$ in this particular solvent.
2. Successive recrystallisations of impure $S_3N_2Ph_2$ (Experiment 9) gave samples of melting points 95°C (after four recrystallisations), 101°C (after six recrystallisations), 101°C (after seven recrystallisations), and 97-98°C (after eight recrystallisations). The fact that the melting points increased to 101°C and then dropped to 97°C suggested either compound formation or excessive destruction of $S_3N_2Ph_2$ to S_4N_4.
3. Infra Red spectra (FIG. SP.10b, 10c) showed absorptions at 10.75, 18.10 and 18.30 microns which are common to S_4N_4 (FIG. SP.7a). However, the region 13.5 to 15 microns did not appear to resemble the I.R. spectrum of S_4N_4 in the same region. Close examination of the I.R. spectrum of pure $S_3N_2Ph_2$ (FIG. SP.14) with the I.R. spectrum of a mixture of S_4N_4 and $S_3N_2Ph_2$,

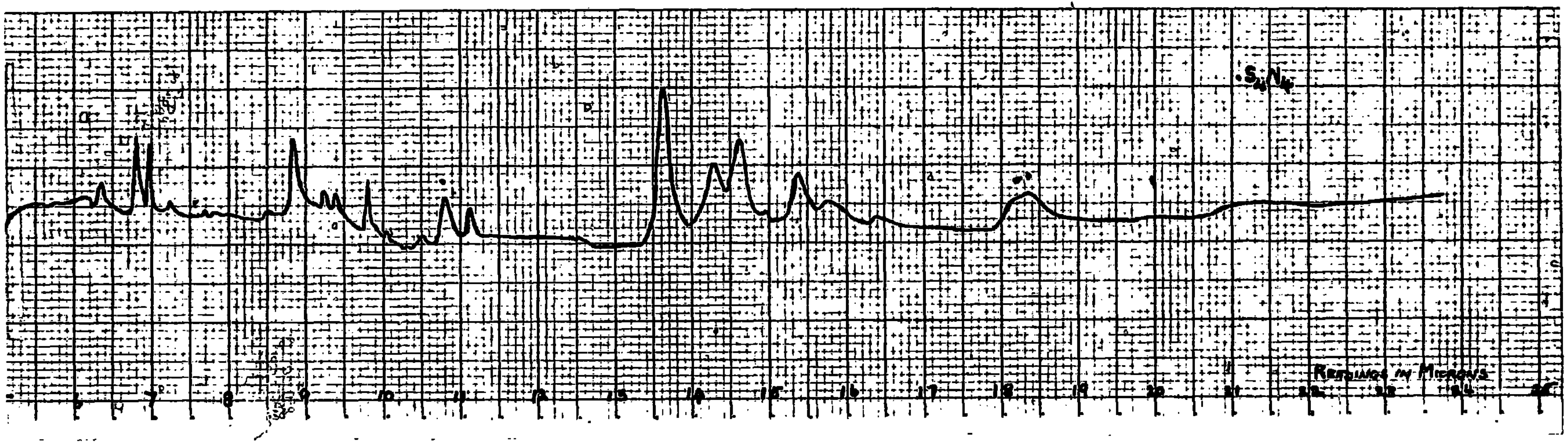


FIG SP. 16.

I.R. SPECTRUM OF $S_4N_4 + S_3N_2Ph_2$ MIXTURE IN APPROXIMATE RATIO 1 : 5

in the ratio 1:5 showed that the 14.21 micron absorption (FIG. SP.14b) was present as a shoulder in FIG. SP.16, while the 14.33 micron absorption (FIG. SP.16) was absent from the spectrum of the pure product (FIG. SP.14). Comparison of the spectra of pure S_4N_4 and $S_3N_2Ph_2$ (FIG. SP.16) and the samples where adduct formation was suspected (FIGS. SP.13b and 13c) showed them to be identical in the 13.5 to 15 micron region, both in intensity and position of absorption. This does not disprove that $S_3N_2Ph_2$ could not form adducts with S_4N_4 but suggests that adduct formation did not occur.

Three coloured forms of $S_3N_2Ph_2$ have been obtained; gold, orange and brown. The gold and orange samples tended to form leaflet crystals while the brown sample had a needle formation. A P.S.R. spectrum of a carbon tetrachloride solution of the gold (FIG. SP.10c) and orange (FIG. SP.10b) samples gave two identical spectra. It is unknown whether there is any difference between these species but it was thought that the difference in colour of the leaflet crystals may have been due to reflected light in the gold sample and transmitted light in the orange sample.

When phenyl magnesium bromide in ether was added to the S_4N_4 benzene solution, an orange/brown precipitate formed immediately. The instant formation and the fact that it is broken down by acid hydrolysis or excess Grignard reagent suggests that the orange/brown precipitate is a complex of S_4N_4 and PhMgBr with donation occurring through the sulphur or nitrogen atoms, (see Figs. 4 and 5). Precisely how hydrolysis breaks the complex

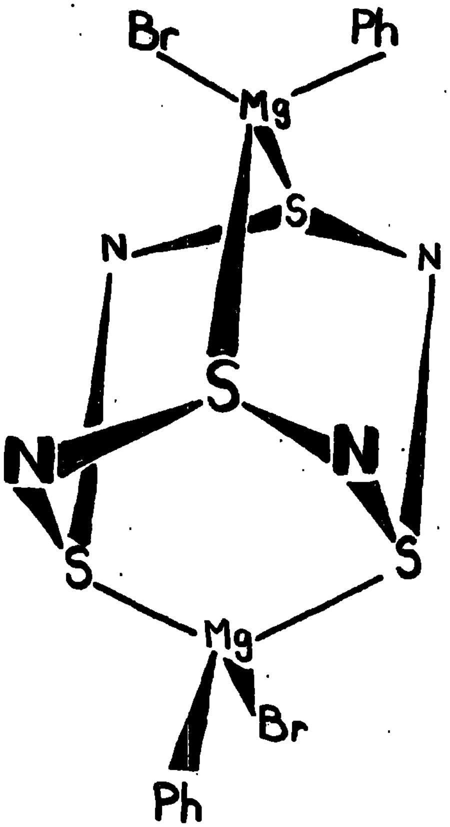


FIG. 4

HYPOTHETICAL COMPLEX BETWEEN S_4N_4 AND PhMgBr

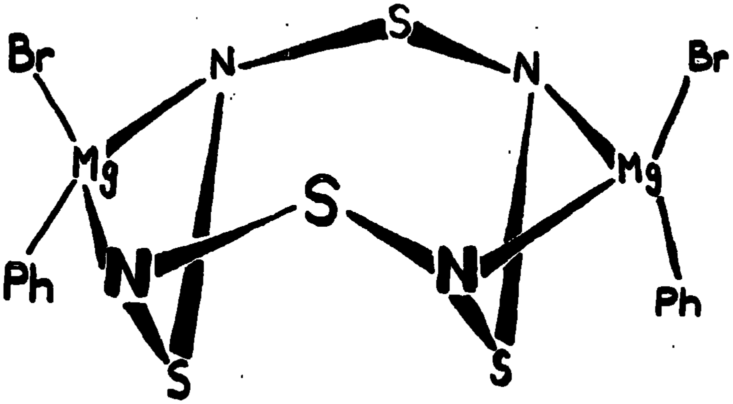
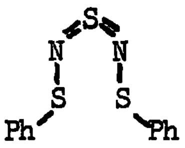


FIG. 5

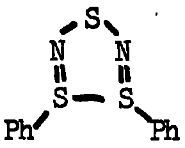
HYPOTHETICAL COMPLEX BETWEEN S_4N_4 AND PhMgBr to give $S_3N_2Ph_2$ is difficult to envisage if donation occurs through sulphur (Fig. 4). Examination of Fig. 5 shows that on hydrolysis the phenyl groups could migrate to the sulphur atoms to give $S_3N_2Ph_2$ and therefore this structure is more feasible, particularly in view of the fact that nitrogen to magnesium donation is stronger relative to its sulphur counterpart[124].

Mass spectral data of $S_3N_2Ph_2$ showed the presence of the ions given in FIG. SP.17 and Table 21. Each ion was 'weighed' to 6ppm. The breakdown pattern, Fig. 6, was deduced from a spectrum obtained while the ion repeller voltage was high, thus amplifying metastable species in the spectrum. The dotted lines (Fig. 6) represent unconfirmed breakdown paths; the curved lines represent confirmed but minor breakdown routes, and the full straight lines represent the major breakdown route. Since the main breakdown is by loss of SN_2, it would seem possible that the structure of $S_3N_2Ph_2$ could be either



(a)

or



(b)

Comparison of the I.R. spectrum of $S_3N_2Ph_2$ (FIG. SP.14b) with the I.R. spectrum of diphenyl disulphide shows many similarities. Scrutiny of these spectra enabled the author to assign tentatively certain absorption frequencies of $S_3N_2Ph_2$ to S=N and S-N stretching frequencies (see Tables 13-15, 17, 18 for $S_3N_2Ph_2$; Table 16 for Ph_2S_2). Furthermore, the

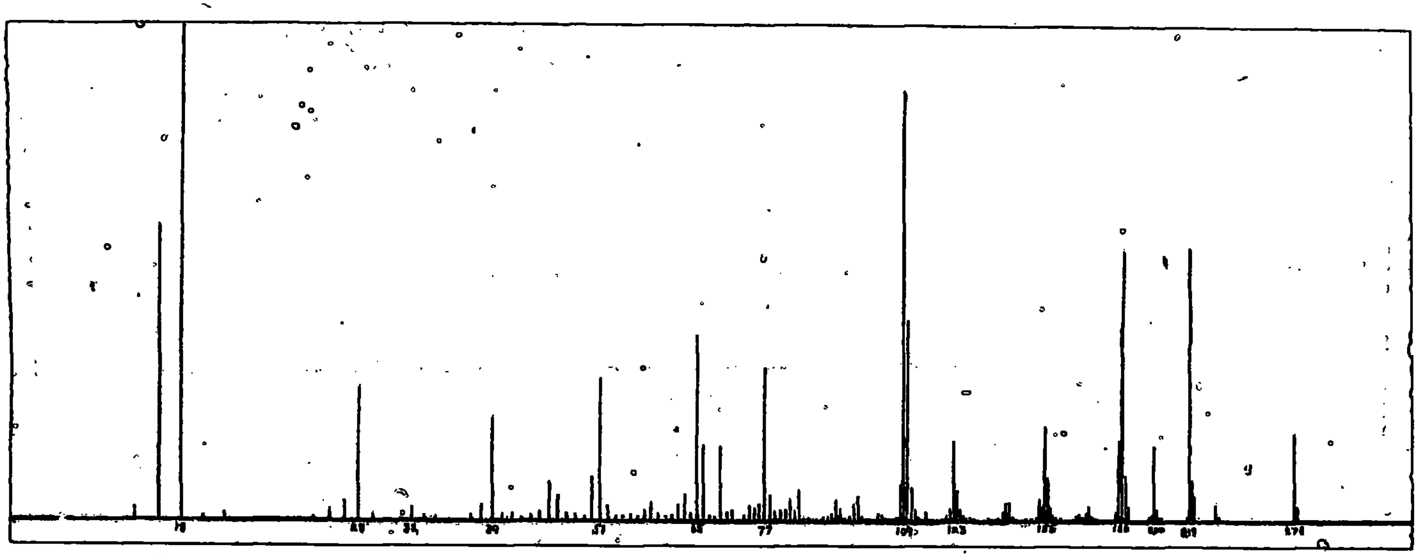


FIG. SP. 17.

MASS SPECTRUM OF $S_3N_2Ph_2$

Table 21

Mass Number	Assigned Ion Ion Source Temp. 230±10°C
28	N_2
32	S (v. small because charge carried by Phenyl groups)
46	(Probably some S-N)
39, 45 51, 65 66, 69	Mainly Phenyl breakdown
77	Ph
109	SPh
123	SNPh
154	Ph_2
155	S_2NPh
186	Ph_2S
200	$SNPh_2$
218	S_2Ph_2
232	S_2NPh_2
250	S_3Ph_2
278	$S_3N_2Ph_2$

Mass Spectrum of Brown Crystalline

$S_3N_2Ph_2$

(See FIG. SP.17)

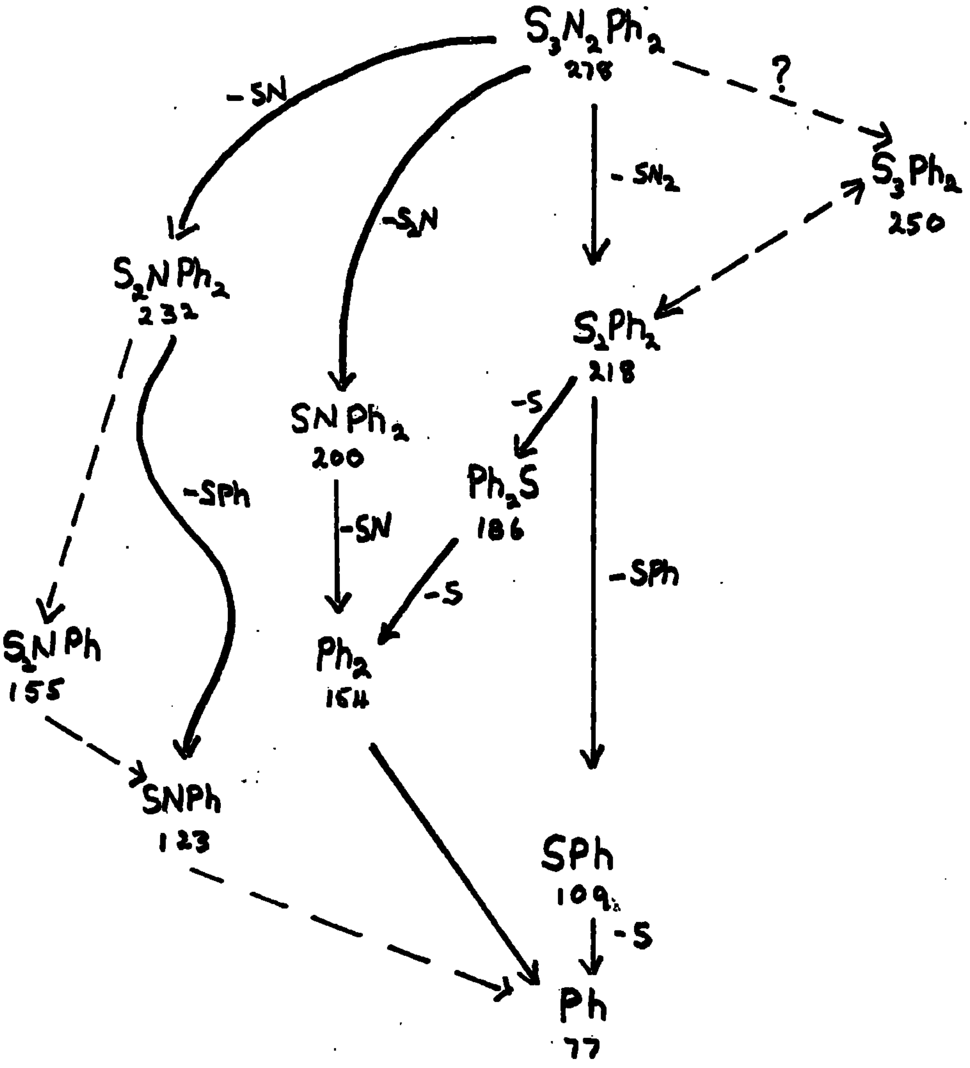


FIG. 6

MASS SPECTRAL BREAKDOWN OF $S_3N_2Ph_2$

(see FIG. SP.17)

similarity of the weak absorptions in the 20.5-21.5 microns ($S_3N_2Ph_2$ - FIG. SP.14b) and 21.0-22.0 microns (Ph_2S_2 - FIG. SP.12b) could suggest that the S-S bond is present in $S_3N_2Ph_2$, thus favouring structure (b) above.

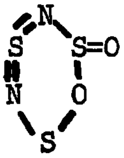
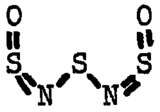
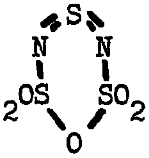
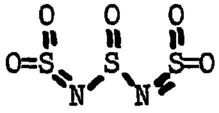
Using Robinson's and Gillespie's method of plotting absorption frequencies versus bond lengths, and taking an average value of the stretching frequencies of S=N and S-N given in Tables 13-15, 17 and 18, the predicted 'sulphur-nitrogen' bond lengths in $S_3N_2Ph_2$ are:

$S{=}N = 1.52 \pm .02\text{Å}$ $\quad$ $S{-}N = 1.82 \pm .04\text{Å}$

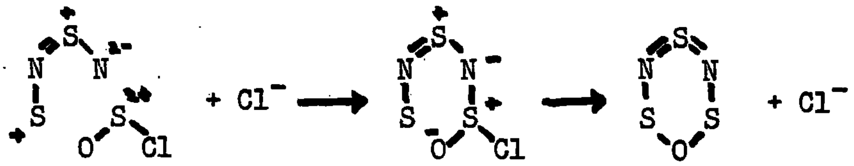
APPENDIX

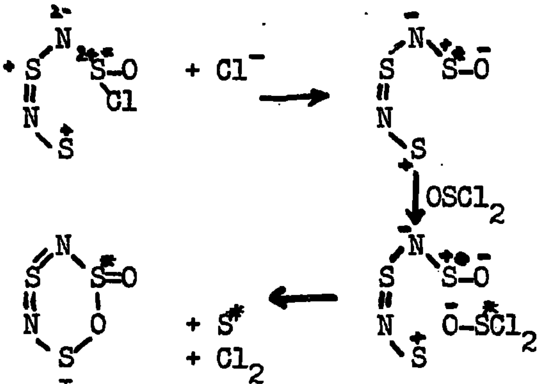
Thiodithiazyl Oxides

It will be recalled that in the introduction structures for S_3N_2O, $S_3N_2O_2$ and $S_3N_2O_5$ were recorded as given by Goehring[48], and that alternative structures were given for these compounds. The structures are given again below:

	Structure		
Formula	Goehring	Alternative	
S_3N_2O			See Ref. 33
$S_3N_2O_2$			Structure known[54]
$S_3N_2O_5$			

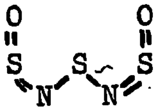
The formation of S_3N_2O and $S_3N_2O_2$ occurs, according to Goehring, via an S_2N_2 unit as follows:





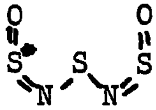
I

The structure of $S_3N_2O_2$ is known to be:



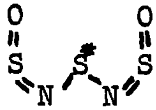
and consequently one might expect the formation to occur as above, but with structure I opening to give:

II

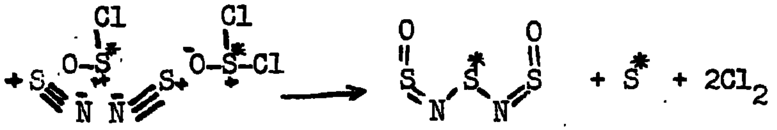


However, Goehring reports that on heating $S^*S_2N_2O_2$ gives S^*O_2 and $\frac{1}{2}S_4N_4$. If $S_3N_2O_2$, II, formed as suggested, there seems no reason why all the SO_2 should contain the labelled sulphur. Indeed one would logically expect that on heating four moles of $S_3N_2O_2$, the products would be $2SO_2 + 2S^*O_2 + S_4N_4 + S^*S_3N_4$. Since only the SO_2 contains the labelled sulphur, one can only suggest from the known structure of $S_3N_2O_2$, that the labelled sulphur atom is in an environment common only to itself, i.e. structure III.

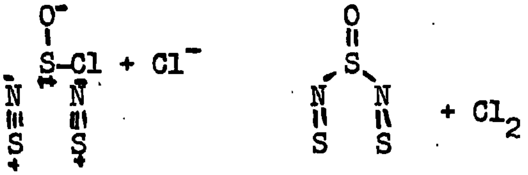
III



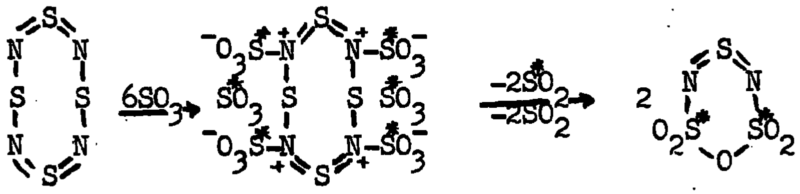
If this is true the formation must occur via S–N units



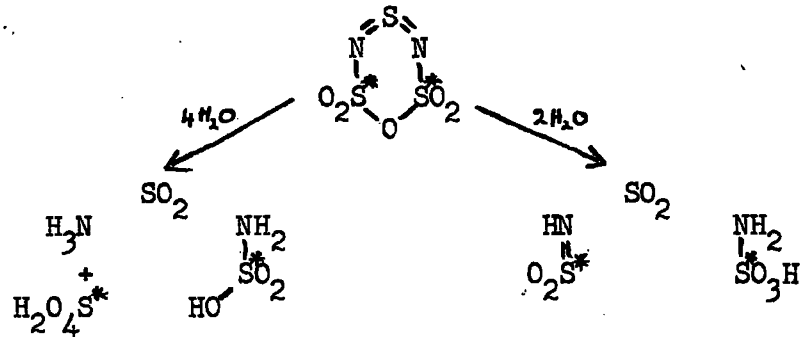
The formation of S_3N_2O, having the alternative structure suggested by Meuwsen[33], could be formed in a similar manner



$S_3N_2O_5$ having the structure suggested by Goehring, was formed from S_4N_4 and S^*O_3 as follows:

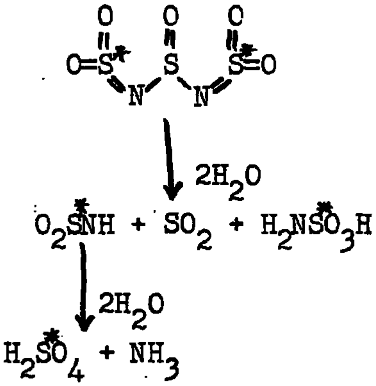


The structure was based on the hydrolysis products formed as shown



Hydrolysis of the alternative structure for $S_3N_2O_5$, IV, could also give the required products, providing the terminal sulphur atoms were the ones labelled

IV



S_4N_4 and $\overset{*}{S}O_3$ could initially form a complex $S_4N_4.4\overset{*}{S}O_3$ (c.f. Goehring), which could then be oxidised, by further $\overset{*}{S}O_3$ attacking the sulphur atoms of the S_4N_4 unit, thereby giving $S_3N_2O_5$ as shown in structure IV.

The Mass Spectrum of S_4N_4

The mass spectrum of S_4N_4 was recorded using the direct insertion probe technique. The spectrum obtained varied a little depending on the time the sample was in the ion source, prior to recording the spectrum. Thus if the time was short, S_3N_2 (124 mass units) was absent. The mass spectral data of S_4N_4 is recorded in Table 22, and the abundance of each ion, relative to S_4N_4 equal to unity, is recorded in Table 23.

It is interesting to note that the abundance values of S_3N_3 and SN are large and approximately equal. These values are not only a measure of the quantity of each ion present, but also, presumably, some indication of their stabilities. If this is so, the $S_3N_3^+$ ion should be more stable than the $S_4N_4^+$ ion, and the SN ion could be $S_3N_3^{3+}$ rather than $S_4N_4^{4+}$. Possible structures for the S_3N_3 ions are given below:

$S_3N_3^{3+}$

$S_3N_3^{+}$

The abundance value for the SN ion does not ofcourse nec~~c~~essarily indicate that the ion is $S_3N_3^{3+}$. Indeed, the fact that S_2N_2 is present to 2.7 times the abundance of $S_4N_4^+$ indicates either, the ease with which S_4N_4 ionizes to $S_4N_4^{2+}$, or the ease with which S_4N_4 breaks down to give $S_2N_2^+$. Thereforethere would seem no reason why S_4N_4 should not break down to SN^* or form $S_4N_4^{4+}$.

Closer examination of the spectrum reveals that masses 185, 186, 187

Table 22

Assigned Ion	Mass Number
N_2	28
S	32
SN or $S_4N_4^{4+}$	46
$S_3N_2^{2+}$	62?
S_2	64
S_2N	78, 80
S_2N_2 or $S_4N_4^{2+}$	92, 93, 94
S_3N	110, 112
S_3N_2	124, 126
S_3N_3	138, 139, 140, 141, 142
S_4N_4	184, 185, 186, 187, 188

Mass Spectrum of S_4N_4

(Ion Source Temp. 230±10°C)

Table 23

Assigned Ion	Mass Number	Abundance
SN	46	7.92
$S_3N_2^{2+}$	62?	0.15
S_2	64	0.25
S_2N	78	3.00
S_2N_2	92	2.71
S_3N	110	0.50
S_3N_2	124	0.15
S_3N_3	138	8.60
S_4N_4	184	1.00

Abundance of Species Present in Mass Spectrum of S_4N_4

(Relative to $S_4N_4 = 1$)

and 188, for S_4N_4, and masses 93, 94, 95 and 96, for S_2N_2, are all doublets, while the masses for S_3N_3, 138-142, and SN, 46-48, are all singlets. This may be a further indication that the S_2N_2 mass unit corresponds to $S_4N_4^{2+}$, and that the SN mass unit corresponds to $S_3N_3^{3+}$.

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