Some derivatives of trithiatriazine

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SOME DERIVATIVES OF TRITHIATRIAZINE

by

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1967 and July 1970. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference. Part of this thesis has been the subject of the following publication

Synthesis of Some Trimeric Sulphanuric Compounds: Methylsulphanuric Dichloride, Bis(dichlorophenyl)-sulphanuric Chloride, Di(n-octylamino)- and Bis(diethylamino)sulphanuric Fluorides by A.J. Banister and (Miss)B. Bell.

Journal of the Chemical Society, Section A, 1970. p.1659.

ABSTRACT

This thesis can be conveniently divided into two parts (a) the reactions of trimeric sulphanuric chlorides and fluorides, and (b) the investigation of reactions of trithiazyltrichloride, thiodithiazyldichloride and their derivatives with epoxides and with nitriles and other unsaturated systems.

(a) Reactions of Sulphanuric Halides

The replacement of chlorine and fluorine in the sulphanuric halides $(NSOCl)_3$ and $(NSOF)_3$ by aliphatic, aromatic, amino and thioalkoxy groups has been investigated. The bromination and iodination of $(NSOCl)_3$ was attempted, and the following new compounds were identified: $(NSO)_3Cl_2Me$, $(NSO)_3Cl(C_6H_3Cl_2)_2$, $(NSO)_3F(NEt_2)_2$, $(NSO)_3F(NC_8H_{18})_2$. Evidence was found for the existence of $(NSONMe_2)_3$, $(NSO)_3(SEt)_nCl_{3-n}$, $(NSOBr)_n$, $(NSOI)_n$ and $(NSO)_3Ph_2(o\text{-}C_6H_2Cl_3)$. The mass spectral fragmentation pattern of $(NSO)_3Ph_2F$ was investigated.

(b) Reactions of $(NSCl)_3$, $S_3N_2Cl_2$ and their derivatives

The investigation of the reactions of $(NSCl)_3$ with epoxides and nitriles commenced by Dr. G.G. Alange (Ph.D. Thesis, University of Durham, August 1969) was continued, and extended to other strained and unsaturated systems, namely episulphides and isocyanates. The reaction with nitriles yielded products of the type S_2N_2CClR where R is phenyl, t-butyl and

trichloromethyl. This system, S_2N_2CClR is compared with that of 1,2,5-thiadiazoles and $S_3N_2Cl_2$. A study of the reaction of $S_3N_2Cl_2$ with sulphuryl chloride led to a convenient new synthesis of trithiazyl trichloride. The reactions of $S_3N_2Cl_2$ with thionyl chloride and trichloromethylacetonitrile were also investigated. The reaction of epichlorohydrin with "$(NSCl)_3$" - prepared by rapid chlorination by chlorine gas of S_4N_4 - was investigated.

Results of both sections are generally discussed and an appendix covers the use of the chlorine isotope pattern for identifying fragments in the mass spectrum.

CONTENTS

Chapter 5 Reactions of trithiazyltrichloride, thiodithiazyldichloride and their derivatives. I. Experimental

Chapter 1

Introduction

This introduction reviews the chemistry to June 1970 of the sulphur-nitrogen ring systems based on (i) thiodithiazyl dichloride, $S_3N_2Cl_2$, (ii) trithiazyl trichloride, $(NSCl)_3$ and (iii) sulphanuric chloride $(NSOCl)_3$. Possible schemes of nomenclature of cyclic unsaturated sulphur-nitrogen compounds are discussed and a short summary of the reactions of aryl and alkylsulphenyl chlorides is included for comparison with trithiazyl trichloride.

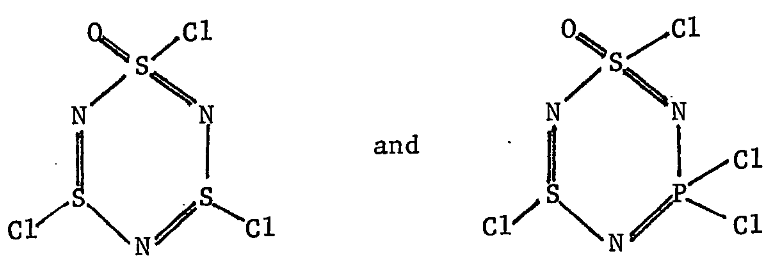
Nomenclature

Although the six-membered sulphur-nitrogen ring has been known since the end of the nineteenth century, no one systematic form of nomenclature has been evolved; compounds tend to be still called by their trivial names, e.g. sulphanuric chloride which was originally[1] proposed by analogy with cyanuric chloride, and trithiazyl trichloride which is based on the repeating unit (thiazyl, SN) in the ring. Two other systems have been proposed: 1) a cyclothiazene nomenclature, similar to that introduced by R.A. Shaw[2] for phosphonitrilic compounds, and described in the latest (1970) draft IUPAC rules for rings of repeating units. This system has been accepted by the Chemical Society.[3] 2) a nomenclature according to the 1957 IUPAC heterocyclic rules[4,5] but specifying 'abnormal' valencies of the heteroatoms. These will be discussed in turn.

For present purposes an acceptable system must specify (a) the cyclic or linear nature of each compound, (b) the degree of polymerisation of the skeleton, (c) the presence or absence of valency unsaturation, (d) the order of naming of the skeletal elements, (e) the method of designating or numbering the skeletal atoms and (f) the presence of carbon in the skeleton.

1) In the method adopted by the Chemical Society (as from January 1970)[3] the repeating unit in the ring is given based on root names, thia for sulphur, aza for nitrogen, e.g. azathiane for -S-NH- or phosphazene for -P=N-, the more electronegative element is placed last and the linear or

cyclic nature is shown by the presence or absence of the prefix cyclo. Unless otherwise specified any unsaturation is assumed to be uniform and of the Kékulé type (delocalised) or conjugated (localised π bonds); the position of the multiple bonds is therefore not specified. On this system trithiazyl trichloride would be a derivative of the hypothetical cyclotrithia(IV) azene, and α-sulphanuric chloride a derivative of the hypothetical cyclotrithia(VI) azene; being in fact S-trichlorocyclotrithia(IV) azene and S-trioxytrichlorocyclotrithia(VI) azene respectively. This system breaks down when the sulphurs have different substituents or show different valencies in the skeleton itself, or when there is not solely one repeating unit in the ring, e.g.



This system does not specify the number of atoms in the ring.

2) The method according to 1957 IUPAC heterocyclic rules specifies the number of atoms in the ring indicating the position of the heteroatoms and also follows established rules[6] for numbering the ring. In this system α-sulphanuric chloride would be 1,3,5-trichloro-1,3,5-trioxo-1,3,5,2,4,6-trithia(1,3,5 S^{VI})triazine a derivative of the hypothetical

1,3,5-trihydro-1,3,5-trioxo-1,3,5,2,4,6-trithia(1,3,5 S^{VI})triazine; prefixes a or e can be used to denote axial or equatorial substitution respectively. For rings with repeating units with equivalent valencies, the former system does provide the more manageable names, and in fact the trivial names are adequate for simple derivatives, e.g. diphenylsulphanuric chloride for 1-chloro-3,5-diphenyl-1,3,5-trioxo-1,3,5,2,4,6-trithia(1,3,5 S^{VI})triazine and trivial names will be used where possible in this thesis. The 1957 IUPAC system has the main advantage of describing exactly what the molecular formula is, which is not so with the trivial names used here.

The chemistry of thiodithiazyl dichloride

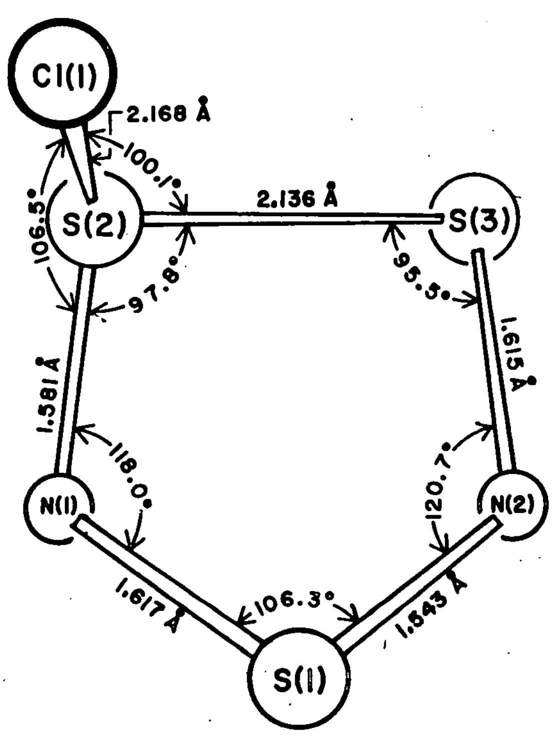
Thiodithiazyl dichloride, an ionic compound containing a five-membered sulphur-nitrogen ring as its cation (Fig.1) is the simplest unsaturated SN ring compound to prepare. It is conveniently prepared in an inert atmosphere by the reaction between ammonium chloride, disulphur dichloride and sulphur,[7] the yield being approximately 17% based on the disulphur dichloride.

$$NH_4Cl + S + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + HCl + S$$

In the absence of excess sulphur the reaction product is thiotrithiazyl chloride S_4N_3Cl. $S_3N_2Cl_2$ can also be obtained by warming a solution of trithiazyl trichloride in disulphur dichloride[8] and then allowing it to cool. The rust brown crystals separate on cooling. Pure $S_3N_2Cl_2$ is an orange crystalline solid (m.p. 89·5-90·5° decomposition[7]) which is extremely sensitive towards moisture. It cannot be kept indefinitely in the absence of moisture, although in a sealed tube under vacuum decomposition is apparently very slow, (approx. 50% in one year).[9] Jolly[10] reported that it will last in an inert atmosphere up to ten days without decomposition. When heated it decomposes with a flash of light.[11] Being ionic it is insoluble in most organic solvents;[7] it reacts instantly with water[7] yielding sulphur dioxide, ammonia and sulphur. X-ray diffraction[12] shows it to contain the five-membered ring cation $S_3N_2Cl^+$ (Fig.1).

Fig.1

Bond lengths and angles in the thiodithiazyl chloride cation



No two sulphur (or nitrogen atoms) are structurally equivalent, in contrast to $(NSCl)_3$ and $(NSOCl)_3$. It is therefore not surprising that the SN ring distances are no longer equivalent. The closest approach of the second chlorine, the anion, to the sulphur is 2·90, 2·93 and 3·04Å (S_1, S_2, S_3 respectively).

TABLE 1

SULPHUR-CHLORINE BOND DISTANCES

Oxidation State(s)	Compound	d_{SCl} Å	refs.
+1	S_2Cl_2	2·07 ± 0·01	88(b)
+2	SCl_2	2·00 ± 0·02 1·99 ± 0·03	88(a)
	CCl_3SCl	2·03 ± 0·03	88(c)
+4	$SOCl_2$	2·07 ± 0·03	88(a)
	$(NSCl)_3$	2·084 (2) 2·150	32
+6	SO_2Cl_2	1·99 ± 0·02	88(a)
	SF_5Cl	2·03	
	$(NSOCl)_3$	2·003	35

It can be seen from Table 1 that the SCl bond length generally falls in the region 1•99-2•15Å. The shortest of the three SCl distances for the final chlorine in $S_3N_2Cl_2$ (2•90Å) is considerably longer than this. The ionic radius of the chloride ion is 1•81Å, (the Van der Waal's radius of chlorine is 1•80Å [13]) the Van der Waal's radius of sulphur(II) is 1•85Å, giving an anticipated SCl distance in the case of ionic chlorine of approximately 3•66Å. The distance in all three cases is much shorter (~ 0•7) indicating a significant amount of interaction between the chloride ion and all three sulphur atoms of the cation.

<u>The Chemistry of trithiazyl trichloride and its derivatives</u>

Trithiazyl trichloride, $(NSCl)_3$, was first prepared by Demarçay[14] in 1880. Of the many unsaturated, cyclic sulphur-nitrogen compounds known it is now one of the easiest to prepare. Demarcay prepared trithiazyl trichloride by passing a stream of chlorine through 'sulphur nitride' (i.e. S_4N_4) in chloroform solution and gave the yellow crystalline product the correct empirical formula, NSCl. In 1931 Meuwsen[15] reported the preparation from a suspension of tetrasulphur tetranitride in carbon tetrachloride and chlorine gas, and from cryoscopic molecule weight determination in benzene gave it the correct formulation of $(NSCl)_3$ rather than $(NSCl)_4$ as had been suggested by Andreacci[16] and Muthmann and Seitter.[17] It is interesting to note in this context that S_4N_4 and chlorine do in fact react to give the tetramer,[18] which subsequently rearranges to give $(NSCl)_3$. The eight membered ring also remains intact on reacting S_4N_4 and AgF_2 to give $(NSF)_4$.[19]

Preparation of trithiazyl trichloride

a) From tetrasulphur tetranitride and chlorine:[20,21] trithiazyl trichloride is obtained in the form of yellow needles by passing chlorine gas slowly (15 min.) through a suspension of S_4N_4 in carbon tetrachloride at room temperature. Schröder and Glemser[22] reported a melting point of $162{\cdot}5^o$. Other workers have reported much lower melting points for samples prepared from S_4N_4, $77\text{-}78^o$ [23a], $95\text{-}96^o$ [23b], $89\text{-}91^o$ [25], these are more in agreement with the melting point obtained for samples prepared by other methods (b,c,d,e). This material shows a complex but distinct near infrared spectrum.[25b] Patton[23c] has investigated the high melting point reported by Schöder and Glemser and finds it difficult to believe. He suggests that, as $(NSCl)_3$ melts it decomposes giving rise to other yellow solids which themselves form S_4N_3Cl which melts with decomposition at $180\text{-}200^o$ when pure. Schroder and Glemser may therefore have overlooked the original melting point, and in fact noted the melting point of impure S_4N_3Cl.

b) From tetrasulphur tetranitride and sulphuryl chloride:[28] On stirring (24 hr.) a suspension of S_4N_4 in sulphuryl chloride the S_4N_4 slowly goes into solution and the pale yellow trithiazyl trichloride, m.p. $90\text{-}91^o$ is precipitated out. Evaporation of the filtrate to dryness under reduced pressure (2mm.Hg) yields an orange solid which is a slightly more impure sample of trithiazyl trichloride:

$$3S_4N_4 + 6SO_2Cl_2 \longrightarrow 4S_3N_3Cl_3 + 6SO_2$$

c) From thiodithiazyl dichloride and chlorine:[29] quantitative conversion (based on nitrogen) of thiodithiazyl dichloride to trithiazyl trichloride can be achieved by passing chlorine gas over crystals of $S_3N_2Cl_2$ and periodically pumping off the sulphur dichloride formed in the reaction.

$$3S_3N_2Cl_2 + 3Cl_2 \longrightarrow 2S_3N_3Cl_3 + 3SCl_2$$

d) From thiodithiazyl dichloride and sulphuryl chloride: (details p.54)

e) From disulphur dichloride and active nitrogen:[30] when a stream of S_2Cl_2 gas is passed into a stream of active nitrogen, a blue glow is emitted and yellow brown solids are formed in a trap cooled in liquid nitrogen. One of these solids is NSCl which slowly polymerises in the absence of S_2Cl_2 (rapidly at room temperature) to give trithiazyl trichloride. A 34% conversion to NSCl of S_2Cl_2 can be achieved, based on the equation

$$2N + S_2Cl_2 \longrightarrow 2NSCl$$

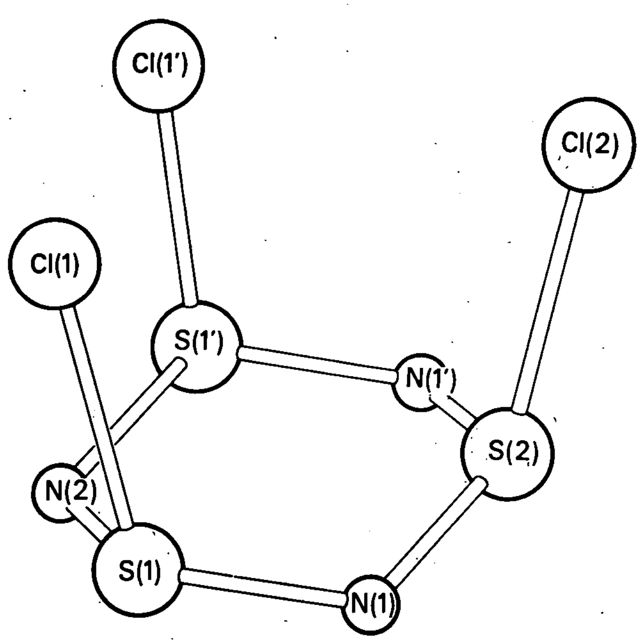
Physical Properties

Trithiazyl trichloride is a pale yellow crystalline solid, whose molecular structure leaves open the possibility for various isomers. When it is prepared from S_4N_4 or $S_3N_2Cl_2$ and chlorine it shows a comparably complex near infrared spectrum; that prepared from S_4N_4 or $S_3N_2Cl_2$ and SO_2Cl_2 shows a much simpler spectrum. The two forms also differ in their behaviour when exposed to the atmosphere, the former turning black and the latter white.[31]

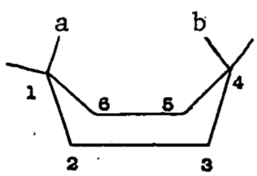
Wiegers and Vos[32] have accurately determined the crystal structure of a crystalline form obtained from the S_4N_4 and chlorine preparation. These proved to be monoclinic plates containing two molecules per unit cell. Each molecule has only one direct sulphur nitrogen distance of 1·605 ± 0·005Å indicating delocalisation[32,20] of the π bonds and therefore a pπ-dπ aromatic system. The six-membered sulphur-nitrogen ring is in a chair conformation with all the chlorines axial, (Fig.2).

<u>Fig.2</u>

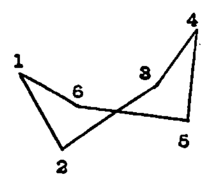
<u>Structure of trithiazyl trichloride</u>



This is the expected arrangement for the thermodynamically most stable conformational isomer, as in the case of cyclohexane.[33] Of the two other possible forms, the boat form (I) is least stable having hydrogens on carbons 2 and 3, 5 and 6 eclipsed respectively and also repulsion between hydrogens a and b (the latter alone amounting to approximately 3kcals.). The skew-boat (II) (twist boat) conformate is more stable;



(I)



(II)

the 'flagpole' hydrogens are further apart and the hydrogens along the sides are largely but not completely staggered, but even this arrangement is believed to be about 5 kcal less stable than the chair form. Axial chlorines in $(NSCl)_3$ are to be expected on similar grounds; a lone electron pair generally exerts a larger electron repulsion effect than a bond pair[34] and so for minimum overall repulsions the sulphur lone-pairs will adopt equatorial positions, leaving the chlorine bond pairs in axial positions. The SCl bonds are not parallel (contrast cyclohexane) but are splayed out making angles of 104^{o} and two of $101{\cdot}5^{o}$ with the plane through the three sulphur atoms. This is possibly due to the chlorine lone-pair-chlorine lone-pair repulsions.

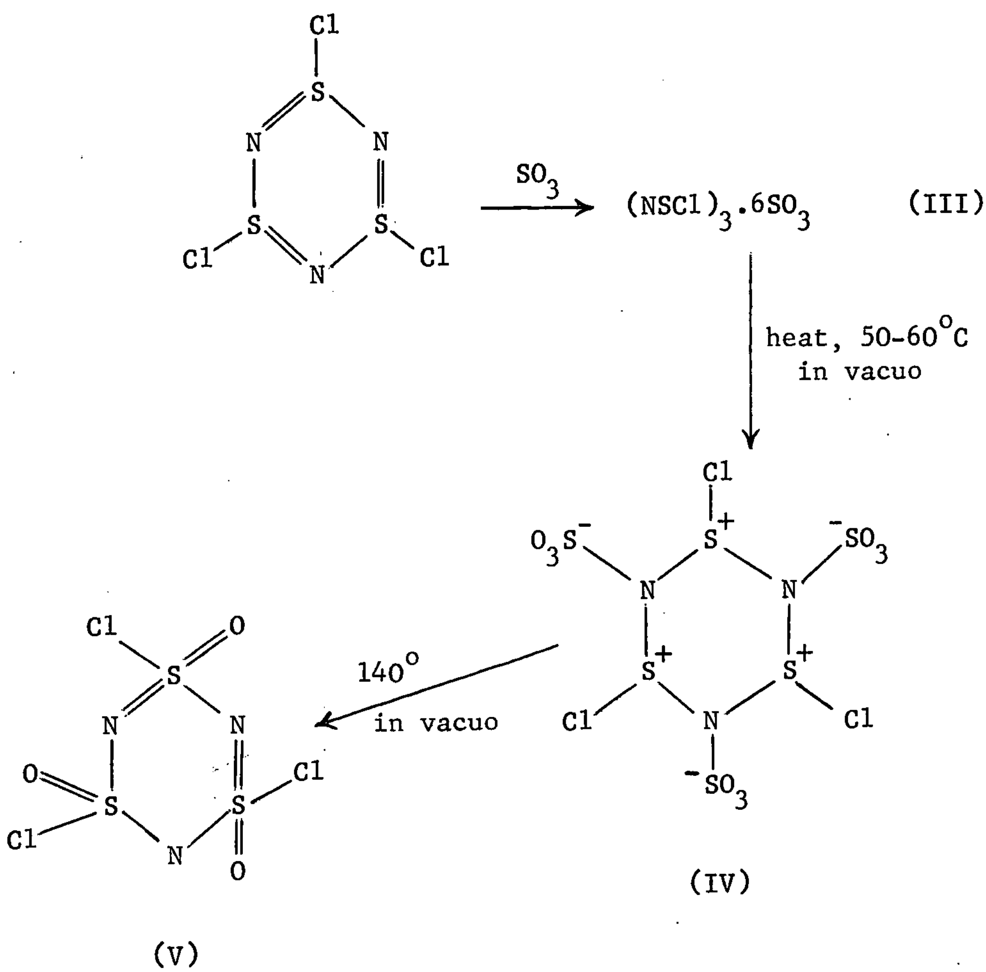
The two SCl bond lengths (Table 1) in trithiazyl trichloride[32] (2·084 (x2) and 2·150Å) and the considerably shorter one found for α-sulphanuric chloride[35] (2·003Å) can be compared with the SCl bond lengths of thionyl chloride (2·07Å) and sulphuryl chloride (1·99Å). Increasing the sulphur oxidation state (from 4 to 6) results in a shorter bond. The difference in bond lengths in $(NSCl)_3$ may be due to weak interactions between neighbouring molecules in the lattice. The sulphur atom of the longer SCl shows a considerable interaction with a nitrogen atom of the neighbouring molecule in the unit cell, the S --- N distance of 3·01Å is 0·34Å shorter than the sum of the Van der Waal's radii of nitrogen and sulphur, (N,1·5Å, S,1·85Å).[37] These differences in chlorine environment are too slight to be picked up by N.Q.R. The quadrupole spectrum[38] of chlorine-35 in $(NSCl)_3$ was found to have only one weak absorption line at 29·842 Mc/sec (285°K) which is close to that of thionyl chloride.

Reactions of trithiazyl trichloride

In the majority of reported reactions of trithiazyl trichloride the six membered ring is destroyed. Hydrolysis by either acid[39] or base[40] leads to the formation of sulphur dioxide or sulphites; all the sulphur can be accounted for in this way. However in a number of cases the ring remains intact; these are summarised below.

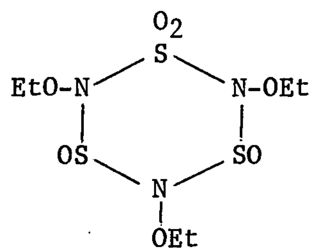
a) <u>Reaction with sulphur trioxide</u>[41]

On reaction with excess sulphur trioxide, $(NSCl)_3$ gives the adduct (III) which on heating loses sulphur trioxide to give the adduct (IV); on further heating in vacuo this gives sulphanuric chloride (V). (Overall yield is only 4%).



b) <u>With ethyl hypochlorite</u>[39]

The ring system is allegedly maintained on reaction with ethyl hypochlorite; the structure (VI) was proposed for the product; it is no longer 'aromatic'.

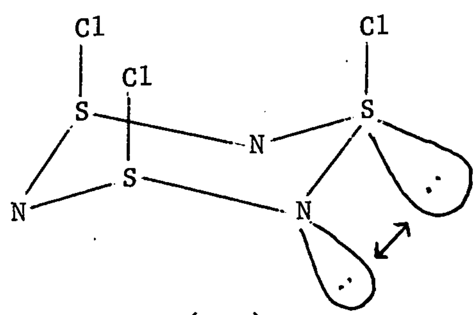


(VI)

Other oxidants, e.g. nitrogen dioxide[39] and nitric oxide[42] cause ring breakdown. Reduction of trithiazyl trichloride with tetrasulphur tetra-imide[41] or with heptasulphurimide[20] in the presence of pyridine give S_4N_4. In the absence of pyridine a brown-red adduct, S_4N_4.4NCl is formed which reacts rapidly with traces of water to give S_4N_3Cl. It has been shown that $(NSCl)_3$ reacts rapidly with 1,2-epoxides to give esters where the six-membered ring remains intact.[43] (pp.95,113).

<u>Bonding in trithiazyl trichloride</u>

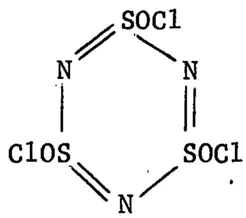
The SN bond distances (1·605Å) in the ring are equal within the limits of experimental error, though they are slightly longer than the SN distance in α-sulphanuric chloride (1·571Å). Glemser[44] computes a bond order of 1·4 and even allowing for some error in the method of calculation it is still considerably shorter (~0·14Å) than a single bond, indicating strong pπ-dπ bonding in the ring. The bonding and overlap schemes for trithiazyl trichloride are similar to those for α-sulphanuric chloride (p.31) except that the oxygen is replaced by a lone pair, which as well as removing a p-electron and reducing the electronegativity of the sulphur thus reducing the $N^{\pi}\!:\longrightarrow S$ back donation, is probably effective in actually lengthening the bond by lone pair-lone pair repulsion between nitrogen and sulphur (VII) (cf. the NN bond length in hydrazine[45]).



(VII)

The Chemistry of Sulphanuric Chloride and its Derivatives

Sulphanuric chloride was first prepared in 1950 by Kirsanov[46] whilst investigating the reaction between sulphamic acid and phosphorus pentachloride. He originally suggested that it was a trimeric ring of NSO units, and followed up the original preparation with further work,[1] including the isolation of two isomers (α and β). The following structure was proposed:



(VIII)

The sulphur-nitrogen ring was presumed to be flat and the α and β compounds were taken to be cis and trans isomers. Later X-ray investigations[48] showed that the ring is in the chair form and that α and β sulphanuric chloride are two of the four possible isomers. Becke-Goehring[49] prepared sulphanuric chloride in 1953 from the reaction between sulphuryl chloride, thionyl chloride and ammonia. Eleven years later Seel and Simon[50] published their preparation of sulphanuric fluoride by halogen exchange using potassium fluoride. Sulphanuric chemistry had begun.

<u>Preparation of α- and β-sulphanuric chloride</u>

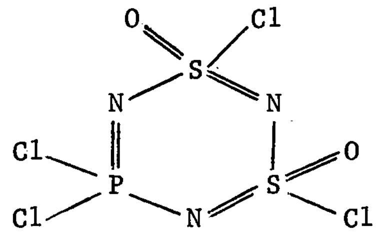
α-Sulphanuric chloride has been prepared in three ways but only one, method (i) below, is of any synthetic value. This is the original method due to Kirsanov and is apparently the only one which gives significant quantities of the β isomer. Other sulphanuric compounds, with the exception of the fluoride high polymer[51] are obtained directly or indirectly from the α or β chloride.

(i) From sulphamic acid and phosphorus pentachloride.[1] Phosphorus pentachloride reacts with a suspension of sulphanuric acid in refluxing carbon tetrachloride to give trichlorophosphazosulphuryl chloride, which decomposes on heating (~135°C 6 mm.Hg) to give the sulphanuric chlorides.

a) $$H_2NSO_3H + PCl_5 \xrightarrow[\text{reflux}]{CCl_4} Cl_3P{=}NSO_2Cl$$

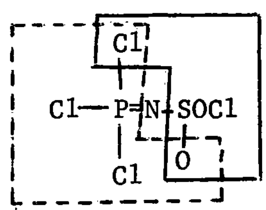
b) $$Cl_3P{=}NSO_2Cl \xrightarrow[135^{o}]{\text{heat}} (NSOCl)_3 + POCl_3$$

Decomposition is considerably more complex than the simple equation suggests. The isomeric α- and β-sulphanuric chlorides are fairly easily obtained from the reaction mixture. The β isomer can be sublimed out. The α-sulphanuric chloride is obtained by slowly pouring the pyrolysis product on to ice-water taking care to keep the temperature below 8°C, filtering of the solid, drying it, then recrystallising from hexane under a nitrogen atmosphere. However Kirsanov reported in the crude product the presence of at least three other compounds, none of which were characterised or have been since. Moeller[52,53] modified the Kirsanov route in that the trichlorophosphazosulphuryl chloride was never actually isolated, the pyrolysis following straight on from the preparation. The required purity of the Cl_3PNSO_2Cl was obtained by using excess sulphanuric acid in reaction (a). Van de Grampel and Vos[54] were unable to obtain sulphanuric chloride in the manner reported by Kirsanov, they reported that pyrolysis of the intermediate, Cl_3PNSO_2Cl in the presence of ultraviolet light gave a phosphorus containing compound (IX)



(IX)

Sulphanuric chloride has been prepared by the Kirsanov method on many occasions without any reported difficulty. Typical yields for α-sulphanuric chloride are: 11·3,[55] 20[53] and 24%[1,42b] based on nitrogen, and for β-sulphanuric chloride 14·3[53] and 18·5%.[1] But it seems that the presence of impurities raises the decomposition temperature to give $(NSOCl)_3$ until ultimately it exceeds the temperature of other side reactions and the sulphanuric chloride yield drops sharply



In the pyrolysis of PCl_3NSO_2Cl the relatively volatile $POCl_3$ is generally eliminated (as enclosed by -----). If the presence of impurities raising the temperature results in the elimination of SO_2Cl_2 (as enclosed by ——) an $NPCl_2$ unit is formed which could result in the formation of (IX).

(ii) From thionylchloride, sulphuryl chloride and ammonia[49]

Becke-Goehring prepared α-sulphanuric chloride from the decomposition of thionyl chloride and sulphuryl chloride with ammonia at low temperatures in petroleum ether, but the yield was extremely low (~1%).

(iii) From trithiazyl trichloride and sulphur trioxide[41,57]

α-Sulphanuric chloride can be prepared from the pyrolysis of the sulphur trioxide adduct of trithiazyl trichloride (p. 13) (4% yield based on $(NSCl)_3$).

Physical Properties

α-Sulphanuric chloride is a white crystalline solid, m.p.144-5° [53] without decomposition. It is generally soluble in organic solvents, e.g. benzene, hexane, acetonitrile and carbon tetrachloride, but hydrolyses slowly when dissolved in wet alcohol (Table 2). X-ray studies[48,35] have shown the crystals to be orthorhombic and to contain four molecules per unit cell. The distribution of bonds around each sulphur atom is roughly tetrahedral, the ring taking up a chair configuration (p.11) with the chlorine atoms arranged axially (Fig.3). This is the expected conformation for the thermodynamically most stable isomer. On account of axial bond pairs experiencing higher electron repulsion than equatorial bond pairs (cf. cyclohexane [33]), the doubly bound oxygen atoms will

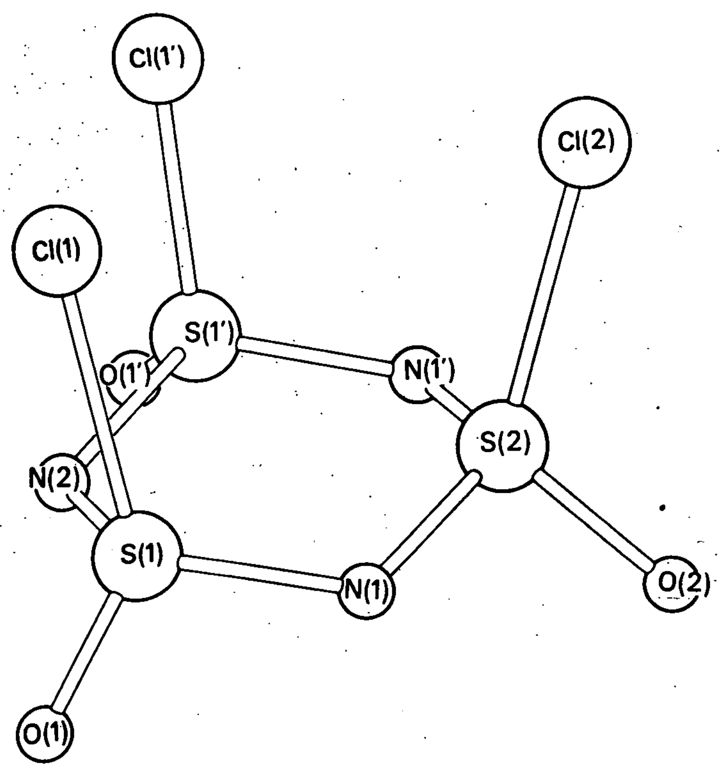
TABLE 2

SOLUBILITY DATA FOR α-SULPHANURIC CHLORIDE AT 25° [53]

Solvent	Solubility g/100g. Solvent
Benzene	22·5
Acetonitrile	13·15
Carbon disulphide	4·10
Carbon tetrachloride	2·95
Petroleum ether (90-110°)	2·32
Cyclohexane	1·63
n-heptane	1·56

Fig.3

Structure of Sulphanuric Chloride



preferentially occupy equatorial positions. The next most stable isomer should have two equatorial oxygen atoms, this is the conformation of β-sulphanuric chloride deduced from dipole moment measurements. The SO bond distance (1·407 ± 0·007Å) indicates[58] an SO bond order of 1·98. The SN bond distances are equal within the limits of experimental error (1·571 ± 0·004Å) and correspond to a bond order of 1·5.[44]

Chlorine 35 nuclear quadrupole resonance[59] showed two frequencies for α-sulphanuric chloride at 36·993 and 37·225 Mc/sec, the intensity ratio being 2:1. This is not in disagreement with the X-ray analysis. There are four molecules in the unit cell, and for any ring one of the chlorines is crystallographically different from the other two, one being adjacent to an oxygen atom of another molecule, whilst two are adjacent to chlorine atoms. The chlorine adjacent to the oxygen atom can draw electron density from that oxygen by charge transfer and release it in its σ-bond to the ring, thus increasing the n.q.r. frequency, this should result in a very slightly different d_{S-Cl} which is not detected by the X-ray method. The n.q.r. results and those from X-ray analysis are therefore consistent.

The infrared absorption frequencies reported by different workers show a slight variation: these are summarised in Table 3.

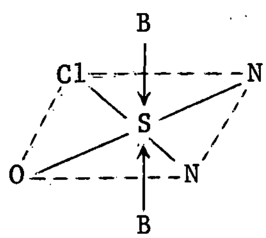
β-Sulphanuric chloride is a white crystalline solid m.p.46-7°C [53] and has in general a much higher solubility in organic solvents than its α-isomer. It is stable in the solid state and in non-polar solvents,

TABLE 3

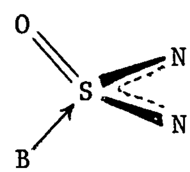
INFRARED ABSORPTIONS OF α-SULPHANURIC CHLORIDE

Source	Absorption frequency cm^{-1}										
Vandi, Moeller and Brown[53]		1365w	1344vs		1110vs	816m	700vs	665s			
McKenney and Fetter[55]	1915w 1810m	1445m	1324vs	1155sh	1080vs	800m	695vs	650vs	630sh	530s	420m
Banister and Bell[60]	1808w		1342s 1326s		1107s	812m	730sh 714m	701ms	671m 665ms	541ms 524ms	
Moore[42c]	1812m		1335s 1326s		1100s	812m	713ms	702ms	663s	540ms	

e.g. benzene and cyclohexane, but in the more polar solvents, e.g. acetonitrile and diethyl ether its isomerisation to the α-isomer is rapid. The role of a basic solvent in effecting the isomerisation is probably to assist the re-orientation of the bonds about the sulphur through the formation of an adduct of either a neutral molecule (e.g. X) or a cation (e.g. XI).

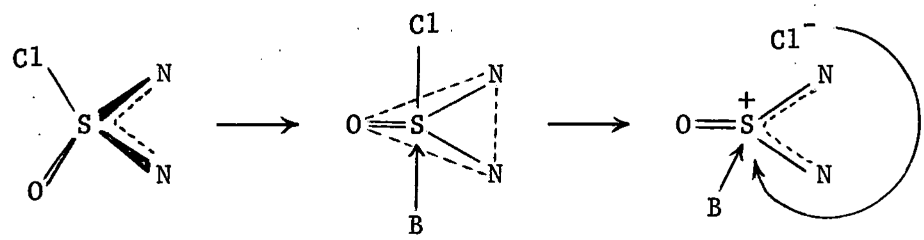


or



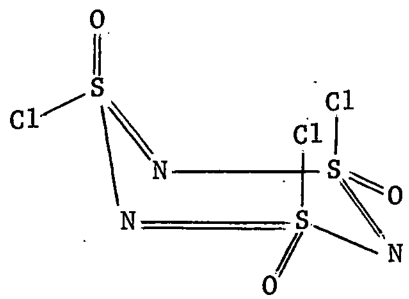
(X) (XI)

Vandi, Moeller and Brown[53] favour a transition state which does not involve bond breaking either in the ring or SO or SCl since this could lead to degradation of the compound, and suggest a five-co-ordinate transition state (one solvent molecule attached). If it passes through a 5-co-ordinate transition state it is difficult to see how bond breaking could be avoided. Isomerisation via a 5-co-ordinate transition state would conceivably proceed as follows:



which leaves a chloride ion free to be picked up by another molecule

Vandi, Moeller and Brown[53] suggested the following structure (XII) on the basis of dipole moment measurements. There is as yet no other structural information.



(XII)

<u>Reactions of α-sulphanuric chloride</u>

<u>Halogen exchange</u>

α-Sulphanuric chloride will undergo halogen exchange with potassium fluoride in carbon tetrachloride[50] or acetonitrile.[52] Two isomers are formed, the <u>cis</u>-sulphanuric fluoride (b.p. 138-4°) and the <u>trans</u>-sulphanuric (b.p. 130·3°) fluoride, which can be separated by distillation using a 50 cm. column or by gas chromatography. Both the isomers are colourless liquids at room temperature with a density of 1·92 g./ml. The fluorine-19 nuclear magnetic resonance spectra[50] show that in the case of the _cis_ isomer all the fluorine atoms are environmentally equal, whereas with the _trans_ isomer this is not the case. It is therefore likely that the _cis_ and _trans_ fluorides correspond in structure to the α and β-sulphanuric chlorides respectively. The infrared absorption spectra of the two isomers is shown below (Table 4). Sulphanuric fluoride is considerably more stable to hydrolysis than even α-sulphanuric chloride. It has been reported[50] that on boiling with water for 7 hr. 50% of the compound is hydrolysed by the breaking of the SF bonds but without rupture of the SN ring but no products were characterised. Sulphanuric fluoride undergoes reactions with amines (p.27) and phenyl lithium (p.28) which would result in the formation of adducts or breakdown of the ring if α-sulphanuric chloride was used.[42d]

Hydrolysis

Sulphanuric acid $(NSO.OH)_3$ should be the first hydrolysis product of sulphanuric chloride, but like its isomer trisulphimide $(HNSO_2)_3$ it is unknown. Malz[63] found that even on very careful acid hydrolysis of sulphanuric chloride, imidosulphamide, sulphuric acid and hydrochloric acid were formed immediately. The rate of hydrolysis by water diminishes with reduction in temperature. It is slow in the atmosphere and in water below $15^{o}C$, and very slow at 0^{o} (p.51).

TABLE 4

INFRARED SPECTRA OF CIS- AND TRANS-SULPHANURIC FLUORIDE

cis-$(NSOF)_3$ [52]	trans-$(NSOF)_3$ [50]
cm^{-1}	cm^{-1}
2700w	
2050w	
1940w	
1870w	
1780w	
1670w	
1550w	
1415sh	
1390vs	1389vs
1250m	1245w
1190sh	
1170vs	1172vs
1070w	1060w
945w	
895m	899vs
870s	875m
780sh	789vs
770s	781s
700w	
560sh	553s
520s	522s

a) With secondary amines

Failli, Moeller, Kresge and Allen[64] reported the preparation of two isomeric morpholine derivatives of sulphanuric chloride; with this exception sulphanuric chloride generally undergoes solvolysis followed by ring breakdown with secondary amines.

b) With diphenyl mercury

Although in general sulphanuric chloride reacts with organometallic compounds with resulting ring breakdown,[62] McKenney and Fetter[55] prepared diphenylsulphanuric chloride (m.p.120°C) from the reaction of diphenyl mercury and α-sulphanuric chloride in good yields ($>$ 50%). The reaction takes place slowly in benzene at room temperature. This was the second reported derivative apart from the cis and trans sulphanuric fluoride.

c) With tertiary bases R_3N, R_3P, R_3As and R_3Sb[42e,66]

α-Sulphanuric chloride reacts with tertiary bases to give adducts of the general formula $(NSOCl)_3.3B$. The adducts with nitrogen bases are readily formed on mixing benzene or toluene solutions of the amine and sulphanuric chloride at room temperature. The products, are insoluble, involatile viscous oils which are readily hydrolysed when exposed to the atmosphere and from which it has not been possible to recover the α-sulphanuric chloride.[65]

Reactions of sulphanuric fluoride

It is from sulphanuric fluoride, either one isomer or a mixture of the two that most of the known sulphanuric derivatives have been prepared. Sulphanuric fluoride reacts with phenyl lithium without substantial ring disintegration (yield of $(NSO)_3FPh_2$ is 79%) and its action with amines results in substitution of the fluorine by an amino group without solvolysis and ring breakdown (yields usually 90 to 98%, before separation of isomers). A table of these derivatives is given below (Table 5). The final fluorine atom is difficult to remove as seen in the table.

Diphenylsulphanuric chloride and fluoride

The diphenylsulphanuric halides are more stable to hydrolysis than the parent trihalide. Diphenylsulphanuric fluoride is prepared directly from the trifluoride (see Table 5) or by the reaction of the chloride with potassium fluoride in acetonitrile[55] (p.65). They are less soluble in polar and non-polar solvents than the parent trihalide.

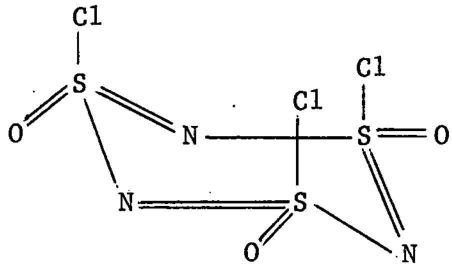
Bonding in the sulphanuric system

The only sulphanuric compound of known structure is α-sulphanuric chloride (XIII). The SO bond distance of 1·407Å corresponds to a bond order of 1·98.[58] The SN bond distances (1·571Å) are equal within the limits of experimental error. Glemser[44] computes a bond order of 1·5 (given earlier[20] as 1·9) and even allowing for some error in the method of

TABLE 5

SULPHANURIC DERIVATIVES PREPARED FROM SULPHANURIC FLUORIDE

Reactant	Product	Yield	Melting Point
NH_3 [50]	$(NSO)_3F_2(NH_2)$		
Me_2NH [50]	$(NSONMe_2)_3$		
Morpholine[52]	$(NSO)_3F(C_4H_8NO)_2$ two isomers	46% 46%	146° 195°
2,6 dimethylmorpholine [52]	$(NSO)_3F(C_6H_{10}NO)_2$ two isomers	51% 42%	129° 166°
piperidine[52]	$(NSO)_3F(C_5H_{10}N)_2$ two isomers	53% 43%	114° 166°
pyrrolidine [52]	$(NSO)_3F(C_4H_8N)_2$ two isomers	23% 66%	127° 148°
phenyl lithium [52] Mole ratio 1:1	$(NSO)_3F_2Ph$	55%	95°
phenyl lithium [52] Mole ratio 2:1	$(NSO)_3FPh_2$	79%	119°
benzene/$AlCl_3$ [52]	$(NSOPh)_3$ two isomers	7% 10%	148° 177°



(XIII)

calculation it is still a short bond and indicates pπ-dπ bonding in addition to the expected contribution from structures such as $(\overset{-}{N}-\overset{+}{S}OCl)_3$. The atomic arrangement is very similar to that of trithiazyl trichloride [32] except that the oxygen atoms have replaced the lone pairs and the SN distances are appreciably shorter (1•605Å in $(NSCl)_3$). Inserting a highly electronegative atom not only increases the sulphur Lewis acidity but also removes the repulsion between the S and N lone pairs The SCl bonds are also significantly shorter (2•150Å in $(NSCl)_3$, Table 1). This all suggests that in sulphanuric chloride the presence of the highly electronegative oxygen decreases the electron density on the sulphur [67] enhancing electrostatic and lone pair donation contributions (from N and Cl) to both the SN and SCl bonds.

This situation can be compared with that for $(NPCl_2)_3$ where replacement of the chlorine by fluorine contracts the PN ring distances by 0·03Å, from 1·59 to 1·56Å[68] due to increased N → P donation (termed exocyclic π' bonding[74]). Some idea of the likely $N^{\pi'}$ → M (M is P or S) contribution to bonding in phosphazenes and thiazenes can be obtained from the Lewis acidity of the corresponding halides or oxyhalides of M. The only chloride or oxychloride of S^{VI} is sulphuryl chloride, SO_2Cl_2; this is a considerably stronger[70] Lewis acid than thionyl chloride or phosphorus pentachloride. A significant contribution from π' bonding is therefore to be expected for sulphanuric chloride and this is likely to exceed the π' contributions in the corresponding thiazene $(NSCl)_3$ and phosphazene $(NPCl_2)_3$.

σ-framework

Since each sulphur in S^{VI} is bound to four other atoms a roughly tetrahedral distribution of σ electrons pairs (sp^3 hybridisation) is to be expected. This together with the planar distribution, sp^2, on the nitrogen results in a σ-framework similar to the chair conformation of cyclohexane.

π-bonding[69]

Electrons which are not used in the σ-framework are on sulphur (two in d orbitals), nitrogen (one) and oxygen (one). Including lone pairs the oxygen is three co-ordinate - hence an approximately sp^2 hybridisation and one pπ electron. The sulphur ~~dt~~ d orbitals are available for π bonding and for π' bonding (lone pair donation to sulphur) with both nitrogen and oxygen. The dxz and dyz have the correct symmetry for overlap with the Npπ if the axes are defined as shown (Figs. 4,5, and 6) and the dz^2 for overlap with the Opπ. The remaining two d orbitals, the dxy and the dx^2-y^2 are of the correct symmetry for overlap with the sp^2 lone pair of the nitrogen. The suggested overlap scheme for this bond, an exocyclic bond is shown in Fig.4.

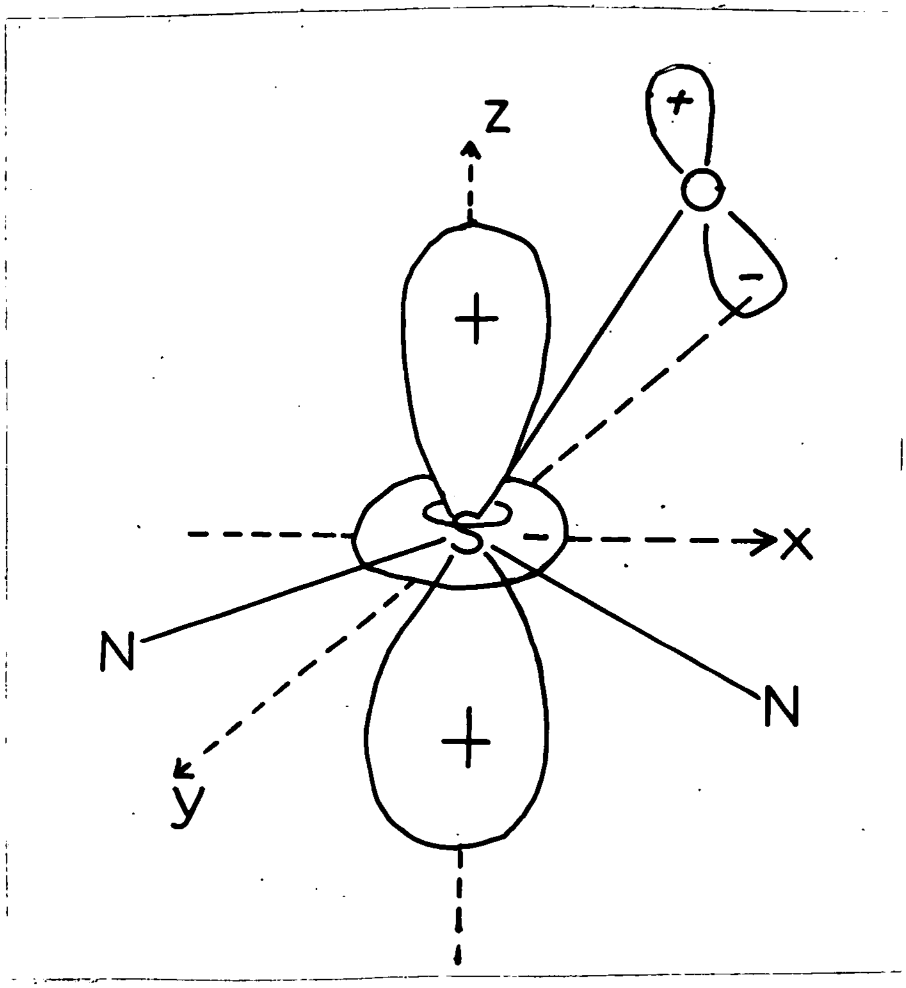


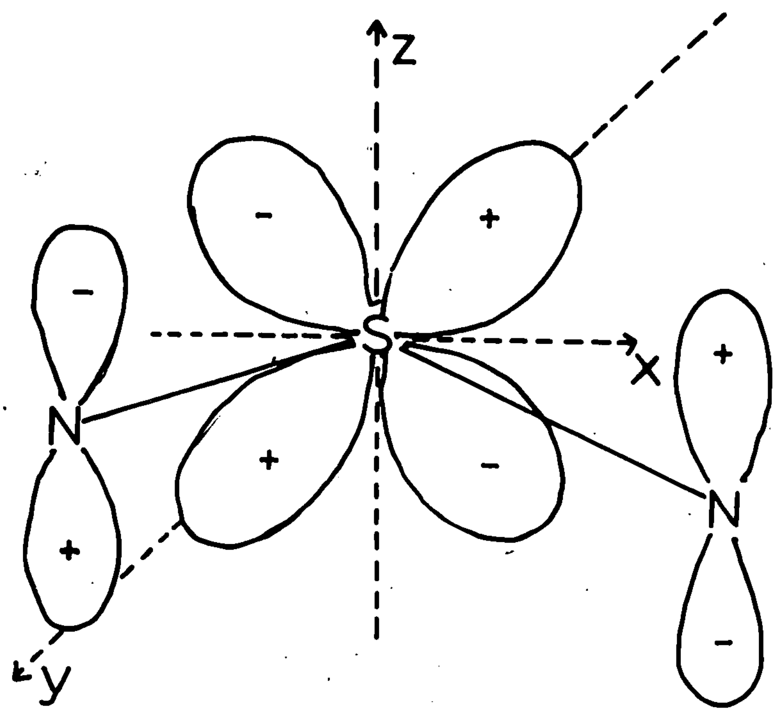
Fig.4.

Exocyclic π-bonding with the oxygen

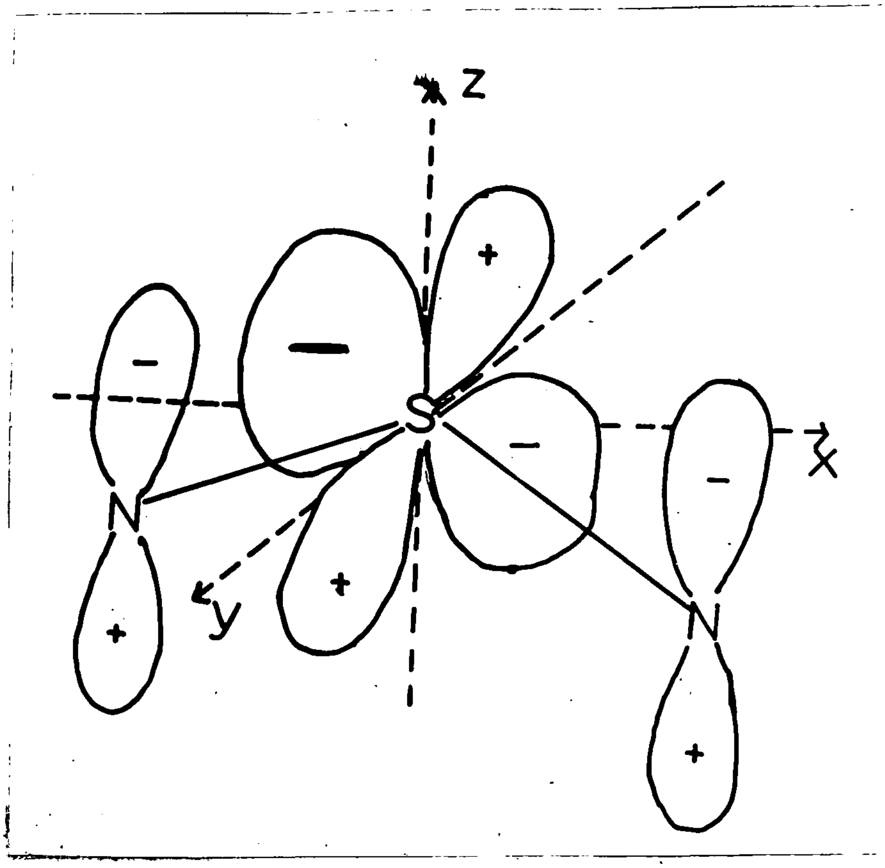
The remaining electron can participate in π-bonding in the ring together with the p electron of the nitrogen. Suggested overlap schemes appear below (Fig.5). Signs of ψ are correct for overlap

Fig.5.

π-Bonding in the sulphanuric ring



a) dxz and pz



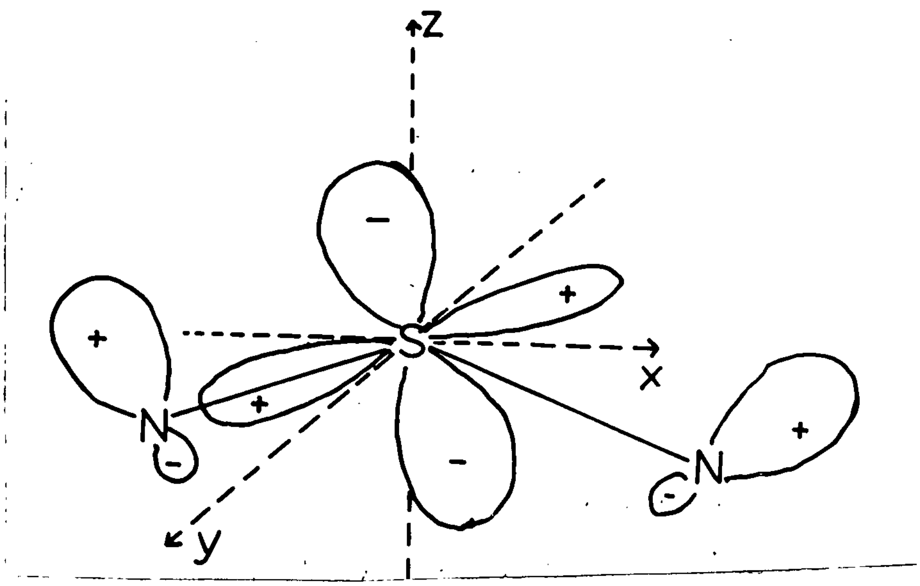
b) dyz and pz

π'-bonding

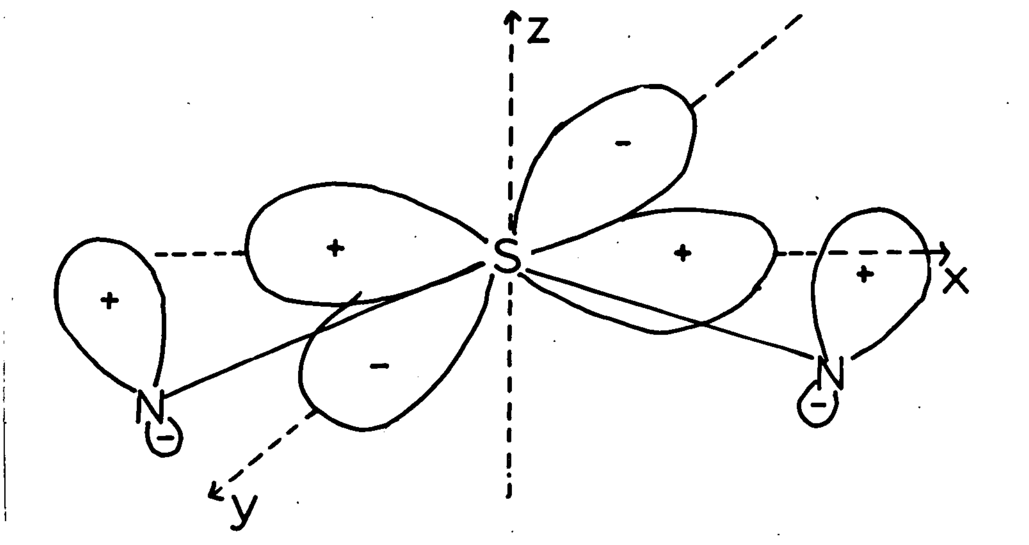
As has been noted earlier (p 31) a significant contribution from π' bonding is to be expected in the sulphanuric ring. Possible overlap schemes are shown in Fig.6.

Fig.6.

π'-bonding in the sulphanuric ring



a) dxy and an $(sp^2)_y$ hybrid lone pair (N)



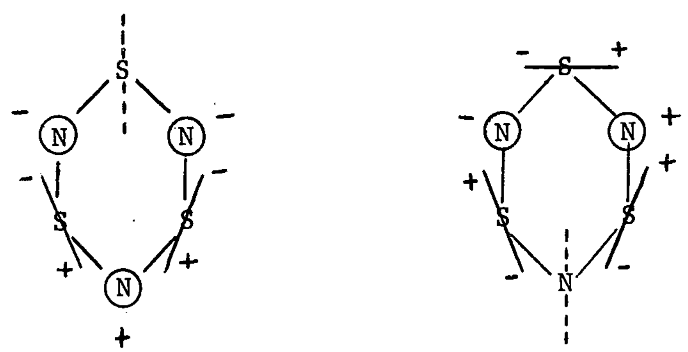
b) dx^2-y^2 and an sp_y hybrid

The combined strength of the π and π' bonding in the ring can be seen by comparing the SN bond distance of 1•57Å with that for $((SO_3)_2NH)^{2-}$ of 1•662 ± 0•005Å[71] where there is thought to be some π bonding, and that for H_3NSO_3K of 1•764Å[72] where the bond order is probably close to one.

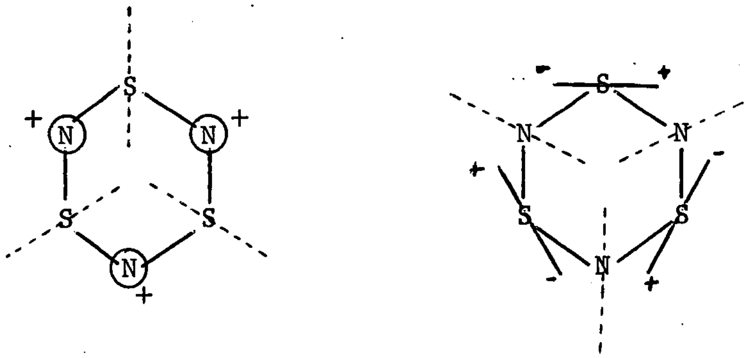
This system is similar to the phosphonitrilic system with the major exception being the extra electron in the d orbitals which is involved in π bonding with the exocyclic oxygen. The d orbital most favourable for such overlap is the dz^2 (Fig.4) although the dyz could participate to a small extent. As the main contribution to the π bonding is the dxy with only a small contribution from the dyz[73] this is unlikely to have a large effect on the resultant molecular orbitals. The suggested molecular orbital symmetries and relative energies are therefore expected to be similar to those for $(NPCl_2)_3$. These are shown in Fig.7.

Fig.7.

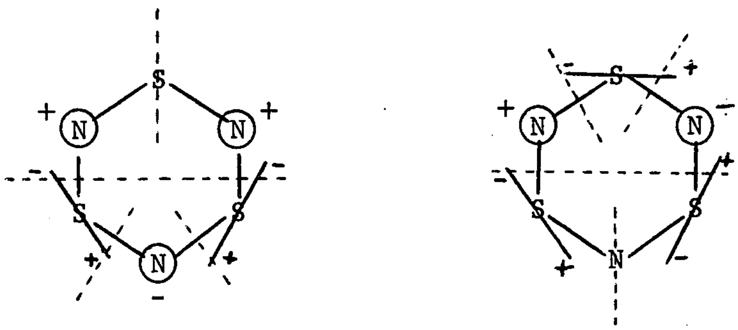
Anticipated ring molecular orbitals in $(NSOCl)_3$



a) bonding orbitals



b) non-bonding orbitals



c) antibonding orbitals

------ (dotted lines) indicate either node or no orbital involvement

——— (red lines) indicate orientation of sulphur d orbitals

The N ⟶ S donation, π' bonding, can similarly be compared to the phosphonitrilic system which gives an exocyclic molecular orbital of the type shown in Fig.8.

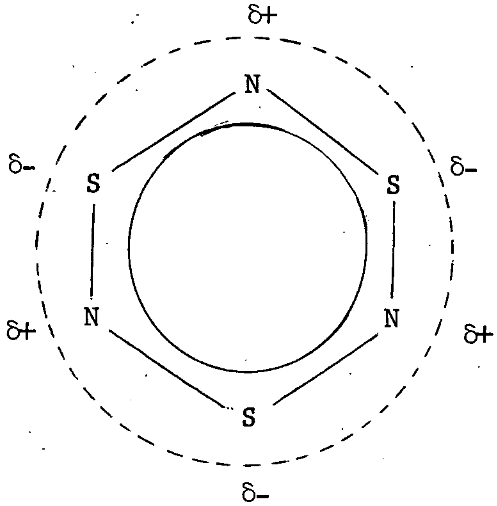


Fig.8.

π' delocalisation

A Summary of the Chemistry of Sulphenyl Chlorides

Sulphenyl chlorides, RSCl, where R is alkyl or aryl are generally yellow or orange liquids which fume in moist air. The alkyl sulphenyl chlorides are much less stable than aryl sulphenyl chlorides and received little attention prior to World War II. They are not usually isolated but prepared in situ. The first alkylsulphenyl chlorides to be isolated were those containing no α-hydrogen, e.g. CCl_3SCl, Ph_3CSCl. C_2Cl_5SCl and Bu^tSCl. This is due to α-hydrogen being easily replaced by chlorine.

The most common preparation of sulphenyl chlorides is from disulphides and chlorine[24] or sulphuryl chloride[24] at low temperatures (-10^o to -20^oC).

$$RSSR + Cl_2 \longrightarrow 2RSCl$$

$$RSCl + Cl_2 \longrightarrow RSCl_3$$

$$RSCl_3 + RSSR \longrightarrow 3RSCl$$

The low temperatures are necessary to prevent chlorination of the organic group by $RSCl_3$.[26] In the case of aryl sulphenyl chlorides it is often advisable to prepare them from the thiol, as scission of the S-S bond frequently requires more energy than chlorination of the ring.[27]

$$ArSH + Cl_2 \longrightarrow ArSCl + HCl$$

$$ArSH + ArSCl \longrightarrow ArSSAr + HCl$$

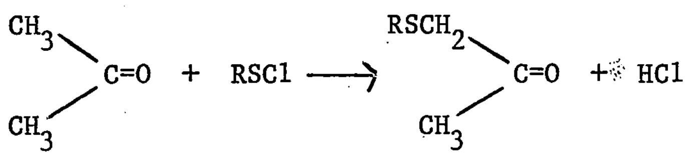
$$ArSSAr + Cl_2 \longrightarrow 2ArSCl \quad \text{(sometimes)}$$

The formation of ArSSAr is kept to a minimum by a constant excess of chlorine. These reactions are generally carried out under anhydrous conditions and in inert solvents, e.g. CCl_4; in the presence of moisture sulphonyl chlorides are formed.

Sulphenyl chlorides react with (a) the elimination of HCl, (b) the precipitation of metal halides and (c) by addition to unsaturated systems. This final type of reaction is their most well-known characteristic.

(a) Elimination of HCl

Most compounds with easily replaceable hydrogens, e.g. acetone[47] acetoacetic ester[56] and malonic ester[24] react with RSCl with the elimination of HCl



Alkyl or aryl sulphenyl chlorides will react with aromatic hydrocarbons[61] in the presence of aluminium trichloride to give sulphides

$$RSCl + ArH \xrightarrow{AlCl_3} ArSR + HCl$$

Phenols[62] and alcohols[65] react to give esters whilst thiophenols[76] and mercaptans[79] give disulphides

$$R'OH + RSCl \longrightarrow RSOR' + HCl$$

$$R'SH + RSCl \longrightarrow RSSR' + HCl$$

Sulphenamides are formed in the reaction between RSCl and primary or secondary amines;[24] with ammonia some alkyl sulphenyl chlorides will in fact replace all the hydrogen to give $(RS)_3N$[78]

$$R_2NH + R'SCl \longrightarrow R_2NSR' + HCl$$

If the reaction is not carefully controlled or if excess amine is used the reactions may lead to guanidines, e.g.[78]

$$CCl_3SCl \xrightarrow[RNH_2]{excess} RN(H)-C(=NR)-NHR\cdot HCl$$

(b) Precipitation of metal halides

Grignard reagents RMgX react with both alkyl and aryl sulphenyl chlorides to give sulphides[77]

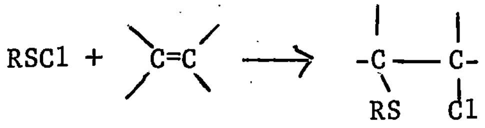
$$RMgX + R'SCl \longrightarrow RSR' + MgXCl$$

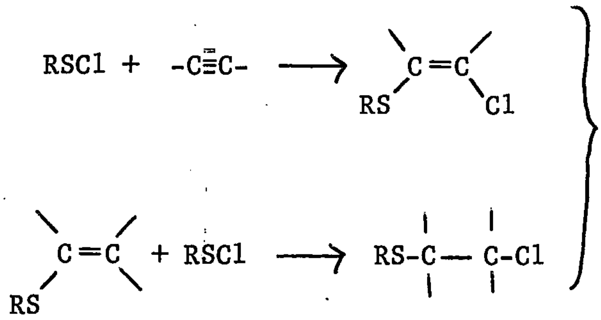
The chlorine may also be replaced by -OR or $-N{=}CR_2$ by reaction with NaOR[79] or $LiN{=}CR_2$[82] with the precipitation of NaCl or LiCl and the formation of esters and sulphenimides respectively

$$LiN{=}CR_2 + R'SCl \longrightarrow R'SN{=}CR_2 + LiCl$$

(c) Addition to unsaturated systems

Sulphenyl chlorides will undergo addition reactions with olefins[80] and acetylenes[81] which generally obey the Markownikoff rule, the more electropositive part, RS, becoming attached to the unsaturated carbon carrying the smaller number of alkyl groups or electron withdrawing entities[83]

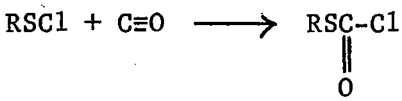




product depends on nature of original acetylene

In the case of addition of aryl sulphenyl chlorides to acetylenes the reaction is not so rapid but can be catalysed by $AlCl_3$.[84]

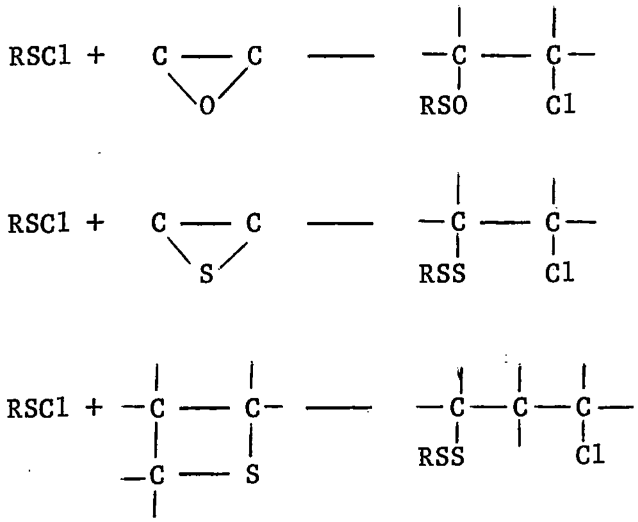
Sulphenyl chlorides react with carbon monoxide[85] to give a series of chlorothioformates, the reaction can be classed as an addition insertion reaction.



The reaction is carried out under a pressure (6000 psi) of CO and a yield > 80% of the chlorothiol formate is obtained.

(d) Insertion reactions with strained ring systems

Alkyl sulphenyl chlorides react with epoxides[86] and episulphides,[87] with ring opening and the formation of esters and disulphides



As can be seen from the preceding summary of reactions of sulphenyl chlorides, they are highly reactive materials from which a range of compounds are preparable.

Chapter 2

Apparatus, Techniques and the Preparation of Starting Materials

(a) Apparatus and Techniques

The Nitrogen Supply

Many of the compounds studied react with moist air fairly rapidly so almost all of the work was carried out in an atmosphere of dry nitrogen either in a glove box or in apparatus so designed that counter current techniques could be used. The nitrogen for the counter-current work was dried by passage through two (30 cm.) traps cooled in liquid nitrogen.

The Glove Box

The glove box (Lintott IIIB) was set up in such a way that its nitrogen atmosphere could be continually recycled, by means of a small pump inside the box, through two traps (50 cm.) cooled in liquid nitrogen and two towers (30 cm.) of copper wire at 600°. As a further precaution against moisture two trays of P_2O_5 were kept in the box. These were also useful as an indicator of the efficiency of the purification system at any time. The transfer tube to the box was thoroughly purged, e.g. 60 min., with dry nitrogen before the introduction of materials into the box.

Infrared Spectroscopy

Infrared spectra over the range 2•5-25μ (4000-400 cm^{-1}) were recorded on a Spectromaster prism grating spectrophotometer. Samples of moisture sensitive materials were prepared for spectroscopic analysis in the glove box. Most samples were prepared in the form of Nujol mulls between potassium bromide discs, but oils were applied as contact films and for some air and moisture stable materials samples were prepared in the form of impregnated potassium bromide discs.

Mass Spectra

Mass spectra were recorded on an A.E.I. (M.S.9) mass spectrophotometer. The samples were mounted in the glove box on to an inert ceramic and introduced into the ion source using a direct insertion probe (temperature $200^{o} \pm 20^{o}$C unless stated otherwise).

Molecular Weights

Molecular weights were measured using a Mechrolab, Vapour Pressure Osmometer (Model 301A) and benzene or chloroform as solvents.

Reaction Vessels

Most of the reactions were carried out in either a Schlenk or a two necked round bottomed flask. In the latter case filtration was effected by pouring from one flask to another through a tube containing a sintered glass disc (porosity 1 or 3, a filter stick). Liquids were introduced from a syringe through 3 mm. straight taps fitted to ground glass joints, B19 or 24.

(b) The Preparation and Purification of Solvents and Starting Materials

All solvents were purified and stored under an atmosphere of dry nitrogen.

A.R. benzene, A.R. toluene, hexane, heptane, pentane and diethyl ether were dried by standing over sodium wire for several days.

Carbon tetrachloride was dried by standing over phosphorus pentoxide.

Sulphuryl chloride and disulphur dichloride were fractionally distilled through a 30 cm. Vigreux column, the fractions with boiling points 69•0-69•5°/760 mm.Hg and 58-9°/760 mm.Hg respectively were used.

Thionyl chloride.[36] Triphenyl phosphite (40 ml.) was added dropwise over 30 min. to technical grade thionyl chloride (250 ml.) with vigorous stirring. The resulting mixture was fractionated through a twelve inch column, packed with glass helices, connected to a reflux distillation head. The receiver was protected by a calcium chloride drying tube. Up to 60% of the thionyl chloride was distilled over the first 10 ml. of the distillate being discarded.

Acetonitrile and benzonitrile were purified by distilling from calcium chloride on to phosphorus pentoxide, then back on to fresh phosphorus pentoxide and finally fractionated on to calcium chloride, over which they were stored in a nitrogen atmosphere.

Epoxides and other nitriles were dried by standing over anhydrous magnesium sulphate, laboratory reagent grades of these materials were used.

Dimethylamine, diethylamine, triethylamine, n-octylamine, morpholine, aniline and pyridine were dried by distilling from potassium hydroxide pellets on to fresh potassium hydroxide and stored under nitrogen, preferably in a dark cupboard.

Sulphamic Acid,[89] technical grade sulphamic acid, (250 g.) was added to distilled water (600 ml.) preheated to 75°. The solution was heated to 75° and maintained at this temperature with stirring until all the solid had dissolved, it was then allowed to cool with stirring to 40° and the residue filtered off and discarded. The filtrate was cooled slowly to 0° and filtered through a sintered glass funnel. The crystals were washed with ice-cold water, 10 ml., and dry analar acetone, 3 x 20 ml. then dried under reduced pressure at 50° for 30 min. and stored in a phosphorus pentoxide vacuum desiccator. A 35% recovery was obtained.

Phosphorus pentachloride - May and Baker Ltd. analar phosphorus pentachloride was used without further purification. This was not possible, with phosphorus pentachloride obtained from other suppliers.as a trace of P-OH changes the course of the pyrolysis of trichlorophosphazosulphuryl chloride

Diphenylamine and 2,4,6-trichlorophenol were purified by sublimation under reduced pressure.

Sulphur was purified where necessary by soxhlet extraction using benzene as solvent.

Potassium fluoride, anhydrous potassium fluoride was heated at 120° under 0·1 mm.Hg for ten hours to remove any moisture.

Potassium thiocyanate, technical grade, was recrystallised from acetone and diethyl ether in a nitrogen atmosphere and dried at 50° under reduced pressure for 1 hr. then stored under dry nitrogen.

Sodium azide,[90] laboratory reagent sodium azide (50 g.) was ground in a pestle and mortar with hydrazine hydrate (5ml.) and left to stand in a fume cupboard for 12 hr. The solid was dissolved in the minimum volume of water (40 ml.) and precipitated by the addition of analar acetone (2 l.). The sodium azide was filtered off, washed with analar acetone (50 ml.) and dried (20°) in vacuo. It was used within 24 hr. of recrystallisation, otherwise it was recrystallised as above.

The preparation of diphenyl mercury[91]

To a suspension of phenyl mercuric chloride (200 g.) in methylated spirits (2 l.) was added hydrazine sulphate (84·5 gm.) and sodium carbonate (126 g.). The reaction mixture was refluxed (48 h.) with stirring. On cooling, white, needle-like crystals formed. The solid was filtered off and extracted with hot chloroform using a soxhlet extractor. 60 g. of white acicular needle crystals were obtained which were recrystallised from a 50:50 chloroform-hexane mixture, m.p.122°.

The preparation of phenyl lithium[92]

To a suspension of lithium (3 g.), in peas, in diethyl ether (100 ml.) was added slowly with cooling and stirring a solution of bromobenzene (35·5 g.) in ether (50 ml.). When all the lithium had dissolved the brown suspension was filtered through glass wool to remove lithium bromide and 100 ml. hexane added. This precipitated more lithium bromide and stabilised the solution which was stored under nitrogen in the 'fridge.

Preparation of N,N-diphenylaminotrimethylsilane [93]

To a solution of diphenylamine in hexane, cooled to -196°C was added the equivalent amount of butyl lithium and the solution allowed to warm up to room temperature. When the evolution of butane had stopped, the solution was cooled again and 1:1 trimethylchlorosilane was added. The solution was warmed to room temperature with stirring, filtered and the solution of N,N-diphenylaminotrimethylsilane used immediately without further purification assuming an 80% yield.[93]

Preparation of N,N-dimethylaminotrimethylsilane[94]

Trimethylchlorosilane was distilled on to excess dimethylamine at -78°C and stirred for 20 hr., the excess dimethylamine and the N,N-dimethylaminotrimethylsilane were distilled off at low temperatures and fractionated. N,N-dimethylaminotrimethylsilane b.p.71-3° was used immediately.

Preparation of lead ethylmercaptide[95]

To a suspension of lead acetate (32 g.) in aqueous alcohol (30 ml., 1:10) was added dropwise ethane thiol (7·5 ml.) with stirring. The yellow solid, the ethyl mercaptide was filtered off, washed with water and dried in vacuo.

Preparation of ethylthiotrimethylsilane[96]

To lead ethylmercaptide (3 g.) was added trimethylchlorosilane (2·8 ml.) and the mixture refluxed until the yellow colour disappeared.

The white precipitate, $PbCl_2$, was filtered off and the resulting colourless liquid distilled under an atmospheric pressure of nitrogen. Ethylthiotrimethylsilane b.p.130^{o} was collected.

Preparation of phenylthiotrimethylsilane[96]

To lead acetate (32 g.) in methanol (20 ml.) was added thiophenol (10·25 ml.), the yellow solid mercaptide which formed immediately was filtered off, washed with water and dried under reduced pressure. 8 g. of this lead phenylmercaptide was refluxed with trimethylchlorosilane (4 ml.) in a nitrogen atmosphere. The white solid was filtered off and the liquid fractionally distilled on a 30 cm. vigreux column. Phenylthiotrimethylsilane was collected b.p.85-6^{o}.

Preparation of t-butylisocyanate

A solution of technical grade pivalic acid (100 g.) in benzene (60 ml.) was refluxed for 48 hr. with excess thionyl chloride (120 ml.). The acid chloride $Bu^{t}COCl$ was separated by fractional distillation and in benzene solution was treated with activated (p.48) sodium azide. The acyl azide was immediately decomposed in warm toluene (100 ml., 60^{o}). Distillation of the resulting liquid yielded a benzene contaminated fraction of t-butylisocyanate which was used in benzene solution. The fraction of benzene present was determined by gas liquid chromatography (p.102). (Solution was 92·5% benzene and 7·5% t-butylisocyanate as determined from relative peak areas).

Preparation of sulphanuric chloride

(i) Preparation of trichlorophosphazosulphuryl chloride[1]

Analar phosphorus pentachloride (250 g.) was loaded into a 500 ml. round bottomed two-necked flask in the glove box. 110 g. of freshly recrystallised (p.47) sulphamic acid and dry carbon tetrachloride (40 ml.) were added by counter current techniques. The mixture was heated in an oil bath at 120^{o} with a reflux water-condenser and outlet bubbler filled with heavy white oil. The evolution of hydrogen chloride started almost immediately and after 3 hr. a clear solution was obtained. When the evolution of HCl had ceased (16 hr.) heating was stopped and the mixture cooled in an atmosphere of dry nitrogen. Carbon tetrachloride and phosphorus oxychloride were taken off at 30^{o} under reduced pressure (through trap at -78^{o} rotary pump under air ballast).

$$PCl_5 + NH_2SO_3H \longrightarrow Cl_3P{=}N{-}SO_2Cl + HCl + POCl_3$$

The resulting oil was cooled in the 'fridge (15 min.) and a white crystalline solid formed (m.p.33-5^{o}). This was used without further purification.

(ii) Pyrolysis of trichlorophosphazosulphuryl chloride[53]

The trichlorophosphazosulphuryl chloride was put in the flask of a distillation apparatus with a 30 cm. vigreux column and heated to 140^{o} at a pressure of $\sim$ 2 mm. Hg. Condensation began at an oil bath temperature of about 100^{o} but the condensed liquid soon solidified and was often in danger of blocking the apparatus. $POCl_3$ eventually began to distil off and the temperature was maintained at 140-145° until solid began to form in the condenser and very little $POCl_5$ was coming over. The solid residue was cooled, and tipped into ice-water to remove hydrolysable material. The buff insoluble material was filtered off dried and recrystallised from hexane then sublimed at 120° and 0·01 mm. Hg. α-Sulphanuric chloride was so obtained m.p.135°. Yield 23 g.,20%. The infrared spectrum showed absorptions at: 1808w, 1342s, 1326s, 1107s, 812m, 730sh, 714m, 701ms, 671m, 665ms, 541ms, 524ms.

Preparation of sulphanuric fluoride [52]

α-sulphanuric chloride (6·1 g., 21mmole) and anhydrous potassium fluoride (7·1 g.) were dissolved in dry acetonitrile (20 ml.) and refluxed with stirring (24 hr.). The potassium chloride was filtered off, washed with acetonitrile and the washings and filtrate combined and distilled at reduced pressure then fractionally distilled, using a 30 cm. plain column, at atmospheric pressure b.p.135°. Yield 4 g., 79%. The infrared spectrum showed absorptions at: 1876w, 1390vs, 1179vs, 889sh, 880s, 781s, 557m, 518s.

Preparation of tetrasulphur tetranitride, S_4N_4

Tetrasulphur tetranitride was prepared in the department as described by P.J. Dainty. [97]

Preparation of thiodithiazyldichloride, $S_3N_2Cl_2$ [7]

Ammonium chloride (100 g.) and powdered sulphur (20 g.) were thoroughly mixed and put in a 250 ml. single necked round bottomed flask with a B24 100 cm. air condenser which led off through a heavy oil bubbler. Disulphur dichloride (50 ml.) was added and the mixture heated slowly until the S_2Cl_2 refluxed into the bottom of the air condenser, 110^o, this temperature was maintained until the reaction mixture was almost dry. Brown crystals formed in the air condenser and HCl gas was given off. The air condenser was removed under a flow of dry nitrogen and the crystals pushed into a nitrogen filled flask and pumped dry. The residue set hard but after soaking with water could be broken up and poured out. 10·5 g. of $S_3N_2Cl_2$ was obtained, m.p.90-92^o. The infrared spectrum showed bands at: 1015m, 936vs, 892sh, 749w, 719sh, 711s, 579m, 457s, 400m(broad).

Preparation of trithiazyltrichloride,$(NSCl)_3$

(i) From tetrasulphur tetranitride, S_4N_4 [28]

S_4N_4 (10 g., 54 mmole) was stirred with sulphuryl chloride (20 ml.) in a nitrogen filled Schlenk, open to an outlet bubbler for 16 hr. The yellow solid was filtered off and recrystallised from dry carbon tetrachloride (1g. $(NSCl)_3$ per 10 ml.). The filtrate was taken down to dryness under reduced pressure and the resulting solid recrystallised from carbon tetrachloride. The two samples of trithiazyltrichloride so obtained, m.p.90-91^o, amounted to 16·5 g. a 93% yield. The infrared spectrum showed absorptions at: 1256w, 1076sh, 1016vs, 800m, 700s, 621mw, 515s.

(ii) From thiodithiazyldichloride[28] (p.103)

Thiodithiazyldichloride (10 g., 51 mmole) was stirred for 24 hr. at room temperature with sulphuryl chloride (30 ml.) in a Schlenk open to an outlet bubbler. After 24 hr. evolution of gas (SO_2) had ceased and yellow solid had formed. The liquid was evaporated under reduced pressure and the yellow solid was recrystallised from carbon tetrachloride. 10·8 g., 91% of trithiazyltrichloride were obtained m.p.90-91°C. The infrared spectrum showed absorptions at: 1017vs, 698ms, 621w, 514m, 493m.

Chapter 3

Reactions of Sulphanuric Compounds

I. Experimental

Reactions of Sulphanuric Compounds

I. Reaction of Sulphanuric chloride with HgR_2

a) α-Sulphanuric chloride and diphenylmercury[55]

Sulphanuric chloride (7·3 g., 25 mmole) and diphenyl mercury (17·7 g., 50 mmole) were dissolved in dry benzene (100 ml.) and the mixture stirred at 30-33° for 72 hr. The white solid was filtered off, washed with benzene and the washings and filtrate combined and taken down to dryness. The resulting buff semi-solid was extracted with 5 x 50 ml. portions of boiling n-heptane until it turned dark green. On cooling, the n-heptane extract yielded white crystals which were recrystallised from heptane m.p.116-7°. Yield 4·2 g., 45%. Analysis, Found: C,38·74; H,2·63; Cl,9·0; calculated for $(NSO)_3ClPh_2$ C,38·35; H,2·68; Cl,9·4%.
The infrared spectrum (Nujol mull) showed absorptions at: 1894w, 1825w, 1760vw, 1630vw, 1582w, 1450s, 1326s, 1274s, 1188s, 1149vs, 1100s, 1083vs, 1073sh, 1024m, 1013m, 992m, 976w, 832m, 823s, 755m, 743s, 727w, 715s, 690m, 680s, 667w, 638ms, 572s, 565sh, 537s, 470w, 452w.
The mass spectrum (p.147) showed a fragmentation pattern with peaks at m/e 375, 377, 340, 249, 141, 139, 127, 125, 110, 109, 85, 83, 81, 77, 64, 48, 46, 36, 38.

b) α-Sulphanuric chloride and dimethylmercury

α-sulphanuric chloride (1·0 g., 3 mmole) was dissolved in dry benzene (10 ml.) and cooled to -78°. Dimethylmercury (1·5 ml., 4·6 g., 20 mmole) was added dropwise under a counter current of nitrogen and the solution allowed to warm slowly to room temperature with constant stirring. After stirring for 24 hr. at room temperature the white precipitate, MeHgCl, was filtered off and the solution taken down to dryness, leaving a white flaky solid which began immediately to turn yellow and sticky. The yellow sticky solid was extracted with boiling n-heptane from which white crystals formed on cooling m.p.148^{o}. Yield 0·4 g., 40%.

The infrared spectrum (Nujol mull) contained absorption bands at: 1812w, 1355s, 1342s, 1307sh, 1263m, 1193w, 1168m, 1130m, 1109s, 1075s, 1025m, 833w, 811m, 795sh, 734m, 719s, 701s, 671m, 666s, 634w, 554m, 540s, 523s.

Analysis Found: C,4·5; H,1·10. $(NSO)_3Cl_2Me$ requires C,4·41; H,1·10%.

II. Reaction of sulphanuric fluoride with amines and sulphanuric chloride with amine derivatives, $(Me_3Si.NR_2)$

a) Morpholine and α-sulphanuric chloride[64]

A solution of α-sulphanuric chloride (0·9 g., 3 mmole) in acetonitrile (20 ml.) was added dropwise under a counter current of nitrogen to a cooled (0^{o}C) solution of morpholine (1·57 g., 18 mmole) in acetonitrile (10 ml.) over a period of 1 hr. No solid, morpholine hydrochloride, formed and the solution was evaporated to dryness under reduced pressure leaving a yellow viscous oil. Infrared (contact film on KBr plates) absorptions occurred at: 2739w, 2702w, 2475w, 2394w, 1615m, 1476m, 1366m, 1293sh, 1262s, 1237sh, 1213w, 1149sh, 1108s, 1069s, 1030s(broad), 925m, 870m, 846m, 815sh, 801s, 773m, 741m, 722m, 706m, 689m, 677w, 671sh, 663w, 652w, 606m, 578sh, 505m(very broad).

b) <u>Pyridine and α-sulphanuric chloride</u> [42c]

Dry pyridine (0•2 ml.,2•6 mmole) was added from a syringe to a stirred solution of α-sulphanuric chloride (0•23 g.,0•8 mmole) in toluene (10 ml.). Immediate clouding of the solution occurred and a viscous oil slowly settled out (3 hr.). The toluene was syringed off and the oil washed with toluene (10 ml.) and chloroform (2 x 5 ml.) then dried in vacuo. Infrared absorptions (contact film) occurred at: 3077m, 3030m, 2924m, 2817sh, 2717s, 2617s, 2083m, 1865w, 1642m, 1634sh, 1538m, 1488m, 1470s, 1404w, 1337sh, 1367s, 1255sh, 1167s, 1126s, 1063s, 1026sh, 962sh, 818m, 800s, 750s, 740sh, 704m, 680s, 658s, 636w, 609m, 591m, 569s, 562sh, 529s, 523s, 487m, 468m.

c) <u>Deuteropyridine and α-sulphanuric chloride</u>

Deuteropyridine (0•2 ml.,2•4 mmole) was added dropwise from a syringe with a counter current of nitrogen to a solution of α-sulphanuric chloride (0•23 g., 0•8 mmole) in toluene (10 ml.). The solution immediately turned cloudy and a golden yellow oil settled out. The toluene was decanted and the oil washed with toluene (10 ml.) and chloroform (2 x 5 ml.) then dried in vacuo. Infrared absorptions (contact film) occurred at: 3182w, 3086m, 2915m, 2808m, 2724sh, 2666s, 2544sh, 2049m, 1595s, 1501w, 1472m, 1406w, 1367sh, 1349sh, 1307s, 1231m, 1158s, 1126s, 1064s, 1036sh, 1005s, 977sh, 868w, 842sh, 828m, 812s, 803s, 773w, 738s, 705m, 699m, 680w, 660s, 651sh, 587m, 570s, 528s, 490m, 467m.

d) Dimethylamine and sulphanuric fluoride

Sulphanuric fluoride (0·5 g., 2 mmole) was cooled to -78^{o} and dimethylamine (0·45 ml., 6 g.) condensed on to it from a graduated tube under reduced pressure (65 cm.). The reaction mixture was allowed to warm to room temperature with stirring and dry heptane (10 ml.) added. The white solid (I) which precipitated out and did not redissolve on warming was filtered off and the heptane removed from the filtrate yielding a white solid (II). Both solids had very similar infrared spectra and analysis, attempts to purify them by recrystallisation from diethyl ether, hydrocarbons and benzene or sublimation at temperatures from 20^{o} to 90^{o} and 1 to 0·001 mm. Hg lead to decomposition or formation of dimethylammonium fluoride.

I showed infrared (Nujol mull) absorptions at: 2040w, 1841w, 1538sh, 1315s, 1281sh, 1264s, 1237sh, 1123s, 1050m, 1020m, 1002w, 963m, 843s, 800m, 734sh, 771s, 691m, 617w, 542w, 524m.

II showed infrared (Nujol mull) at: 2030w, 1538m, 1356s, 1264s, 1237s, 1120s, 1050m, 1023m, 1000w, 968s, 840s, 803m, 734s, 772s, 694m, 610w(broad), 524m.

e) Diethylamine and sulphanuric fluoride

Sulphanuric fluoride (0·5 g., 2·0 mmole) was dissolved in dry heptane (20 ml.) and cooled to -78^{o}C. Diethylamine (1·3 ml., 0·9 g., 12 mmoles) was added with stirring and the solution warmed to 30^{o}. After stirring at this temperature for two hours the solution was cooled to 0^{o} and the white acicular crystals were filtered off. The filtrate was taken down to dryness leaving a colourless oil (0•56 g., 61%). Analysis Found: C,13•6; H,2•96; F,5•8. $(NSO)_3F(NEt_2)_2$ requires C,13•7; H,2•86; F,5•5%. The infrared spectrum (contact film) showed absorption bands at: 3077w, 2941w, 1468w, 1385s, 1370s, 1299s, 1202m, 1150s, 1102m, 1085m, 1070m, 1018m, 966m, 873m, 855m, 820s, 795m, 746s, 727m, 700m, 612w, 552w, 517m, 464w, 457w.

f) n-Octylamine and sulphanuric fluoride

Sulphanuric fluoride (3 g., 12 mmole) was cooled to -46°C and n-octylamine (6 g., 47 mmole) added slowly from a syringe with a counter current of dry nitrogen. The mixture was then allowed to warm gradually to room temperature where it was maintained with stirring for two hours. Dry toluene (40 ml.) was added and the suspension warmed until all the white solid had dissolved. On cooling the precipitated white solid (I) was filtered off, washed with toluene (4 x 10 ml.) and dried. The filtrate and the washings were combined and the toluene removed under reduced pressure leaving a colourless oil (II) which over the period of a week continued to precipitate white solid, n-octylammonium fluoride, which was soluble in the desired product and in many organic solvents. In an attempt to remove all the ammonium salt the oil was dissolved in toluene, (20 ml.) then the solution washed three times with distilled water (3 x 20 ml.), dried over anhydrous magnesium sulphate and the toluene removed. The infrared spectra showed that the oil so obtained contained hydrolysis product. Analysis indicated the absence of F and S. The oil, II also proved too involatile to distil, even under reduced pressure. After standing for two weeks in a nitrogen atmosphere and filtering all the solid out the oil gave analyses of C,41·1; H, 7·8; N,14·9; F,4·32; S,8·5%.

Calculated for	n-octylammonium fluoride	monsubst.	disubst.	trisubst.
C	64·38	27·3	41·6	50·5
H	13·51	5·1	7·9	9·5
N	9·38	15·9	15·2	14·7
F	12·73	10·8	4·1	
S		27·3	20·8	16·8

The infrared spectrum (contact film) showed absorptions at: 3185w, 3049w, 2941m, 2232m, 1631w, 1613w, 1506w, 1470m, 1381w, 1362ms, 1348ms, 1266m, 1240m, 1142s, 1111s, 1075s, 935m, 850m, 802m, 783m, 730s, 713m, 697m, 616w, 552w, 517m, 464w, 457w.

g) Aniline and sulphanuric fluoride

Sulphanuric fluoride (0·86 g., 3·5 mmole) in heptane (10 ml.) was cooled and aniline (2·2 g., 23·5 mmole) added. After stirring at room temperature for 24 hr. there was no noticeable change and no precipitate of aniline hydrofluoride. The reaction mixture was refluxed for 24 hr. and the heptane removed. The infrared spectrum of the oil so obtained showed no reaction had taken place, it was a superimposition of sulphanuric fluoride and aniline.

h) <u>N,N-diphenylaminotrimethylsilane and α-sulphanuric chloride</u>

α-sulphanuric chloride (45 g., 1•5 mmole) in toluene (10 ml.) was added to a solution of N,N-diphenylaminotrimethyl silane (p.49) freshly prepared and the mixture stirred at room temperature for 6 hr. The black solution was taken down to dryness under reduced pressure leaving a dark green intractable solid, insoluble in hydrocarbons, ethers, alcohols, actone and water, and involatile at 100^o and 0•001 mm.Hg. The infrared spectrum of this solid was ill defined, a mull with Nujol being impossible to achieve. Analysis found: C,37•0; H,4•21; Cl,21•9; S,12•8; N,11•21% which gives an atomic ratio of C:H:Cl:N:S of 40:31:6:4:8 which indicates that a polymeric material of variable constituency had probably been formed. Repetition of the reaction gave a product with very similar infrared spectrum and analysis. The infrared spectrum (Nujol mull) of the green powder contained absorptions at: 1398w, 1385w, 1310s, 1266s, 1176m, 1149m, 1089s, 1071s, 1052sh, 1029s, 1013s, 902w, 818s, 781s, 694s, 569s.

i) <u>N,N-dimethylaminotrimethylsilane and sulphanuric chloride</u>

α-Sulphanuric chloride (1•0 g., 3•4 mmole) in dry toluene (10 ml.) was cooled to -78^o and N,N-dimethylaminotrimethyl silane (p.49) (1•2 g., 10•2 mmole) was added dropwise with stirring. The solution was stirred at room temperature for an hour then heated to 60^o at which temperature a liquid distilled off which was shown by infrared spectroscopic analysis to be trimethylchlorosilane. The solution was pumped to dryness leaving a golden-red, viscous, involatile oil. Analysis Found: C,22·3; H,5·82; N,25·8; Cl, 0. $(NSONMe_2)_3$ requires C,22·7; H,5·76; N,26·4%. The infrared spectrum contained bands at: 3012m, 2967m, 2924m, 2890m, 2849w, 2801w, 1700w, 1628w, 1459ms, 1408w, 1351w, 1319sh, 1257s, 1146sh, 1084s, 941s, 849s, 814ms, 757ms, 693ms, 598w, 544mw, 529m, 525m, 483mw.

III. Substitution by SR

a) α-Sulphanuric chloride and ethanethiol

α-Sulphanuric chloride (0·6 g., 2 mmole) was dissolved in dry carbon tetrachloride (30 ml.) and cooled. Ethanethiol (1 ml., 0·84 g., 13 mmole) was added dropwise with a counter current of nitrogen and the solution allowed to warm to room temperature. After two hours a white feathery precipitate formed which was filtered off and washed, m.p.339-40^{o}. Infrared spectrum has peaks at 3310s, 1721m, 1358w, 1398s, 1158m, 943w (broad), 721vw, which was identical with ammonium chloride. 0·3 g. were obtained which corresponded to 91% conversion of the nitrogen of α-sulphanuric chloride. The filtrate on evaporation under reduced pressure gave an oil which analysed to diethyldisulphide. Analysis found: C,40; H,8·1; S,53. Calculated for Et_2S_2: C,39·3; H,8·2; S,52·4. Its infrared spectrum contained bands at: 2962s, 2912s, 2869m, 2812m, 1709w, 1447s, 1420m, 1375s, 1277sh, 1252s, 1221w, 1183w, 1158w, 1113w, 1111w, 1062sh, 1050m, 1029w, 969m, 807w, 780m, 753s, 692w, 666w, 639w, 478m.

b) α-Sulphanuric chloride with lead ethylmercaptide

α-Sulphanuric chloride (0·5 g., 1·7 mmole) was dissolved in dry carbon tetrachloride (15 ml.) and excess lead ethylmercaptide (5 g.) (p.49) added. The resulting suspension was stirred for 48 hr. at 24^{o}. After 20 hr. a slight darkening was noticeable and the mixture eventually turned to a brown colour. The solid was filtered off, washed with carbon tetrachloride and analysed. Analysis Found: C,3•64; H,0•97; Cl,20•56. Some exchange had therefore taken place. Eavporation of the carbon tetrachloride solution gave a red, intractable tar, whose infrared spectrum contained bands at: 3139m, 3048m, 2971m, 2928m, 1692w, 1543w, 1447m, 1408m, 1379m, 1312s, 1269sh, 1246sh, 1182s, 1164s, 1082s, 1050s, 1026s(broad), 790m, 736m, 694m, 666sh, 660m, 631m, 619w, 550m, 543m, 515m, showing that the sulphanuric ring was no longer intact.

c) <u>α-sulphanuric chloride and ethylthiotrimethylsilane</u>

To α-sulphanuric chloride (0•75 g., 2•5 mmole) in a 100 ml. two necked RB flask, cooled in liquid nitrogen, was added ethylthiotrimethyl silane (p.49) (3•4 g., 25 mmole) with a counter current of nitrogen and the reaction vessel warmed slowly to room temperature. As the mixture warmed a violent reaction took place when the temperature was in the region -50-40^{o}, a deep red mobile liquid being formed, which was stirred at room temperature for a further two hours. The liquid was pumped dry, removing any trimethylchlorosilane and ethylthiotrimethylsilane. The dark red oil was extracted with hot n-heptane (2 x 10 ml.) which yielded a minute quantity of yellow needle-like crystals on cooling,m.p.96^{o}. The infrared spectrum showed absorption bands at: 1404w, 1331s, 1307vs, 1265w, 1237vw, 1132m, 1102s, 1057m, 1033s, 1025s, 961m, 885w, 788m, 774m, 721m, 699s, 657ms, 610s, 515s, 508s, 495s.

The infrared spectrum of the red oil remaining contained bands at: 3184m, 2976w, 2923w, 1700m, 1550w, 1443m, 1404m, 1315s, 1243sh, 1161s, 1072s(broad), 1008sh, 853w, 807m, 791m, 763m, 689m, 663s, 631m, 617w, 558sh, 544s, 514m, indicating that the sulphanuric ring had opened up.

IV. Halogen Exchange

a) α-Sulphanuric chloride and lithium bromide

α-Sulphanuric chloride (1·0 g., 3·4 mmole) in dry acetonitrile (20 ml.) was added dropwise to a cooled solution of anhydrous lithium bromide (0·9 g., 10·5 mmole) in acetonitrile (20 ml.). The resulting solution was gradually warmed to room temperature where it was maintained with stirring for 48 hr. The white solid was filtered off, washed with dry acetonitrile (20 ml.), the filtrate and the washings were combined and taken down to dryness. The resulting yellow-brown solid was extracted with warm (50^{o}) toluene, the red solution so obtained yielded red crystals when cooled overnight in the fridge, m.p.152-4^{o}.

The infrared spectrum contained absorptions bands at: 1267ms, 1108s, 806ms, 723m, 469ms(broad).

Analysis found: N,8·94; S,24·4; Br,61·8 (assuming no chlorine).

$(NSOBr)_3$ requires N,9·88; S,22·6; Br,56·3%.

b) <u>α-Sulphanuric chloride and lithium iodide</u>

α-Sulphanuric chloride (1·0 g., 3·4 mmole) and lithium iodide (1·37 g., 10·3 mmole) were mixed and dissolved in acetonitrile (10 ml.) under a nitrogen atmosphere. The initial exothermic reaction on dissolving the solids resulted in a deep red solution and an orange solid. The suspension was stirred for 48 hr., filtered and the filtrate taken down to dryness. Excess iodine was sublimed out of the red solid leaving a light brown solid which was insoluble in hexane and toluene. Analysis found: N,8·42; S,16·76%. $(NSOI)_3$ requires N,7·42; S,16·95.

The infrared spectrum contains peaks at: 1280sh, 1263s, 1164s, 1101s, 803m, 721m, 568w(broad), 474w(broad).

On exposure to the atmosphere the solid turned green and deliquesced with decomposition.

V. <u>Reactions of diphenylsulphanuric chloride</u>

a) <u>With potassium fluoride</u>

Diphenylsulphanuric chloride (1·8 g., 5 mmole) and potassium fluoride (0·6 g.) in dry acetonitrile (30 ml.) were refluxed in a two necked round bottomed flask fitted with a reflux condenser (48 hr.) protected from atmospheric H_2O by bubbler filled with heavy white oil. A cloudiness of the solution appeared soon after refluxing commenced and a white solid slowly precipitated out. The white solid (KCl) was filtered off, washed, the washings and the filtrate were combined and taken down to dryness under reduced pressure. The white solid residue was extracted with hot (70°) n-heptane. On cooling the extract, white crystals formed which were recrystallised from heptane, m.p.115°. Yield 0·95 g., 53%. Analysis found: C,39·91; H,2·83; F,5·28. Calculated for $(NSO)_3FCl_2$ C,40·1; H,2·79; F,5·29%.

The infrared spectrum showed absorptionsbands at: (p.82) 1914w, 1883w, 1821w, 1757w, 1678w, 1585w, 1452s, 1359s, 1299sh, 1284s, 1189s, 1171vs, 1157vs, 1135vs, 1129vs, 1082s, 1045sh, 1025w, 1000m, 932w, 835s, 786ms, 762m, 749ms, 725sh, 720sh, 715vs, 693w, 683m, 678ms, 669w, 631ms, 611w, 569vs, 533s, 526ms, 512w, 481w.

b) <u>With lithium iodide</u>

To $(NSO)_3ClPh_2$ (1·0 g., 2·7 mmole) in acetonitrile (30 ml.) at 0° was added dropwise with stirring anhydrous LiI (0·36 g.) in acetonitrile (15 ml.). The clear colourless solution immediately began to turn red-brown and a white solid was precipiated. The solid (LiCl) was filtered off and washed with acetonitrile, the washings and filtrate when combined and taken down to dryness under reduced pressure gave a red, toluene soluble oil. The infrared spectra showed absorptions at: 3333s(broad), 2304s, 2272s, 2061w, 1620s, 1538m, 1408m, 1285m, 1253m, 1180w. On exposure to air the oil turned rapidly brown and iodine could be sublimed off.

c) With potassium thiocyanate

Diphenylsulphanuric chloride (0·6 g., 1·6 mmole) and anhydrous KNCS (0·34 g., 3·2 mmole) were dissolved in acetonitrile (40 ml.) and refluxed in a nitrogen atmosphere for 24 hr. On removal of the acetonitrile under reduced pressure, a rich yellow solid was obtained which was insoluble in hydrocarbons, and ethers but a white solid could be extracted with boiling ethanol which contained no chlorine and 17·2% C. The infrared spectrum (KBr disc) showed absorptions bands at: 3400m, 2778m, 2326m, 2162m, 2047vs, 1602w, 1477w, 1447w, 1433w, 1325w, 1242sh, 1227s, 1160w, 1105s, 1065m, 1019m, 997m, 968s, 950m, 814w, 747s, 730sh, 727m, 724m, 708w, 693m, 682m, 667w, 617w, 607m(broad), 543w, 483s, 469m.

d) With chlorine

Chlorine gas was bubbled through a solution of $(NSO)_3ClPh_2$ (0·5 g.) in dry carbon tetrachloride (40 ml.) with iodine (0·1 g.) as catalyst for 1 hr. The chlorine saturated solution was stirred at 22° for 15 hr. under a chlorine atmosphere. The solution was then pumped to dryness and the white residue extracted with boiling n-heptane. On cooling white crystals came out of the heptane, m.p.72°. Yield 0·47 g., 68% of recrystallised product. Analysis found: Cl,34·0; C,27·8; H,1·18; S,19·1%. Calculated for $(NSO)_3Cl(C_6H_3Cl_2)_2$ Cl,34·5; C,28·1; H,1·18; S,18·8%. The molecular weight calculated from osmometry in benzene was 511. The infrared spectrum showed peaks at: 1326s, 1274m, 1183s, 1152s, 1139s, 1096m, 1083m, 1023m, 998m, 840m, 815m, 755w, 742m, 718m, 690w, 680w, 666m, 639m, 625m, 573m, 563m, 538m, 488w.

e) With bromine

To diphenylsulphanuric chloride (0•6 g., 1•6 mmole) and iodine (0•1 g.) in dry carbon tetrachloride (40 ml.) was added excess bromine (10 g.) and the brown solution stirred for 20 hr. at room temperature. The solution was taken down to dryness under reduced pressure and the resulting white solid extracted with boiling heptane. The white solid, m.p.73-4^{o}, which crystallised from the heptane on cooling contained both chlorine 8•65 and bromine 1•48%, but substitution either was incomplete or halogen exchange was the only reaction which had taken place. Analysis found: C,34•2; H,2•5 (p. 89) N,9•7; S,21•0; Cl,8•7; Br,1•5%. The mass spectrum showed fragments containing bromine. The infrared spectrum consisted of the following absorptions: 1449m, 1326s, 1312m, 1279m, 1188s, 1166m, 1156s, 1142s, 1101m, 1086m, 1028m, 998w, 853w, 840m, 832w, 821m, 756w, 743m, 717s, 690w, 680m, 670w, 666m, 639s, 628sh, 573s, 564s, 545sh, 539s; 489m.

f) With 2,4,6-trichlorophenol

Diphenylsulphanuric chloride (0•5 g., 1•3 mmole) and trichlorophenol (0•26 g., 1•3 mmole) were heated to 80^{o}, fusion taking place at ~ 50^{o}. A gas was evolved which turned damp litmus red and gave white fumes with ammonia. The white liquid turned deep red and on cooling formed a red sticky solid. Excess trichlorophenol was sublimed out and the dark red tar slowly solidified (3 days) to give a deep pink powder on grinding, m.p.52^{o}. Analysis found: C,39•3; H,2•36; Cl,20•03%. Calculated for

$(NSO)_3Ph_2(C_6H_2Cl_3O)$ C,40•27; H,2•25; Cl,19•8%. The infrared spectrum contained absorption bands at: 1953w, 1890w, 1818w, 1754w, 1689w, 1600m, 1541m, 1449s, 1437s, 1326s, 1276s, 1226w, 1188m, 1140s, 1103s, 1183s, 1025sh, 1020m, 998m, 952w, 913w, 857m, 821s, 805m, 756m, 743s, 728s, 724s, 717m, 692m, 681m, 640m, 611w, 572s, 555w, 537s, 454m, 452m.

g) With pyridine

To a solution of diphenysulphanuric chloride (0•2 g., 0•5 mmole) in toluene (10 ml.) was added pyridine (0•5 ml.; 2•6 mmole) under an atmosphere of dry nitrogen. The solution immediately turned cloudy and a pale yellow oil slowly settled out. The solvent was decanted and the oil washed with toluene (5 ml.), chloroform (2 x 5 ml.), and finally hexane (5 ml.), then dried in vacuo. Infrared absorptions (contact film) occurred: 3226m, 3058s, 2976s, 2849s, 2597s(broad), 2803m,2000m, 1631m, 1607s, 1529s, 1481s, 1458w, 1376m, 1316sh, 1299vs, 1280sh, 1250sh, 1199sh, 1179sh, 1163vs, 1121vs, 1056s, 1029s, 1001m, 930w, 905w, 823sh, 812m, 800m, 749s, 705m, 678s, 657m, 647m, 606m, 561s(broad), 518s(broad).

h) With diethylamine

Diphenylsulphanuric chloride (0•4 g., 1•0 mmole) were dissolved in diethylamine (10 ml.) and the mixture refluxed for 20 hr. with rapid stirring. The diethylamine was then removed under reduced pressure leaving a red oil which was insoluble in heptane and other hydrocarbon solvents (hexane, benzene and toluene). The infrared spectrum showed absorptions at: 3390m, 2907s, 2841s, 2487m, 2404m, 2273w, 1818w, 1667m, 1618ms, 1470s, 1450s, 1394s, 1294m, 1242s(broad), 1102s(broad), 1034s(broad)

926m, 862w, 845w, 805s, 758m, 740m, 730m, 695s, 670w, 626m, 615m, 561s(broad), 516m(broad).

i) Diphenylsulphanuric fluoride and dimethylamine

Dimethylamine (3 ml.) was condensed on to a solution of diphenylsulphanuric fluoride (0·5 g., 1·3 mmole) in heptane (20 ml.) and the mixture stirred at 0^{o} for 6 hr. On removal of the solvent and excess amine from the clear colourless solution, a white solid formed m.p.114-5^{o}, whose infrared spectrum was identical with that of diphenylsulphanuric fluoride, the starting material.

j) With ethylthiotrimethylsilane

To diphenylsulphanuric chloride (0·3 g., 0·8 mmole) in dry carbon tetrachloride (10 ml.), ethylthiotrimethyl silane (p. 49) (0·15 ml., 1·0 mmole) was added dropwise with stirring. The solution was stirred at toom temperature for 20 hr. then taken down to dryness under reduced pressure. Extraction of the remaining buff solid with n-heptane gave a white crystalline solid whose m.p.115-6^{o}, and infrared spectrum showed it to be unchanged diphenylsulphanuric chloride.

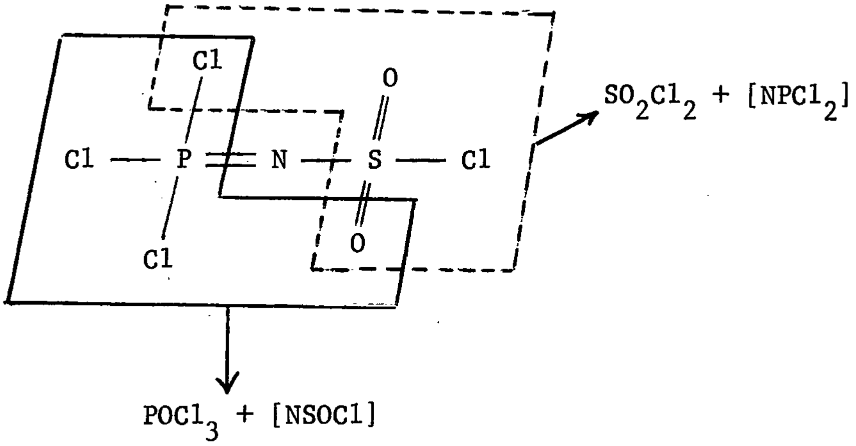
Chapter 4

Reactions of Sulphanuric Compounds

II. Discussion

a) <u>Synthesis of the Sulphanuric System</u>

The usual preparation of α-sulphanuric chloride involves the pyrolysis of trichlorophosphazosulphuryl chloride under reduced pressure. This method has been reported to give yields as high as 24% with little difficulty although van de Grampel and Vos[54] could not obtain sulphanuric chloride from this pyrolysis; they found that in the presence of u.v. light a six membered sulphur-nitrogen-phosphorus ring was obtained. In this work difficulty in obtaining $(NSOCl)_3$ has been periodically encountered. The difficulty probably arose from impure PCl_5, a slight amount of hydrolysis of the PCl_5 resulted in the pyrolysis product being a dark brown oil rather than a light brown semi-solid, which was extremely moisture sensitive. The temperature of pyrolysis was much higher, the Cl_3PNSO_2Cl often subliming out of the reaction vessel before pyrolysis commenced. The pyrolysis temperature to give $(NSOCl)_3$ apparently increases with the amount of hydrolysis of the original PCl_5 and it looks as though this temperature gradually overtakes the temperature of formation of other hydrolysable compounds. The $Cl_3P{=}NSO_2Cl$ can conceivably decompose in two ways, each eliminating a volatile liquid $POCl_3$ or SO_2Cl_2 (p.16). If sulphuryl chloride is eliminated an $NPCl_2$ unit remains which would account for the more highly exothermic hydrolysis of the residue. The presence of condensation products from P-OH in the $Cl_3P{=}NSO_2Cl$ would reduce the volatility of any phosphorus entity that could come off with the result that elimination of SO_2Cl_2 would be more favourable leaving the $NPCl_2$ fragment.



In the cases where the yield of sulphanuric chloride was either low or non-existant some HCl was usually condensed in the trap even though the 'bleed' was of dry nitrogen so presumably the hydrogen was from impurities in the reaction mixture, e.g. from impure PCl_5.

After washing out the hydrolysable material the α-sulphanuric chloride was recrystallised from boiling heptane then sublimed. On sublimation a considerable quantity of a buff amorphous solid remained which was insoluble in hot heptane and unchanged by water, it would not mull with Nujol indicating that it was polymeric. At the sublimation temperature (~ $100^{\circ}C$) it seems likely that slight impurities cause polymerisation to occur.

In the reported synthesis of sulphanuric fluoride[52] catalytic water was added; we found that the yield of the trimer increased if carefully dried solvents and reagents were used but the time necessary for complete reaction increased. It was found that in the reported preparation a considerable amount of polymeric material - a yellow semi-solid which hardened on drying - remained after the first distillation; when no catalytic water was added the amount of this yellow material was practically nil.

Reaction of α-sulphanuric chloride with HgR_2

Until McKenney and Fetter[55] reported the preparation of diphenyl-sulphanuric chloride from diphenyl mercury and sulphanuric chloride the only route to aryl sulphanuric compounds was from sulphanuric fluoride and phenyl lithium,[52] which yields either the mono- or di-substituted trimer. Moeller et al[52] had prepared the sulphanuric triphenyl by a Friedal Crofts reaction with aluminium trichloride in refluxing benzene; this is still the only known way to get the trisubstituted aryl derivative. The yield is very low in the order of 7-10%. Moore[42d] found that reactions with lithium alkyls lead to the formation of compounds whose spectra bear no resemblance to those of sulphanuric chloride or other sulphanuric derivatives,[42d] and the reaction of $(NSOCl)_3$ with PhMgBr in an attempt to prepare $(NSOPh)_3$ gave a small amount of an oil whose infrared spectrum was almost identical to that for PhNSO.

It appears therefore that organolithium compounds and Grignard reagents are too reactive for effecting substitution in $(NSOCl)_3$ and as yet only HgR_2 can be used to ~~replace~~ effect this substitution of Cl by R groups.

The work done by McKenney and Fetter was repeated and extended to prepare the first alkyl sulphanuric derivative using dimethyl mercury. The product was highly moisture sensitive and no attempt was made to separate isomers. The formation of the mono- rather than di-substituted derivative may be explained in much the same way as non-geminal substitution in cyclophosphazenes. So long as inductive effects are dominant, replacement of one chlorine by a group of lower electronegativity results in deactivation of the ring with respect to further nucleophilic attack. The monosubstituted derivative is then likely to be the major product.

The action of diaryl or dialkyl mercury compounds on sulphanuric fluoride has not been investigated but in view of its reaction with phenyl lithium there is no apparent reason as to why they should not react smoothly to give reasonable yields of the aryl or alkyl sulphanuric fluorides. The use of organomercury compounds containing substituted organic groups, e.g. amino or nitro groups is a conceivable way of preparing derivatives from which complex and/or biologically active species can be prepared.

Reaction of sulphanuric chloride with amines

The reaction of α-sulphanuric chloride with morpholine, pyridine and deuteropyridine resulted in the formation of viscous yellow oils which were extremely air and moisture sensitive. Moeller reported [64] that with morpholine and α-sulphanuric chloride a trimorpholido derivative could be obtained under carefully controlled conditions. On repeating this work the author could only obtain an oil similar to those prepared by L.F. Moore [42c] in a series of reactions of $(NSOCl)_3$ with amines. The oil obtained portrayed similar charcteristics to those of the adducts prepared by Moore and was assumed to be an adduct of similar structure, i.e. (NSOCl).3B where B is the basic molecule, the donor. The infrared absorption bands of α-sulphanuric chloride can still be seen in the spectrum superimposed on those of the base although most of these bands show shifts of 4 to 10 cm^{-1}.

The reaction between α-sulphanuric chloride and pyridine discussed at length by Moore[42c] was repeated and the infrared spectrum compared with that of the adduct formed with deuteropyridine in an attempt to account for the band at ~2600 cm^{-1} which Moore found difficulty in assigning. It was thought that if this band was a C-H shifted through ~450 cm^{-1} due to hydrogen bonding there would be a noticeable change in the infrared spectrum at this point with the perdeuteropyridine adduct. A strong broad band is found to appear at 2049 cm^{-1} compared with ν_{CD} in deuteropyridine itself at 2252 cm^{-1}. Work on hydrogen bonding has shown that ν_S can shift through 0 to 461 cm^{-1} when the hydrogen is involved in hydrogen bonding.[100]

A —— H ---- B ν_S

← →

These shifts are to lower frequency and are of the order of 10% ν_S. The ν_S mode is also broadened when a hydrogen bond is formed, the ½ width of the new mode being approximately ¾ of the width of the old one.[100] In general ν_H/ν_D is about 1·35.[100] This relationship is obeyed for pyridine and deuteropyridine ν_H/ν_D being 3054/2252 (i.e. 1·35). If hydrogen bonding does in fact occur, the ring being in the same kind of environment the relationship would be expected to hold approximately for the adducts. For ν_H/ν_D to be 1·35, a strong broad peak would be expected in the region of 1925 cm^{-1} (assuming the band assigned by Moore to C-H is correct). In fact a strong broad band appears at 2049 cm^{-1} giving ν_H/ν_D = 1·27 (cf. $CH_3COOH(D)$ 1·29, N-acetylglycine 1·27[100]). Its width is 202 cm^{-1} compared with that of 77 cm^{-1} for deuteropyridine itself. This is again in agreement with the presence of hydrogen bonding.

It looks as though there is a sound case for invoking the presence of CH hydrogen bonding but whether it is with the oxygen or the chlorine of the sulphanuric ring, intermolecular or intramolecular is an open question.

Reaction of Sulphanuric Fluoride with Amines

The majority of sulphanuric derivatives that have been reported in the literature to date have been prepared from the action of sulphanuric fluoride with secondary amines. Seel and Simon[50] reported the preparation of a dimethylamino derivative in the original preparation of sulphanuric fluoride. The reaction with dimethylamine was repeated and two white crystalline solids were obtained, these solids had very similar infrared spectra but attempts at purification by recrystallisation or sublimation (p. 58) led to decomposition and the formation of dimethylammonium fluoride. The formation of Me_2NH_2F is to be expected in the reaction if substitution does occur but when it was removed by sublimation the residue had an i.r. spectrum which gave no evidence of the sulphur nitrogen ring remaining intact. No solvent was found by which separation could be achieved suggesting that any derivative that may have been formed had an extremely similar solubility in organic solvents to that of Me_2NH_2F.

The reactions with diethylamine and the primary amine, n-octylamine were more successful,[60] a disubstituted derivative was isolated in each case although the removal of the amine hydrofluoride proved difficult. These derivatives were colourless which turned slowly yellow on standing; if some amine hydrofluoride remained it was slowly precipitated on standing. It is again noticeable that the final fluorine is difficult to replace.

No reaction occurred between aniline and sulphanuric fluoride in refluxing heptane. Sulphanuric fluoride will react with simple primary and secondary amines at room temperature or below to give disubstituted derivatives but purification of the products proves involved. The separation on an absorbing column may be the answer but the derivatives slowly decompose in the presence of moisture and therefore a completely water free column or thin layer chromatography plate is necessary. The separation would preferably be carried out in an inert atmosphere (e.g. dry nitrogen).

Reaction of α-Sulphanuric Chloride with Me_3SiNR_2

The use of Me_3SiNR_2 for the introduction of NR_2 and the elimination of Me_3SiCl has proved to be of widespread value. Abel and Armitage[101] have reported the reactions

$$RSO_2Cl + Et_2NSiMe_3 \longrightarrow Me_3SiCl + RSO_2NEt_2 \qquad (R = Me \text{ or } Ph)$$

and $$SO_nCl_2 + 2Et_2NSiMe_3 \longrightarrow 2Me_3SiCl_2 + (Et_2N)_2SO_n \qquad (n = 1,2)$$

the trimethylchlorosilane being relatively volatile is therefore easily removed from the reaction mixture. Moore[42d] found that the reaction of Et_2NSiMe_3 with N-sulphanuric chloride gave an oil, the analysis for which approximate to those required for the diethylamino derivative $(NSONEt_2)_3$, but attempts at separating the expected isomers by recrystallisation and sublimation were unsuccessful. The reaction of α-sulphanuric chloride with N,N-dimethylamino trimethylsilane was investigated as the dimethylamino derivative $(NSONMe_2)_3$ had previously been prepared by Seel and Simon.[50] However the product was once again a viscous involatile oil of golden red colour which portrayed the same difficulties in purification as the oily derivatives. However a considerable amount of Me_2NSiMe_3 was distilled off at room temperature under reduced pressure though not sufficient to account for quantitative conversion to the trisubstituted derivative. The analyses of the oil (C,H,N,Cl) were very close to those expected for $(NSONMe_2)_3$ and the infrared spectrum showed the sulphanuric ring to have remained intact.

It was decided that perhaps with a higher molecular weight amine a solid derivative might be obtained so the reaction was repeated using N,N-diphenylaminotrimethylsilane. This reaction however illustrated only the high chlorinating ability of sulphanuric chloride, a dark green intractable solid being formed at room temperature which had an ill defined infrared spectrum suggesting it was a polymeric material. Repetition at lower temperatures yielded the same type of polymeric material.

Substitution by -SR

The commonest methods of replacing Cl by SR are (i) reaction with RSH eliminating HCl,[24] (ii) precipitation of a metal chloride MCl by reaction with MSR,[42] (iii) elimination of Me_3SiCl[109] using Me_3SiSR.[108]

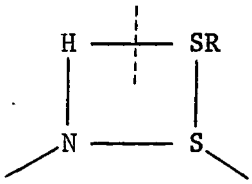
As the preparation of Me_3SiSR involves the preparation of $Pb(SR)_2$ it was decided to attempt method (ii) using $Pb(SEt)_2$. Me_3SiSR was used by analogy with the use of Me_3SiNR_2 by Moore[42d] and in this work. Me_3SiSR has been used by Abel et al[108] to prepare P-SR compounds.

$$(3-n)Me_3SiSR + PX_3 \longrightarrow (3-n)Me_3SiX + P(SR)_{3-n}X_n$$

where X is Cl, Br.

The volatile Me_3SiX is easily removed from the reaction vessel under reduced pressure.

The reaction with ethane thiol resulted, as anticipated, in the formation of an ammonium salt, ammonium chloride the quantity of which corresponded to 91% conversion of the nitrogen and chlorine of sulphanuric chloride to ammonium chloride. The breakdown of the SN ring is probably 'thiolytic', the RSH adding across the SN multiple band of the ring to give NH, this reduction continuing until the nitrogen comes away as ammonia.



An oil was also obtained which corresponded in analysis and infrared spectrum to diethyl disulphide. In the reaction with excess lead ethyl mercaptide some exchange did take place as shown by the analysis of the insoluble lead salt which contained 21% chlorine. However evaporation of the solution yielded a red intractable tar whose infrared spectrum indicated disintegration of the sulphanuric ring.

The reaction with ethylthiotrimethylsilane was more successful, for although a red oil was obtained, a small quantity of yellow acicular crystals were extracted, the infrared of which showed the SN ring to be intact, but insufficient were obtained for analysis on the then available methods. These crystals were extremely air and moisture sensitive and soon discoloured on storing in a nitrogen atmosphere. The infrared spectrum showed a strong peak at 659 cm^{-1} which was assigned to ν_{C-S} but the amount of substitution was not determined owing to the lack of analyses and molecular weight measurements. The infrared spectrum of the oil from which the crystals were obtained showed that once again the SN ring had disintegrated. The instability of the compound can be accounted for in terms of the electronegativity of the substituents. The SEt group has a group electronegativity of 2•31[106] on the Allred Rochow scale compared with 2•83 for chlorine and 4•10 for fluorine on the same scale.[107] The resulting decrease in electron withdrawal from the sulphur of the SN ring will reduce the tendency for N $\longrightarrow$ dπ donation so weakening the bonds in the ring and making the nitrogen more basic thus allowing co-ordination to other molecules at the expense of ring bonding. Low electronegativity values of the new substituent can account for monosubstitution in the reaction with dimethylmercury, (p. 73) and by a similar argument - low electronegative substituent results in higher electron density on sulphur and therefore less N $\longrightarrow$ S donation and instability of the SN ring - substitution would be expected to be only mono- or disubstitution in the case of SEt as their electronegativities are correspondingly low (Me, 2•28, SEt, 2•31).[106] On this basis trisubstutution would not be expected unless accompanied by ring breakdown.

Halogen Exchange

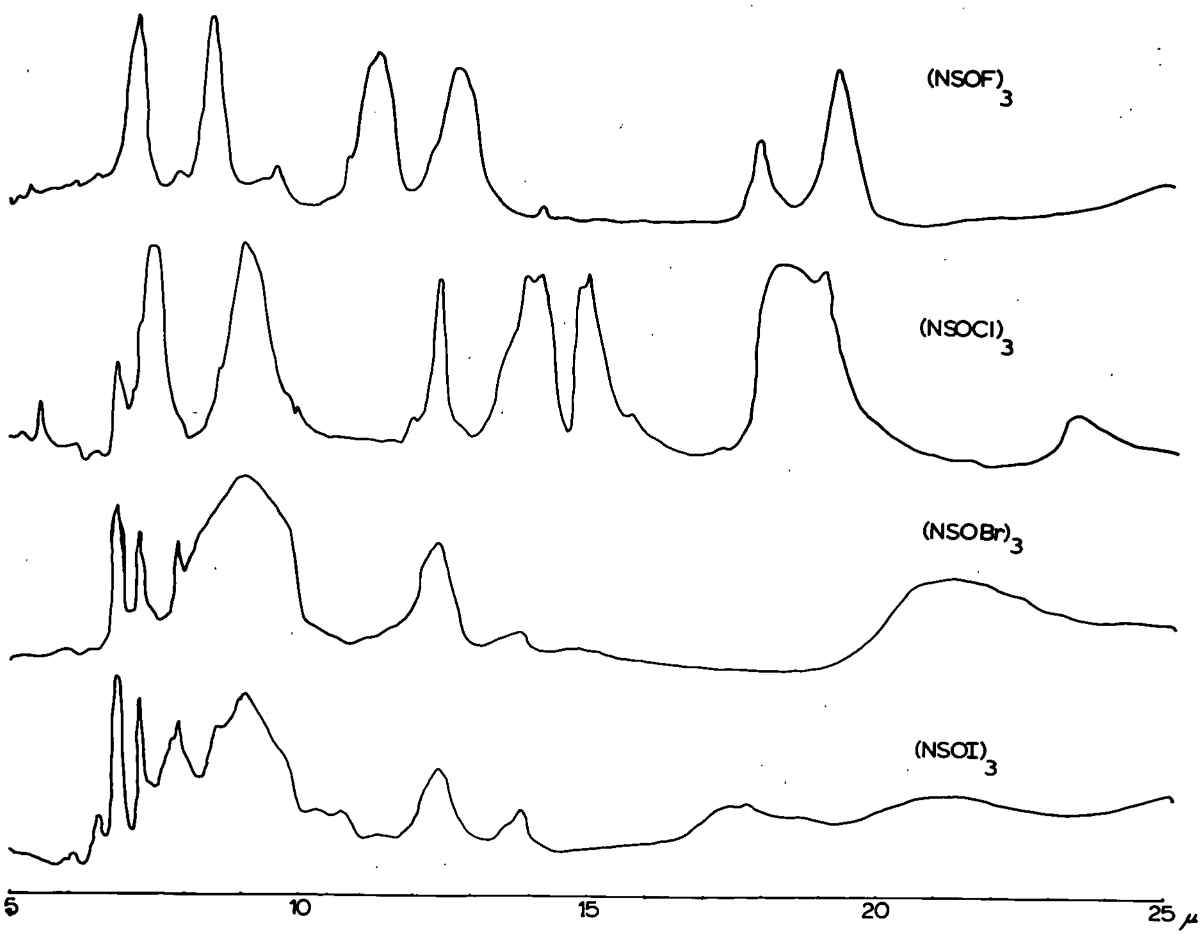
Potassium fluoride will undergo halogen exchange with α-sulphanuric chloride to give sulphanuric fluoride in reasonably high yields but there is no reported investigation of the similar reaction of lithium bromide and iodide which should result in the preparation of sulphanuric bromide and iodide respectively. These two reactions were investigated.

Lithium salts were used as the smallest anion and the smallest cation pack into a crystal to give the higher lattice energy, of the two possibilities LiCl would have a higher lattice energy than either LiBr or LiI and so its formation would be thermodynamically more favourable.

The reaction of α-sulphanuric chloride with LiBr (p.64) gave an intractable moisture sensitive solid at the major product from which a very small quantity of red crystals were obtained by solvent extraction with hot toluene. The analyses (N, S and Br) approximated to those of $(NSOBr)_n$ assuming the absence of chlorine.

In the reaction with lithium iodide a red solid was obtained out of which iodine could be sublimed at room temperature. The resulting light brown solid which was insoluble in hexane and toluene deliquesces in the atmosphere, turning green and decomposing. Again its analysis approximate to those of $(NSOI)_n$. Both these materials were insoluble or too unstable to obtain repeatable molecular weight measurements. However their infrared spectra were remarkably similar to those of $(NSOCl)_3$ and $(NSOF)_3$ but the SO and SN bands had shifted slightly (Fig.9).

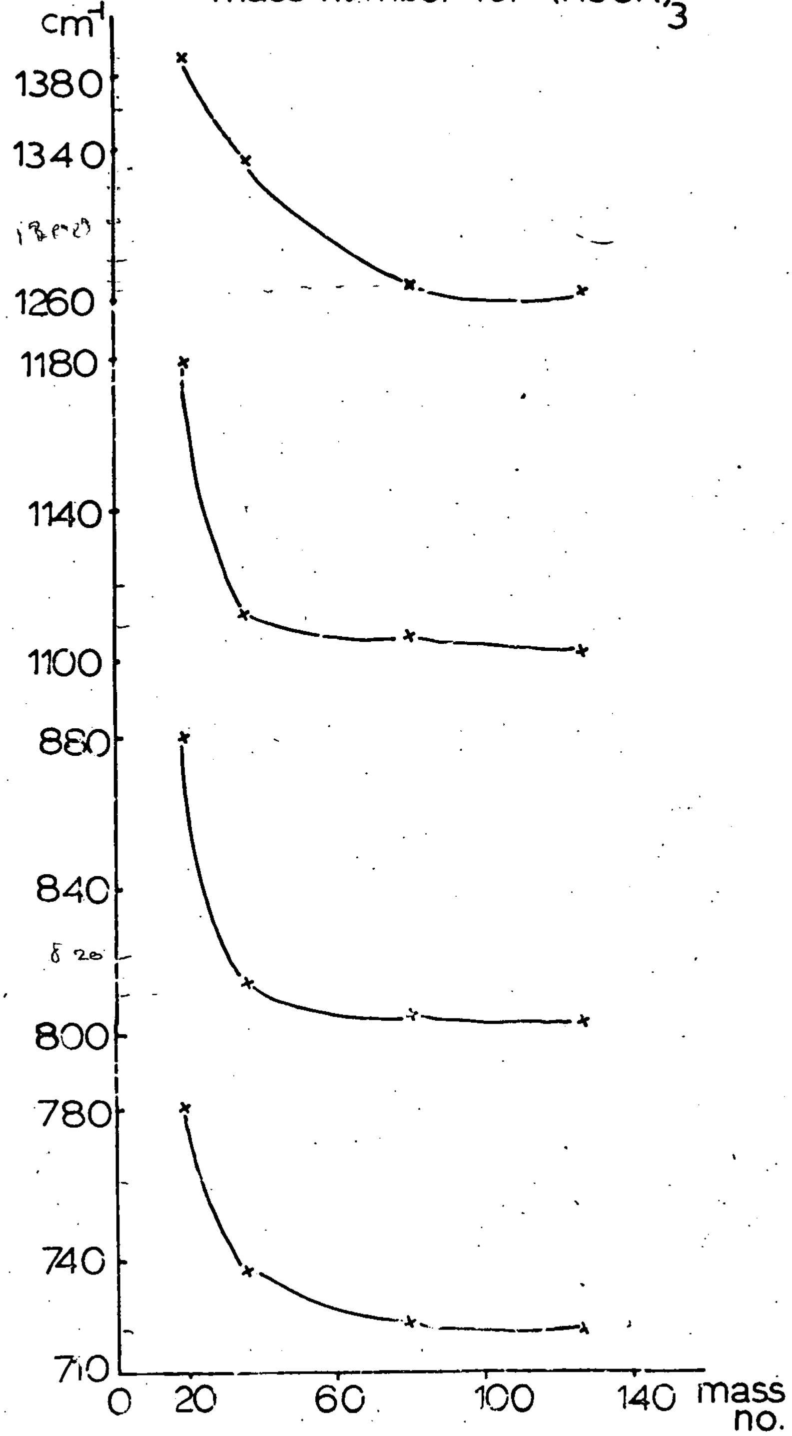
FIG. 9 INFRARED SPECTRA OF $(NSOX)_3$



A correlation was attempted with the four peaks assignable to SO and SN over the halogen group, and a smooth curve found in all four cases when the absorption frequency was plotted against mass number. (Fig.10).

This is an indication that the sulphanuric bromide and iodide were prepared although there is the obvious possibility that it was polymeric material rather than trimeric compounds that were obtained.

FIG.10 Plot of absorption frequency against mass number for $(NSOX)_3$



Reactions of diphenylsulphanuric chloride

Diphenylsulphanuric chloride $(NSO)_3ClPh_2$ is considerably more stable to air and moisture than α-sulphanuric chloride although its solubility in many organic solvents is lower. First prepared by McKenney and Fetter,[55] it is an interesting starting material for either building on to the phenyl groups or replacing the chlorine to give, or increase biological activity. Reactions have been investigated in this work which can be divided into the following types: (i) Reaction with metal salts to replace the chlorine, (ii) halogenation of the aromatic rings, (iii) reaction with amines, (iv) elimination of HCl in reaction with phenols, (v) other reactions which have previously been investigated in sulphanuric chloride chemistry. These reactions are discussed below.

(i) Reaction with metal salts

McKenney and Fetter reported the preparation of diphenylsulphanuric fluoride by the reaction of potassium fluoride with diphenylsulphanuric chloride; though having a similar melting point to the sample prepared by Moeller and Ouchi[52] its infrared spectrum was noticeably different. As with the preparation of sulphanuric fluoride,(p.52), the addition of catalytic water was recommended in the reported synthesis; the author found (p.71) that the yield was increased if carefully dried solvents and reagents were used although the reaction time was slightly longer. There was also a noted decrease in the amount of polymeric material formed during the reaction. Diphenylsulphanuric fluoride is more stable to hydrolysis by water than the chloride (cf. $(NSOCl)_3$ and $(NSOF)_3$) and can be kept for three to four months in an open container with negligible decomposition. The mass spectrum of this compound reveals the stability of the remaining SF bond. A fragmentation pattern is shown in Fig.11. The sulphanuric ring disintegrates before the fluorine breaks away.

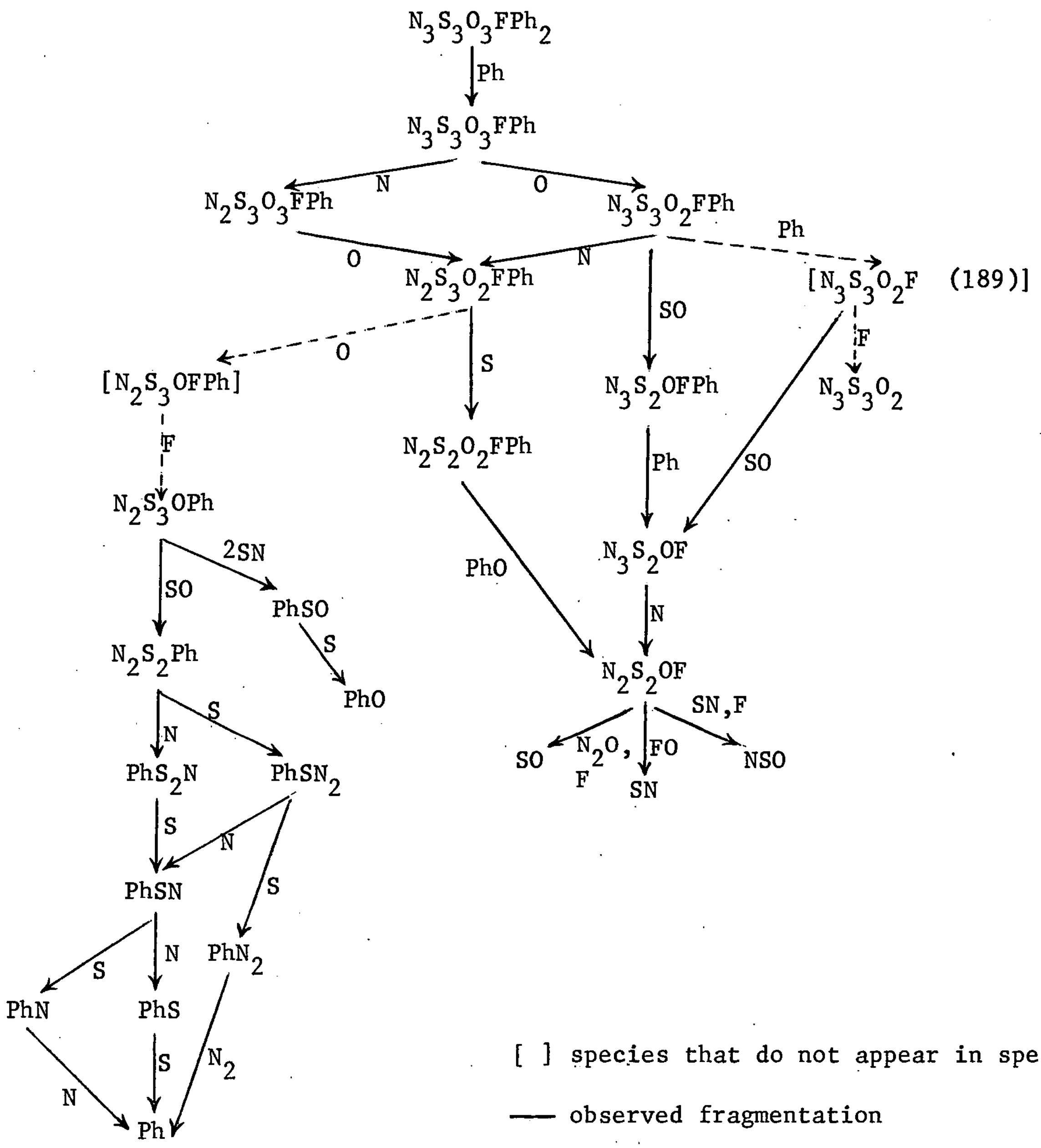
Potassium thiocyanate reacted with $(NSO)_3ClPh_2$ to give a rich yellow solid which was insoluble in most organic solvents. Excess KNCS was removed by washing with boiling ethanol but neither the residue nor the extract contained chlorine. The residue gave an infrared spectrum which showed the presence of phenyl groups, and N=C=S. That the sulphanuric ring remained intact was a little doubtful owing to the very high background on the spectrum. The use of an alcohol as an extracting solvent may have complicated the reaction as alcohols react with isothiocyanates to give thiocarbamates.[102]

$$\text{Y-SCN + ROH} \longrightarrow \text{Y-S-}\underset{\displaystyle\text{OH}}{\underset{|}{\text{C}}}\text{=NR}$$

Sublimation was attempted as an alternative but decomposition occurred. Reaction of some type must have taken place but a complex product was obtained as occurred when Moore[42d] investigated the reaction between KNCS and sulphanuric chloride, when the orange solid formed was insoluble in organic solvents and the by-product KCl could not be separated. Here again the sulphanuric ring differs from the phosphazenes which react with KNCS giving an isothiocyanate[103] derivative.

Fig. 11

Fragmentation Pattern of $N_3S_3O_3FPh_2$



[ ] species that do not appear in spectrum

—— observed fragmentation

--- transitions which are not observed

The reaction with potassium iodide yielded a red oil, which was air sensitive turning brown with the formation of iodine. The infrared spectrum of the oil indicated disintegration of the ring, by an absence of the characteristic 'ring' modes, ν_{SO} and ν_{SN} in the region 7-8μ and 9-10μ respectively.

(ii) Halogenation of the aromatic ring

A phenyl group can be chlorinated at room temperature by molecular chlorine in the presence of $AlCl_3$, $FeCl_3$, pyridine or iodine as a catalyst. Aluminium trichloride and ferric chloride were not used in this case as they also catalyse Friedel Crafts type reactions which Moeller used in the preparation of $(NSOPh)_3$. The use of pyridine was also discarded as tertiary bases form adducts with sulphanuric chloride and pyridine reacts to give an oil with diphenylsulphanuric chloride itself. Hence by a process of elimination iodine was used as the catalyst. Chlorination in the presence of iodine gave a white crystalline solid which analysed to $N_3S_3O_3C_{12}H_6Cl_5$, four chlorine atoms had been introduced, an average of two per phenyl group. The mass spectrum gave no parent peak, but fragments were assignable to the higher peaks as follows (source temperature $\sim 140^oC$).

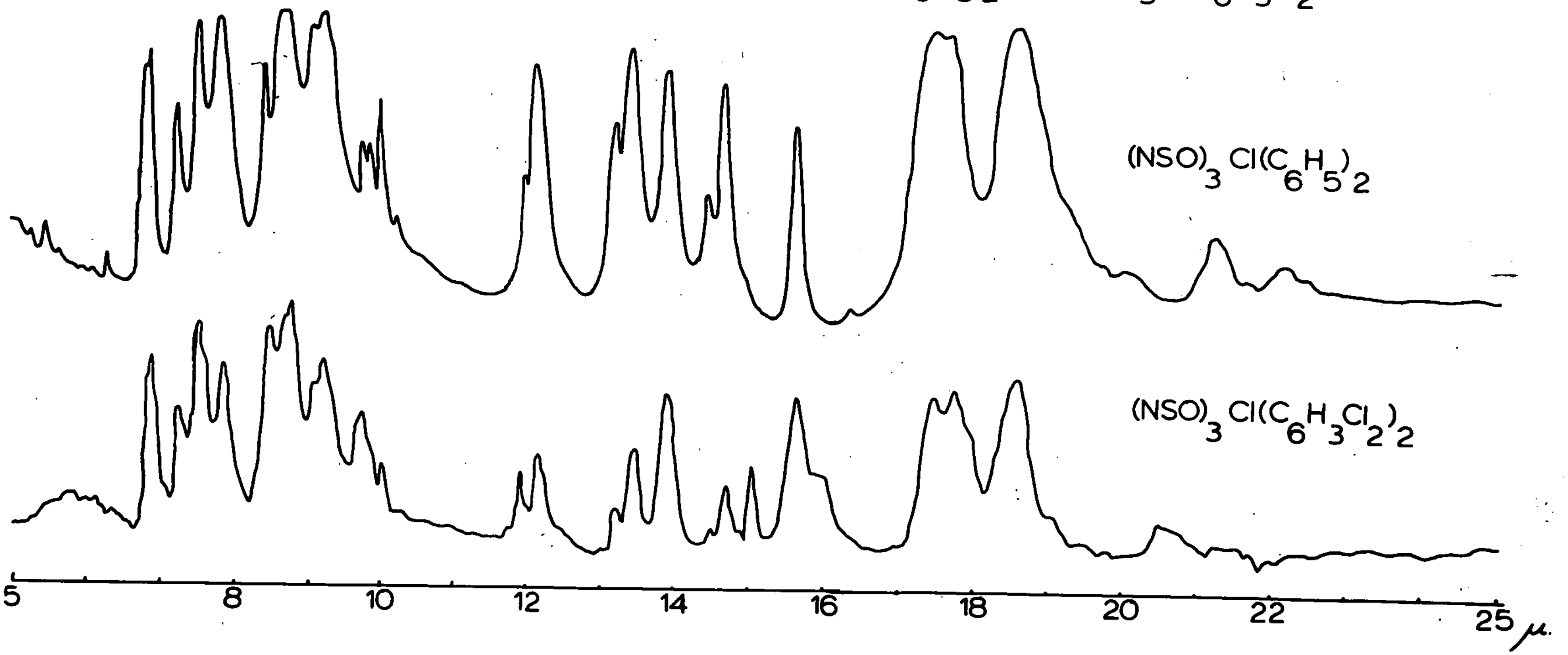
$N_3S_2O_2(C_6H_3Cl_2)_2$	428, 430, 432
$N_3S_2O(C_6H_3Cl_2)_2$	412, 414, 416, 418, 420
$NS_2O(C_6H_3Cl_2)_2$	384, 386, 388, 390, 392
C_6H_3Cl	110, 112

These peaks showed the isotope splitting pattern for 4Cl and Cl as shown on p.144 and p.145.

The substitution could be 1,2,3-, 1,2,4-, 1,2,6- or 1,3,5- depending on the directive effects of the α-sulphanuric ring. Changes in the infrared spectrum from the starting material are noted in the regions 1183-976 cm^{-1}, 850-815 cm^{-1}, 690-666 cm^{-1} and 639-610 cm^{-1} (Fig.12). The sulphanuric ring is expected to be strongly electron attracting and hence meta directing to electrophilic substitution (cf. SO_2R and $CONH_2$ which are also meta directing[104]) and so the phenyl groups in bis-(dichlorophenyl)sulphanuric chloride are probably 3,5-disubstituted.

The infrared spectra of compounds containing 1,3,5 trisubstituted phenyl groups show characteric absorptions in the regions 830-850 cm^{-1} and 680-700 cm^{-1},[105] 1,2,3 and 1,2,4-trisubstituted compounds show absorptions at 760-780 cm^{-1} and 870-885 cm^{-1} respectively. In the new compound the areas 760-780 cm^{-1} and 870-885 cm^{-1} are completely clear of absorption in the spectrum of this derivative. There is a new, medium intensity peak at 840 cm^{-1} which falls within the region characteristic of a 1,3,5-trisubstituted compound. This supports the theory that the substitution is 1,3,5 but the argument cannot be taken further as some of the characteristic areas for 1,3,5-substitution of the spectrum are populated by bands arising from the sulphanuric ring. (Fig.12).

Fig.12 Comparison of infrared specta of $(NSO)_3Cl(C_6H_5)_2$ & $(NSO)_3Cl(C_6H_3Cl)_2$



Bromination in the presence of iodine was not as successful. Some bromine was introduced into the molecule but only a very small proportion (1·48%) of this could be in fact simply halogen exchange. The only evidence for it having substituted into the phenyl ring was that from the mass spectrum, where peaks could be tentatively assigned to the following fragments, but this was not a high resolution spectrum and no accurate masses could be obtained.

Fragments observed (180^{o} source temp.) were:

	Mass	Intensity (strongest peak)
$N_3S_3O_3Cl$	221,223	10
$N_3S_3O_3ClC_6H_4Br$	221,223	50
$N_3S_3O_3C_6H_4Br$	342	60
$N_3S_3O_3BrC_6H_5$	343	20
$N_3S_3O_3Ph_2Cl$	375,377	100
C_6H_4Br	156	50

On repetition of the reaction with refluxing bromine there was no improvement in the yield or degree of substitution

(iii) Reaction with amines

With both pyridine and diethylamine, diphenylsulphanuric chloride reacted to give oils which were remarkably similar to the sulphanuric chloride amine adducts in physical properties. Though initially pale yellow they slowly darkened to a golden red colour. Their infrared spectrum showed the SN ring had remained intact but the amine could not be removed by heating in vacuo without disintegration of the ring and formation of the amine hydrochloride. This evidence supported the idea that it would be inadvisable to use amines as catalysts in reactions replacing the final chlorine atom, e.g. to remove HCl.

Diphenylsulphanuric fluoride did not react with dimethylamine under conditions similar to those used for metatheses on $(NSOF)_3$ with amines.

(iv) Reaction with 2,4,6-trichlorophenol

When a mixture of t.c.p. and $(NSO)_3ClPh$ were fused at 80^o a gas was evolved and a deep red liquid was formed which on cooling gave a red sticky solid which lost most of the stickiness after standing a few days in a nitrogen atmosphere. It was insoluble in hydrocarbon solvents although slightly soluble in acetone. Excess t.c.p. could be removed by sublimation at room temperature. The analysis of the remaining pink powder approximated closely to that of $(NSO)_3Ph_2(C_6H_2Cl_3O)$ and the infrared spectrum agreed with this identity showing a new peak at 692 cm^{-1} characteristic of a 1,3,5-trisubstituted benzene ring, together with phenyl substitution peaks of t.c.p. The peak at 660 cm^{-1} tentatively assigned to ν_{SCl} had disappeared. A molecular weight was not measured because of its insolubility and the resulting difficulty in purification.

(v) Reaction with $EtSSiMe_3$

The reaction between α-sulphanuric chloride and ethylthiotrimethylsilane resulted in the formation of a small quantity of a crystalline derivative, the remainder of the product being an intractable oil (i.r. shows ring breakdown, p. 80), so the reaction was attempted with diphenylsulphanuric chloride which has improved ring stability (see higher ν_{SN}). This is probably due to steric protection by the phenyl groups and the π electron being delocalised over the three ring systems (two phenyl group and the sulphanuric ring). No reaction occurred; the $(NSO)_3ClPh_2$ was recovered unchanged. This lack of reaction can be credited to (a) steric effects (b) reduced sulphur electrophilicity due to the lower electronegativity of phenyl compared to chlorine (Ph, 2·4;[99] Cl,2·83) and the delocalisation of the S δ+ charge. The replacement of chlorine by the 2,4,6-trichlorophenoxy group (p.93) suggests that any steric effects will be kinetic in nature rather than thermodynamic.

Chapter 5

Reactions of trithiazyltrichloride, thiodithiazyldichloride and their derivatives

I. Experimental

Reactions of trithiazyl trichloride

I. Reaction with epoxides

a) With cyclohexene oxide

To a stirred suspension of trithiazyl trichloride (1•5 g., 6 mmole) in dry hexane (20 ml.) at-23^{o} was added dropwise cyclohexene oxide (3 ml., 4•3 g., 44 mmole) and the reaction mixture allowed to warm to room temperature. After 4 hr. a green solution was obtained which slowly turned red over 72 hr. depositing a buff solid. The solid was filtered off, washed with hexane (20 ml.) then with ethanol (2 x 10 ml.) and dried under reduced pressure. The resulting white solid, m.p.93-4^{o}. Analysis found: C,40,1; H,5•4; N,7•61; S,17•45. $(NSClC_6H_{10}O)_3$ requires C,40•1; H,5•49; N,7•79; S,17•8; Cl,19•7%.

The infrared spectrum showed absorptions at: 2941s, 2865m, 1453m, 1403vw, 1372m, 1340vw, 1274w, 1222w, 1209w, 1125vw, 1042s, 1014m, 993vs, 953s, 945vs, 901m, 869s, 850w, 816vw, 801m, 774vw(sh), 743s(sh), 737vs, 723m, 693s, 690s, 688vs, 648w, 607vw, 570m, 563m, 506vw, 500vw, 450vw.

b) With butylene oxide

To trithiazyl trichloride (1•8 g., 7•3 mmole) suspended in hexane (10 ml.) was added butylene oxide (10 ml., 0•19 mmole) at 22^{o}. After about 5 mins. there was a vigorous reaction, the initial green solution turned orange and then slowly red over 15 hr. The excess butylene oxide and hexane were pumped off leaving a red oil. (p.113).

Analysis found: S,20•84; N,9•16; Cl,22•70; C,31•33; H,5•11.

$(NSOCH_2CHClCH_2CH_3)_3$ requires: S,20·84; N,9·12; Cl,23·11; C,31·25; H,5·20%. The infrared spectrum showed bands at: 1471ms, 1439vw, 1372sh, 1370w, 1312w, 1352vw, 1205vw, 1042vs, 980sh, 957vs, 917s, 866s, 791vs, 741s (broad), 694vw, 673vs(broad), 556vw, 420ms.

c) With styrene oxide

To a suspension of trithiazyl trichloride (2·0 g., 8 mmole) in hexane (20 ml.) at 0^o was added dropwise styrene oxide (2·9 g., 24 mmole). An emerald green solution quickly formed which slowly turned red depositing an orange brown solid (6 hr.). The solid was filtered off and recrystallised from carbon tetrachloride. The orange solid had an infrared spectrum identical with S_4N_4. The hexane solution was evaporated to dryness leaving a red oil which decomposed to a white solid on exposure to the atmosphere. Infrared absorptions of the red oil occurred at: 3390s, 3067m, 3040m, 2967s, 2932m, 2882m, 1965w, 1894w, 1821w, 1764w, 1739w, 1695w, 1613w, 1600w, 1504m, 1460s, 1395m, 1361w, 1295w, 1263w, 1209m, 1163w, 1109sh, 1088sh, 1042s, 990s, 957vs, 918m, 882s, 848s, 805m, 758sh, 738s, 699vs, 617m, 568w, 555w, 526m.

d) With 3-(p-chlorophenoxy)-1,2-epoxypropane

To a solution of trithiazyltrichloride (1·7 g., 7 mmole) in dry carbon tetrachloride (40 ml.) at 0^o was added 3-(p-chlorophenoxy)-1,2-epoxypropane (2 ml., 3·8 g., 22 mmole) and the reaction mixture allowed to warm to room temperature. After 72 hr. a red solution was obtained which yielded a red oil on removal of the carbon tetrachloride. Analysis found: N,5·6;

S,11·6; C,37·8; H,2·8. $(NSClOCH_2\text{-}CHCl\text{-}CH_2\text{-}OC_6H_4Cl)_3$ requires N,5·56; S,12·6; C,38·0; H,2·78%. The infrared spectrum showed absorptions at: 3145m, 3049m, 2941m, 2890w, 1600m, 1587m, 1492ms, 1458m, 1433w, 1412w, 1284m, 1242s, 1172m, 1111sh, 1104sh, 1094ms, 1040s, 1020s, 1008s, 995ms, 954m, 917w, 898w, 855m, 823s, 783m, 763m(broad), 740m(broad), 724m(broad), 702m(broad), 665m(broad), 637w, 630w, 568w(broad), 508sh, 505m.
The red oil decomposed to a white solid when exposed to the atmosphere for 2 hr.

II. Reaction with nitriles

a) With benzonitrile

Trithiazyl trichloride (3·0 g., 12 mmole) was stirred at 60^o for 72 hr. with benzonitrile (25 ml.). The initial apple green solution turned yellow then red and an orange solid precipitated out. The solid was filtered off, washed with benzonitrile (10 ml.) then carbon tetrachloride (2 x 10 ml.) and dried in vacuo, m.p.231-40^o decomp. Analysis found: C,41·7; H,2·4; N,13·1; S,30·1; Cl,14·9. S_2N_2CClPh requires: C,38·9; H,2·32; N,12·98; S,29·7; Cl,16·45%. The infrared spectrum showed peaks at: 1600w, 1392m, 1346w, 1150m, 1073m, 1028m, 1000w, 921m, 893s, 842s, 784s, 702s, 690sh, 549s, 515w, 472w.

b) With trichloroacetonitrile

Trithiazyltrichloride (1·2 g., 5 mmole) was dissolved in trichloroacetonitrile (10 ml.) and heated with stirring at 65^o for 72 hr. The initial

green solution turned claret after 1 hr. and an orange solid began to come out of solution. The orange crystals were filtered off and recrystallised from trichloroacetonitrile, m.p.213-214°.
Analysis found: C,9·3; N,10·85; S,24·5; Cl,55·8; $S_2N_2C_2Cl_4$ requires: C,9·3; N,10·8; S,24·8; Cl, 55·0%.
The infrared spectrum contained absorptions at: 1278sh, 1264w, 1052s, 1020sh, 909w, 856m, 814s, 794s, 760m, 723w, 675s, 669sh, 542m, 535sh, 515w.
The mass spectrum had as its highest peaks, three with (p.122) m/e 221, 223, 225 which showed a Cl_3 isotopic splitting pattern (p.144) and was equivalent to $S_2N_2C_2Cl_3$.

c) With t-butylcyanide

Trithiazyl trichloride (1·0 g., 4 mmole) was stirred for 40 hr. at 60° with t-butylcyanide (5 ml.). The initial green solution turned red after 30 min. and an orange solid slowly precipitated out. The solid was filtered off and recrystallised from t-butylcyanide m.p.235-6°.
Analysis found: C,29·39; N,14·6; S,31·7; H,4·34. Calculated for $S_2N_2CClBu^t$: C,30·3; N,14·3; S,30·7; H,4·5%. The infrared spectrum showed peaks at 1680w, 1406m, 1369s, 1219s, 1211sh, 1906w, 1025w, 981w, 942m, 884vs, 854s, 806w, 732s, 725sh, 553s, 524w.

d) With benzyl cyanide

Trithiazyl trichloride (1·5 g., 6 mmole) was stirred for 24 hr. at 60° with dry benzyl cyanide (20 ml.). The resulting wine red solution was chilled in ice and a red sticky solid precipitated out which was insoluble in hydrocarbons and diethyl ether. A white solid was obtained on dissolving in benzonitrile which was ammonium chloride. On evaporating the benzonitrile off under reduced pressure a red tar was again obtained. The infrared spectrum contained peaks at: 2267m, 2026m, 1776s, 1615w, 1503w, 1168m, 1081m, 1034w, 1003ms, 982w, 943m, 845w, 803w, 774w, 734vs, 697vs, 656w, 615m, 566m, 549w, 463s.

e) <u>With 1-naphthonitrile</u>

To a solution of trithiazyl trichloride (1•0 g., 4 mmole) in carbon tetrachloride (20 ml.) was added 1-naphthonitrile (0•46 g., 3 mmole) and the solution stirred at reflux temperature (76°) for 19 hr. The solution turned mint green after 30 min. and then slowly yellow through to orange. After 19 hr. a yellow crystalline solid was present which showed to be unreacted trithiazyl trichloride. Evaporation of the filtrate to dryness yielded a red oil. Infrared absorptions occurred at: 3100w, 3030ms, 2932m, 2898m, 2825w, 2207s, 1936w, 1824w, 1721w, 1683m, 1615w, 1587m, 1570m, 1503m, 1497m, 1432w, 1406w, 1390m, 1373m, 1337m, 1263m, 1228m, 1210m, 1163sh, 1156m, 1141m, 1090m, 1070m, 1051m, 1029m, 1010m, 980sh, 952w, 916w, 883w, 862m, 836w, 798s, 769s, 736m, 708w, 688s, 571m, 538m,491w, 462m, 449s.

f) <u>With cyanogen bromide</u>

Trithiazyl trichloride (1•0 g., 4 mmole) and bromo cyanogen (0•65 g., 6 mmole) were dissolved in carbon tetrachloride (10 ml.) and the solution stirred at room temperature for 5 days. A red solid came out of solution on cooling in the refridgerator. Analysis found: S,39•5; N,60•2%; total 99•7%. The infrared spectrum consisted of absorptions at: 1663w, 1418m, 1270w, 1173m, 1113w, 1046w, 1018s, 956w, 887w, 809w, 725w, 699s, 669w, 641w, 609w, 590w, 562s, 540w, 471s.

III. Reaction with other strained or unsaturated systems

a) With azobenzene

A solution of trithiazyl trichloride (2•0 g., 8 mmole) in dry carbon tetrachloride (40 ml.) was mixed with a solution of azobenzene (2•2 g., 12 mmole) in dry carbon tetrachloride (40 ml.) and the mixture refluxed for 30 hr. The solution was then cooled and the volume reduced to 20 ml. The orange crystalline solid was filtered off, m.p.83-4^{o}(d). Its infrared spectrum consisted of peaks at: 3076w, 1582m, 1485m, 1474m, 1333w, 1305m, 1265mw, 1222m, 1156m, 1102w, 1074s, 1022m, 1002m, 987w, 925s, 851w, 801w, 775vs, 689vs, 617w, 546s, 522s.
Analysis found: Cl,8•14; H,4•73; C,73•0%.

b) With diphenylketiminolithium

To diphenylketimine (2•55 ml., 15 mmole) in hexane (40 ml.) was added n-butyl lithium (7•5 ml., 2 mmole) at -76^{o} and the solution allowed to warm to room temperature at which point it was stirred for 1 hr. to allow all butane to come off. The orange solution was then re-cooled and a solution of trithiazyl trichloride (2•4 g., 9•8 mmole) in hexane (10 ml.) added dropwise. The mixture was then gradually warmed to 22^{o}

where it was maintained with stirring for two hours. The solution changed from orange to yellow, then gradually darkened precipitating a yellow solid. After 2 hr. a black solution was obtained. The black solid was filtered off, washed with dry carbon tetrachloride and dried. Its infrared spectrum consisted of peaks at: 1941w, 1834m, 1760w, 1650s, 1597s, 1515m, 1315m, 1290s, 1180m, 1161s, 1071m, 1046s, 1000s, 973s, 933m, 887w, 875w, 841w, 795ms, 782m, 765w, 741w, 724w, 701vs, 690vs, 629mw, 618m, 593w, 568ms.

The filtrate was pumped to dryness leaving a black solid which would not mull and its physical appearance remained unchanged when exposed to the atmosphere but after exposure it was insoluble in all common solvents.

c) <u>With propylene sulphide</u>

To a solution of trithiazyl trichloride (2·5 g., 10 mmole) in carbon tetrachloride (30 ml.), cooled to -6^{o} in an ice-salt bath, was added propylene sulphide (1·6 ml., 2·26 g., 30 mmole). The solution immediately turned emerald green, and was left stirring in the ice-bath for 48 hr. After 24 hr. it had begun to turn brown and an orange solid began precipitating out. The solid was filtered off and dried. m.p.80^{o}. The infrared spectrum consisted of peaks at 1677w, 1416m, 1264w, 1203w, 1173w, 1002m, 924ms, 800w, 767w, 761w, 726ms, 700s, 621w, 547s, 529m, 517m, 469m.

d) <u>With phenyl isocyanate</u>

To trithiazyl trichloride (1·0 g., 4 mmole) was added an excess (10 ml.)

phenyl isocyanate at room temperature. After stirring for ten min. a green solution formed which slowly turned brown, then red. After 16 hr. a dark red solid had precipitated from the red solution, which was filtered off and recrystallised from dry diethyl ether. The resulting yellow solid, m.p.172-3^{o}, had an infrared spectrum consisting of peaks at: 1788m, 1763w, 1695s, 1587w, 1307w, 1256w, 1216w, 1162m, 1092w, 998s, 798mw, 765sh, 750m, 737m, 701m, 683ms, 636w, 613sh, 607w, 573m, 544ms, 536m, 505w, 467s, 452m. Analysis found: S,57•4; N,19•22%. Calculated for S_4N_3Cl: S,62•28; N,20•43%.

The ether used for recrystallisation was evaporated to dryness leaving a red solid which analysed: N,13•13; S,7•59; H,3•43; C,51•87; Cl,23•2% (total 99•22%). The infrared spectrum was as follows: 3278w, 3165w, 1779w, 1698s, 1677sh, 1592s, 1545sh, 1524s, 1492sh, 1474sh, 1440s, 1312m, 1261m, 1239m, 1222m, 1183m, 1153m, 1108mw, 1095mw, 1070w, 1026w, 900w, 863w, 824w, 810w, 794w, 757sh, 752s, 733m, 719w, 693s, 685s, 663w, 627w, 614w, 582w, 572sh, 565m, 546w, 539w, 506m.

e) <u>With t-butylisocyanate</u>

Trithiazyl trichloride (3•5 g., 14 mmole) was added to the benzene solution of t-butylisocyanate (150 ml., 7•5% by volume solution i.e. 160 mmole t-butylisocyanate) (p.50), and stirred at 16^{o} (48 hr.). The yellow solution turned khaki then orange depositing a yellow solid m.p.195-6^{o}. Analysis found: S,17•62; N,15•37; C,29•57; H,6•95%. $(NSCl.C_4H_9NCO)_n$ requires: S,17•72; N,15•51; C,33•24; H,4•99%.

Infrared absorptions (hexachlorobutadiene mull) occurred at: 3110s, 2941s, 2869s, 2789s, 2691s, 2591s, 2491s, 2073s, 1950w, 1845m, 1825w, 1754s, 1695s, 1510m, 1477w, 1458w, 1435w, 1401s, 1372s, 1317w, 1302s, 1250w, 1242sh, 1215s, 1090m, 1010m, 1000m, 885w, 733m, 714w, 681m, 670w, 630w, 609w, 563m, 529w, 480m, 469m, 449s, 418m.

Reactions of thiodithiazyldichloride, $S_3N_2Cl_2$

a) With sulphuryl chloride

Freshly prepared thiodithiazyl dichloride (10·1 g., 51 mmole) was stirred at room temperature for 24 hr. with sulphuryl chloride (10 ml.). The brown solution turned slowly red, the brown solid went into solution and a fine yellow solid precipitated out. The yellow solid was filtered off and recrystallised from carbon tetrachloride, m.p.90-1^{o}. Analysis found: S,40·0; N,16·8; Cl,43·1%. Calculated for $(NSCl)_3$: S,39·3; N,17·2; Cl,43·5%. Infrared (Nujol mull) absorptions occurred at: 1017vs, 698ms, 621w, 514m, 493m. Infrared (carbon disulphide) absorptions occurred at 1017vs, 699m, 620w, 512s.

The red solution was pumped to dryness, leaving a bright yellow solid which was recrystallised from carbon tetrachloride. The pale yellow crystals so obtained, m.p.90-1^{o}, had an identical infrared spectrum to the above solid and also analysed the same. Therefore the total yield of trithiazyl trichloride was 7·9 g., 95% based on nitrogen content.

b) With thionyl chloride

$S_3N_2Cl_2$ (6 g., 30 mmole) was stirred for 4 days with distilled (p.46) thionyl chloride (40 ml.). The yellow solid which precipitated out was filtered off and dried. Analysis found: N,20·02; S,63·2; Cl,18·1%. Calculated for S_4N_3Cl: N,20·48; S,62·4; Cl,17·1%. Fractional distillation of the red filtrate under reduced pressure gave components which condensed in traps at 0^o, -23^o and -78^oC and had the infrared spectra I, II and III respectively.

I (Nujol mull): 1700w, 1264m, 1015s, 962s, 803m, 699s, 624m, 546m, 514sh, 476s(broad), 441m.

II: 1404m, 1233vs, 483s, 429s(broad).

III: 1406m, 1233vs, 703w(broad), 661w, 483s, 434vs(broad), showing the presence of thionyl chloride, sulphuryl chloride, sulphur dichloride and trithiazyl trichloride. The solid remaining after distillation was recrystallised from carbon tetrachloride yielding a pale yellow crystalline solid m.p.90-91^o. Infrared (Nujol mull) absorptions occurred at: 1013s, 927s, 804w, 771s, 579s, 458s.

c) With trichloroacetonitrile

Thiodithiazyl dichloride (8·5 g., 43·5 mmole) was stirred with trichloroacetonitrile (20 ml.) for 36 hr. at room temperature. The brown solid was filtered off and dried, m.p.176-7^o. Analysis found: S,33·16; N,19·5; C,2·18; H,1·31; Cl,32·5%. Infrared absorptions occurred at: 1739w, 1256w, 1160m, 1089w, 998s, 959m, 943ms, 799m, 713sh, 708s, 696s, 681m, 637w, 607w, 583m, 564m, 546w, 522w, 473sh, 467s, 451m, 430w. The red solution, the filtrate was pumped to dryness and the mixture of red and buff solids obtained were recrystallised from hot hexane. Buff needle crystals were obtained m.p.72-3^{o}. Analysis found: N,13·0; S,19·6; C,9·0; Cl,60·6%. Calculated for $S_3N_5C_4Cl_9$: N,13·23; S,18·14; C,9·07; Cl,59·56%. Infrared absorptions occurred at: 1691mw, 1613w, 1471m, 1418m, 1300s, 1109w, 1045m, 929s, 882w, 842m, 800s, 753m, 720w, 693sh, 684sh, 677ms, 669sh, 646w, 533ms, 495ms, 483s, 469s. The fragmentation pattern of the mass spectrum contained as its heaviest fragment a group around 529 which showed a multiple chlorine pattern.

Reactions of $S_2N_2C_2Cl_4$

a) With sulphur

$S_2N_2C_2Cl_4$ (0·4 g., 1·5 mmole) in dry toluene (20 ml.) was refluxed for 72 hr. with sulphur (0·19 g., 6 mmole). The solution was cooled and as there was no precipitate, was taken to dryness under reduced pressure. The orange solid was recrystallised from carbon tetrachloride - an insoluble fraction proved to be unchanged $S_2N_2C_2Cl_4$ and from the carbon tetrachloride rhombic crystals of sulphur were obtained.

b) With anhydrous potassium fluoride

$S_2N_2C_2Cl_4$ (0·2 g., 0·8 mmole) and anhydrous potassium fluoride (0·1 g., 1·7 mmole) in dry acetonitrile (10 ml.) were refluxed with stirring for 48 hr. The solution was cooled and pumped to dryness. The yellow solid was extracted with carbon tetrachloride (80 ml.) and the insoluble white portion analysed for chlorine, which was absent. On evaporation of the carbon tetrachloride an orange sticky solid was obtained which had infrared absorptions showing complete disintegration of the ring. Infrared (Nujol mull) occurred at 3279m, 2051ms, 1453s, 1233s, 976m, 735w, 621w.

c) <u>With potassium thiocyanate</u>

To a solution of $S_2N_2C_2Cl_4$ (0•2 g., 0•8 mmole) in analar acetone was added potassium thiocyanate (0•1 g., 1•0 mmole) in acetone. After stirring for 10 hr. at room temperature the solvent was removed under reduced pressure and an infrared spectrum (Nujol mull) indicated hydrolysis had taken place. Infrared absorptions occurred at 3125m, 2087m, 1689m, 1412m, 1264w, 1122s, 1047m, 1020w, 982w, 955w, 827w, 805m, 734sh, 722m, 619s. So separation of the salt KX was not attempted and the investigation discontinued.

d) <u>With diphenyl acetylene</u>

A solution of $S_2N_2C_2Cl_4$ (0•15 g., 0•6 mmole) in dry carbon tetrachloride (20 ml.) was stirred for 5 days at 60^o with diphenyl acetylene (0•1 g., 5•6 mmole). The red solution was cooled and as no solid crystallised out was pumped to dryness. The residual red solid was extracted with hexane (2 x 5 ml.). The orange solid remaining was unchanged $S_2N_2C_2Cl_4$ and diphenyl acetylene was obtained from the hexane extract.

e) With antimony pentachloride

To a suspension of $S_2N_2C_2Cl_4$ (0·2 g., 0·8 mmole) in carbon tetrachloride (10 ml.) was added antimony pentachloride (0·5 ml., 0·9 mmole). The solid $S_2N_2C_2Cl_4$ slowly disappeared as a white solid was precipitated out. This was filtered off, washed with carbon tetrachloride (2 x 10 ml.) and hexane (2 x 10 ml.). At 200° the white solid turned orange and a liquid condensed at the cool part of the melting point tube. The residual orange solid had m.p. > 360°. Analysis found: C,4·4; N,5·6; S,10·96; Cl,58·4%. Calculated for $S_2N_2C_2Cl_3^+.SbCl_6^-$ (p.136): C,4·3; N,5·02; S,11·48; Cl,57·3%. Infrared absorptions (Nujol mull) occurred at: 3389w, 3305w, 3225w, 1692m, 1356m, 1269m, 1253m, 1129s, 1061s, 1039sh, 938w, 925w, 853w, 816s, 797s, 780m, 762s, 719w, 681s, 611m, 548ms.

Reactions of S_2N_2CClPh

a) With epichlorohydrin

To a suspension of S_2N_2CClPh (1·0 g., 4·6 mmole) in hexane (30 ml.) was added epichlorohydrin (5 ml.) at room temperature. The mixture was stirred for 96 hr. and the S_2N_2CClPh slowly went into solution. The red solution was pumped to dryness and the red semi-solid washed with cold (10°) pentane (2 x 5 ml.). The resulting red solid, m.p.45-6°(d) had infrared absorptions (Nujol mull) at 1669w, 1603vw, 1366s, 1180m, 1138s, 1095w, 1076m, 1027m, 965vw, 934sh, 924w, 903sh, 899w, 855m, 839m, 801s, 790s, 779s, 766s, 759s, 739w, 711sh, 708w, 686s, 661m, 654m, 619w, 548m, 516m, 508m, 452w.

The solid was insoluble in ether and carbon tetrachloride but came out of hexane solution as an oil. Exposure to the atmosphere resulted in rapid hydrolysis as seen by the infrared absorptions of a Nujol mull made up on the bench, absorptions occurred in this instance at: 3333s, 3174s, 1953w, 1692s, 1663sh, 1618w, 1533w, 1408m, 1228s, 1142w, 1094w, 1081w, 1018s, 913m, 854m, 839m, 804m, 779s, 770m, 739m, 691s, 655m, 619w, 607w, 574w, 508m.

b) <u>With cyclohexene oxide</u>

Cyclohexene oxide (0•2 ml., 3 mmole) was added at room temperature to a stirred solution of S_2N_2CClPh (0•5 g., 2•3 mmole) in carbon tetrachloride (40 ml.) and the mixture stirred for 40 hr. at 20^o. Evaporation of the solution to dryness under reduced pressure yielded an orange solid, m.p.220-40^o(d) with infrared absorptions (Nujol mull) at 1680vw, 1607w, 1302w, 1264w, 1216vw, 1173vw, 1153m, 1099vw, 1070vw, 1031w, 925m, 894s, 846s, 796m, 785m, 710w, 699vs, 548m, showing it to be slightly impure starting material.

c) <u>With acetonitrile</u>

A suspension of S_2N_2CClPh (0•7 g., 3•2 mmole) in acetonitrile (10 ml.) was refluxed for 22 hr. and the orange solid filtered off, m.p.230-40^o(d). Infrared absorptions (Nujol mull) of the solid occurred at: 1298w, 1212w, 1175w, 1146m, 1067w, 1029m, 921m, 895sh, 888s, 838m, 783m, 721w, 694s, 663w, 546s, 515w.

Evaporation of the filtrate to dryness yielded a red tar whose infrared spectrum (Nujol mull) showed it to be impure starting material.

d) With tetrachloroethylene

A solution of S_2N_2CClPh (0·85 g., 4 mmole) in tetrachloroethylene (40 ml.) was refluxed with stirring for 4 hr. The solution was taken down to dryness under reduced pressure and the orange solid obtained was unchanged starting material.

e) With antimony pentachloride

Antimony pentachloride (0·1 ml., 1·8 mmole) was added to a scrupulously dry solution of S_2N_2CClPh (0·1 g., 0·5 mmole) in carbon tetrachloride. Immediate precipitation of a white solid occurred, which was filtered off and washed with carbon tetrachloride. Infrared (Nujol mull) absorptions occurred at: 3225m, 1669w, 1597w, 1345m, 1239mw, 1149w, 1118m, 1063s, 1019s, 970w, 923w, 901w, 892w, 841w, 785s, 765m, 719w, 694s, 680sh, 664w, 650w, 620w, 600w, 579w, 551m, 512m, 503w, 485w.

The solid turned rapidly green then to a black tar when exposed to the atmosphere.

f) With phenyl lithium

A solution of phenyl lithium (0·48 molar) in ether (16·5 ml.) was added to a cooled solution of S_2N_2CClPh (1·7 g., 8 mmole) in ether (60 ml.) and the mixture stirred at 0^o for 24 hr. then allowed to warm slowly to room temperature with stirring. A deep red-brown solution had formed and a buff precipitate. The solid was filtered off and the filtrate taken down to dryness giving a black oil which dissolved in cold ethanol but no crystals could be obtained. Infrared absorptions for the precipitate occurred at: 1600w, 1294w, 1208w, 1168w, 1148m, 1070m, 1029m, 921m, 893s, 842s, 794m, 782ms, 768m, 719w, 708m, 696vs, 688sh, 659w, 548s, 516w. Showing it to be unchanged starting material.

g) With diphenyl mercury

To a solution of S_2N_2CClPh (0•6 g., 2•8 mmole) in benzene (40 ml.) was added to a solution of diphenyl mercury (1•0 g., 4•0 mmole) in benzene (10 ml.) and the reaction mixture stirred at room temperature for 7 hr. The solution began to turn brown immediately and a light coloured solid precipitated out. The solid was filtered off, washed with benzene and dried, m.p.250°. Analysis found: C,23•7; H,1•96; Cl,11•0%. Calculated for phenyl mercuric chloride: C,23•04; H,1•92; Cl,11•36%. 1•65 g. of phenyl mercuric chloride were recovered which corresponded to 92% reaction.

$$S_2N_2CClPh + Ph_2Hg \longrightarrow S_2N_2CPh_2 + PhHgCl$$

The filtrate and the washings were combined and taken down to dryness under reduced pressure, yielding a black solid, which was recrystallised from absolute alcohol (10 ml.) below 0°C. A minute quantity of black crystals were obtained m.p.71-2°. Analysis found: C,62•6; H,4•1; N,10•4%. Calculated for $S_2N_2CPh_2$: C,60•46; H,3•88; N,10•85%. Infrared (Nujol mull) absorptions occurred at: 1949w, 1886w, 1801w, 1584s, 1540m, 1479s, 1419m, 1351w, 1336w, 1314m, 1283s, 1267s, 1240w, 1191s, 1182sh, 1153m, 1095m, 1070m, 1024s, 1001m, 977w, 963w, 941m, 918w, 905w, 833w, 814sh, 804sh, 798m, 769m, 746sh, 734vs, 699m, 690sh, 683vs, 672m, 660m, 648m, 619w, 614w, 551w, 546w, 539w, 520m, 478m, 469m. On standing in the sunlight at room temperature the black crystals decomposed to give diphenyldisulphide (identified by i.r.) and a black tar.

Reactions of tetrasulphur tetranitride

a) With $CuCl_2.2H_2O$

A mixture of tetrasulphur tetranitride (3 g.,16•3 mmole), cupric chloride (1•5 g., 8•8 mmole) and dimethyl formamide (60 ml.) were heated to 150^{o} and water (1 ml.) added and the mixture refluxed for 3 min. The solution was cooled and benzene (1•5 l.) added, the solid precipitated was filtered, washed with benzene and high vacuum dried. The infrared (Nujol mull) absorptions occurred at: 3144m, 1700w, 1639w, 1101s, 720m, 656s. Analysis found: N,27•8; S,13•0; Cl,15•4%. Calculated for: $S_2N_2CuCl_2$ N,12•36; S,28•30; Cl,31•29%.

b) With chlorine

Chlorine was bubbled rapidly through a suspension of S_4N_4 (4•95 g., 27 mmole) in dry carbon tetrachloride (10 ml.) for ten minutes. A clear deep orange solution initially formed which precipitated a pale yellow solid. The yellow solid was filtered off. m.p.117-8^{o}. Infrared absorptions occurred at: 1695w, 1150w, 1075w, 1014s, 951s, 893s, 781m, 712m, 701m, 689s, 667sh, 664s, 634m, 581m, 577m, 548s, 519m, 505m, 456s. Analysis found: S,47•97; N,20•56; Cl,27•38. Calculated for NSCl: S,39•3;

N,17•2; Cl,43•5%. Calculated for $S_6N_6Cl_4$: S,45•8; N,20•1; Cl,33•9%. The filtrate was pumped to dryness leaving a yellow solid. m.p. Analysis found: S,47•7; N,20•08; S,32•84%. Infrared absorptions (Nujol mull) occurred at: 1695w, 1156w, 1012s, 951s, 894s, 780m, 709m, 699m, 688s, 667sh, 664s, 630m, 580m, 576m, 547s, 541sh, 518m, 505m, 464s, 455s.

Reaction of $S_6N_6Cl_4$ with epichlorohydrin

To $S_6N_6Cl_4$ (2 g., 4•8 mmole) suspended in dry carbon tetrachloride (40 ml.) and cooled to 0^o was added dry epichlorohydrin (10 ml.). A dark green solution actually formed which turned slowly reddish-brown. On evaporation of the solvent and excess epichlorohydrin a red viscous oil was obtained which on washing with absolute alcohol yielded an orange solid. m.p.176. Infrared absorptions (Nujol mull) for this solid occurred at: 1779w, 1264w, 1108w, 1066w, 1007w, 927s, 800w, 767wm, 759wm, 726s, 698s, 621m, 547s, 528ms, 516m. On evaporation of the ethanol a red oil remained which had infrared absorptions at: 3246m, 3086m, 2985m, 2941sh, 2906sh, 1700w, 1470m, 1445sh, 1432s, 1391m, 1366m, 1345w, 1298m, 1252s, 1203s, 1161m, 1117w, 1103m, 1036s, 1000sh, 962s, 932m, 885s, 868s, 851sh, 791sh, 778s, 722sh, 687s(broad), 666sh, 630m, 613m, 576m, 555m, 492m.

Chapter 6

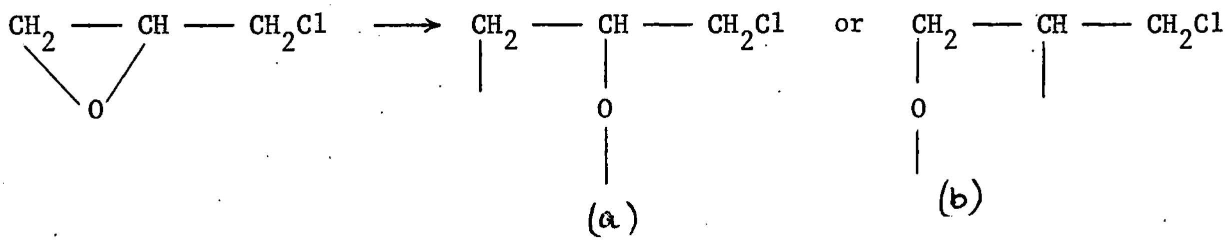
Reactions of trithiazyltrichloride, thiodithiazyldichloride and their derivatives

II. Discussion

The Reaction of trithiazyl trichloride with epoxides

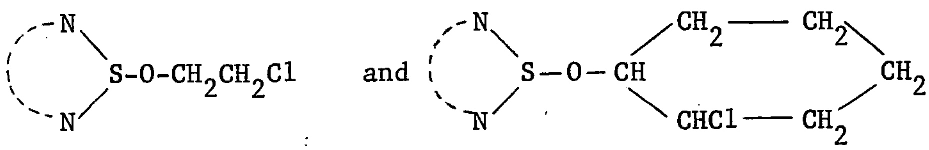
Alkyl and aryl sulphenyl chlorides react with epoxides in an insertion reaction, breaking open the three membered ring[86] (p.43). The reaction of trithiazyl trichloride with epoxides was initially investigated by G.G. Alange who studied the reaction using ethylene oxide, epichlorohydrin, epibromohydrin and butylene oxide. He found that with epichlorohydrin and epibromohydrin air-stable white solids were formed which corresponded in analyses and molecular weight to $(NS\text{-}OC_3H_5Cl_2)_3$ and $(NS\text{-}OC_3H_5ClBr)_3$ respectively, but with ethylene oxide and butylene oxide red oils were obtained which decomposed when exposed to the atmosphere. In this work the reactions of trithiazyl trichloride with cyclohexene oxide, butylene oxide, styrene oxide and 3-(p-chlorophenoxy)-1,2-epoxypropane were investigated. Cyclohexene oxide gave a white solid but the other three epoxides all gave rise to red oils which analysed approximately to those expected for the product $(NS\text{-}O\text{-}R)_n$ where R is a chlorinated group. Peters and Kharasch[86b] found that oils were obtained in some epoxide reactions with sulphenyl chlorides, namely propylene oxide and styrene oxide but attributed this mainly to the inseparability of a mixture of isomers which prevented crystallisation. This could also be the case here, but it should also be taken into account that the styrene oxide reaction gave rise to S_4N_4 so chlorination had also taken place. The oils obtained could therefore be a mixture of isomers of the desired product or a mixture containing chlorinated material whose analysis happens to be near those expected for the derivative.

When the epoxide ring opens it can do so in two ways. Consider for example epichlorohydrin:

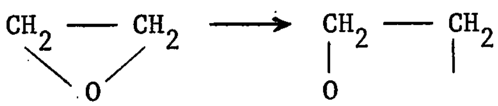


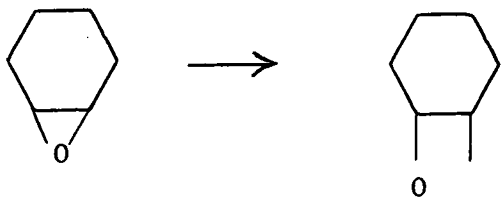
Products may therefore contain (a) and/or (b)

In the reactions of trithiazyl trichloride with epoxides such isomerism is possible in all but the ethylene oxide and cyclohexene oxide cases. The products obtained in these cases are as shown below.



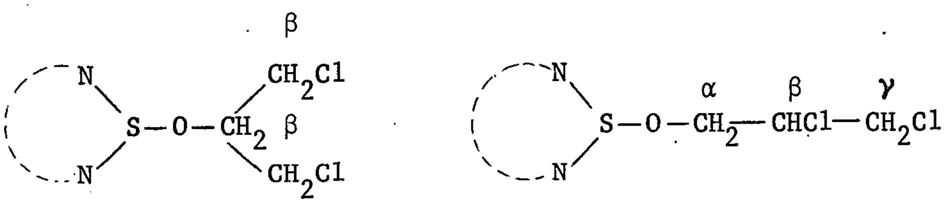
The epoxide rings providing identical organic group whichever way they open (free rotation about C-O is assumed)





To investigate the method of ring opening the P.M.R. spectra of the epichlorohydrin and epibromohydrin products were recorded. Although these samples were practically insoluble in most common organic solvents they were sufficiently soluble in CS_2 to record a P.M.R. spectrum.

When epichlorohydrin reacts with trithiazyl trichloride it can form



I II

Assuming free rotation about O-CH$_\alpha$ the following splitting patterns would be expected

a) for I.

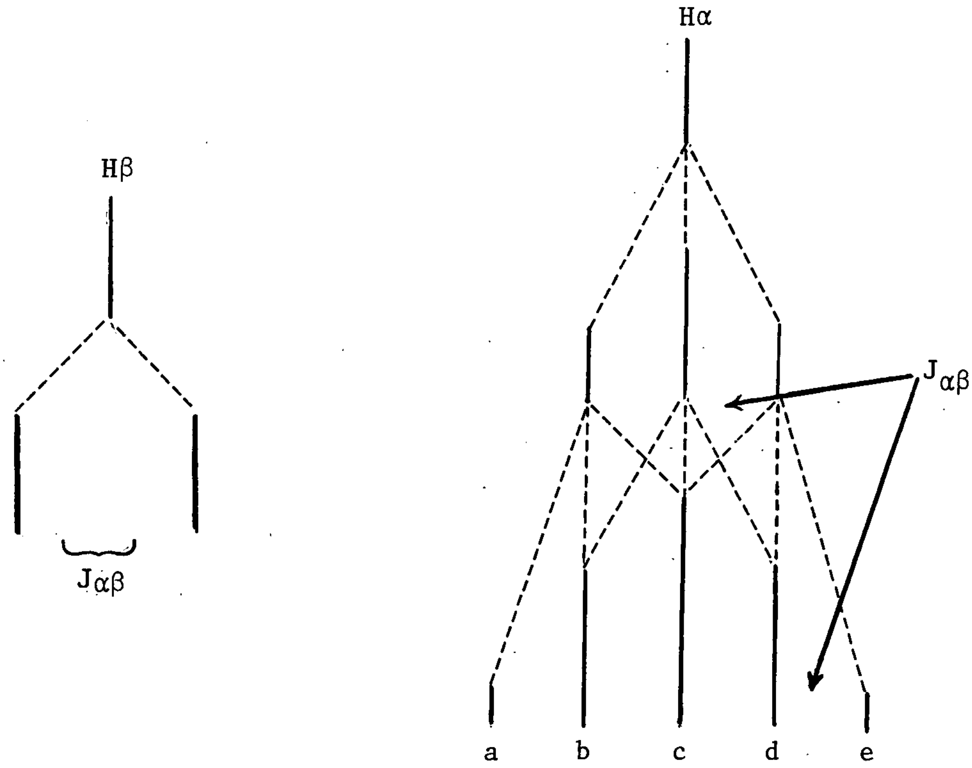


Fig.13

The resulting pattern for the Hα assuming equality of Hβ which would be provided by free rotation would be a quintet. The overall intensity ratio for the doublet to the quintet would be 4:1.

b) for II.

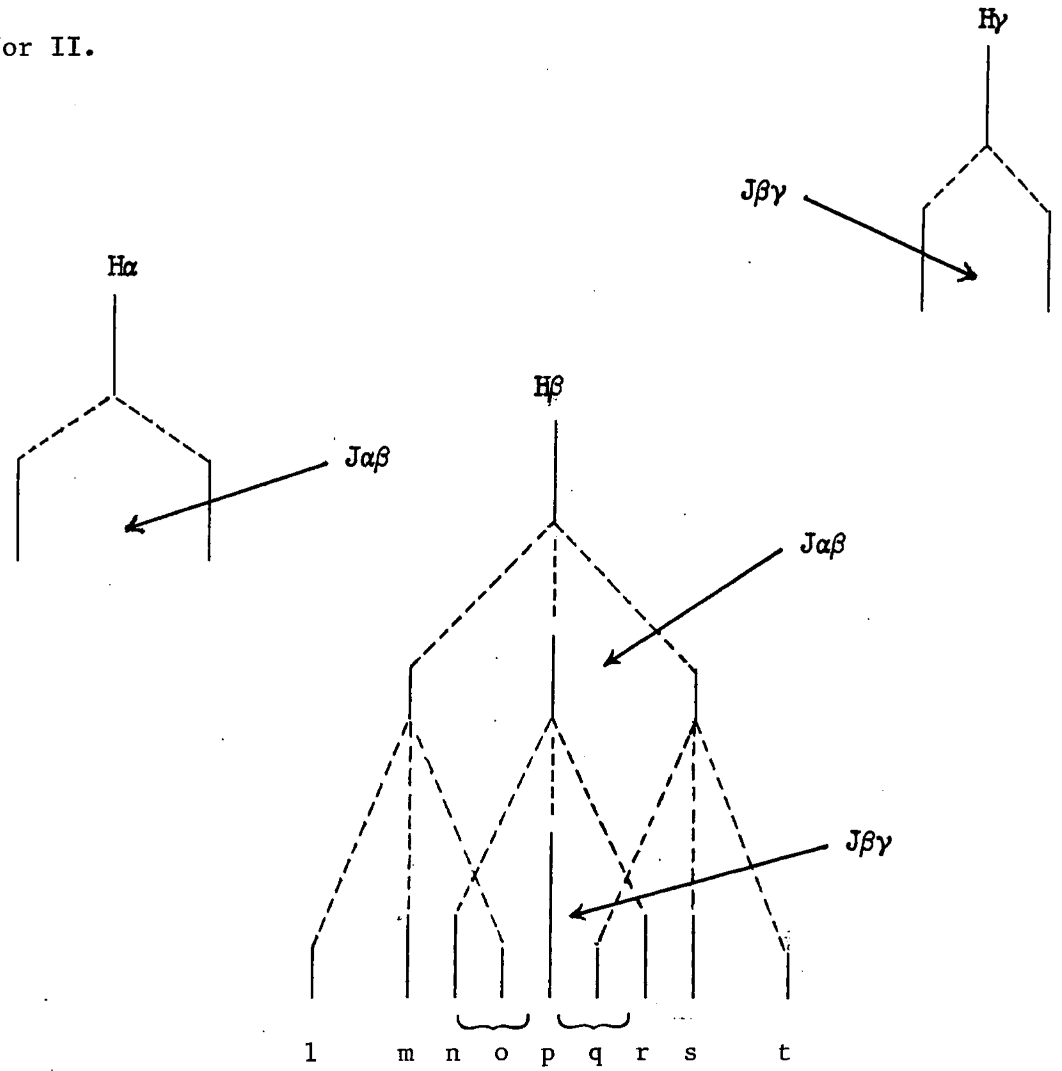


Fig.14.

i.e. two doublets with different splitting constants and a complex nine peak pattern with overall intensity ratios for the doublet:doublet: multiplet: of 2:2:1.

The observed spectrum (Fig.15) showed a triplet and doublet of intensity ratio ~1:4, owing to the weak solution and the relative sizes of the peaks, a and e (Fig.13) had merged into the background. There is no evidence of a second doublet in the spectrum so the compound must contain only the symmetrical group

$$-O-CH\begin{matrix}\diagup CH_2Cl \\ \diagdown CH_2Cl\end{matrix}$$

In the case of the epibromohydrin derivative the situation is more complicated, the organic group may be in the form of

$$-O-CH\begin{matrix}\diagup CH_2Cl \\ \diagdown CH_2Br\end{matrix}$$

or $-O-CH_2-CHCl-CH_2Br$ each of which have hydrogen atoms in different environments. Two doublets would be expected and a nine peak pattern (cf. splitting for Hβ in (Fig.14)In an attempt to decide which isomer had been obtained the chemical shifts obtained were compared with those of similar molecules. The spectrum obtained is shown in Fig.16 and comprises two doublets $\tau 6{\cdot}13$ and $\tau 6{\cdot}30$ and a multiplet centred on $\tau 5{\cdot}43$ showing three broad peaks of separation ~5·4 cps. These broad peaks could arise from (a) m and n, (b) o,p and q (c) r and s not being resolved.

FIG. 15 NMR. SPECTRUM OF $(NSOC_3H_5Cl_2)_3$

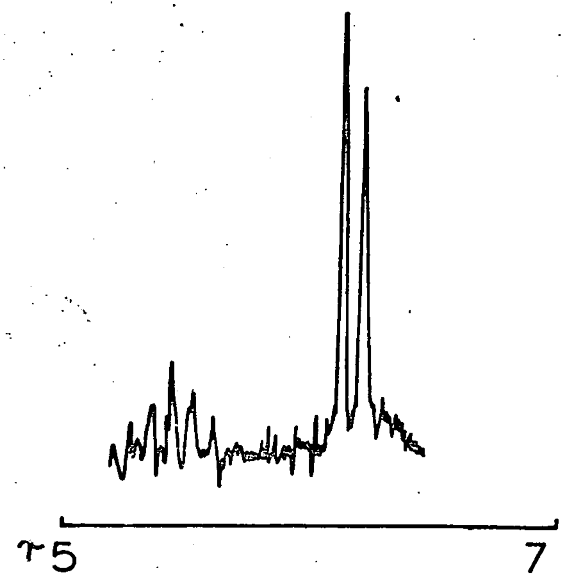
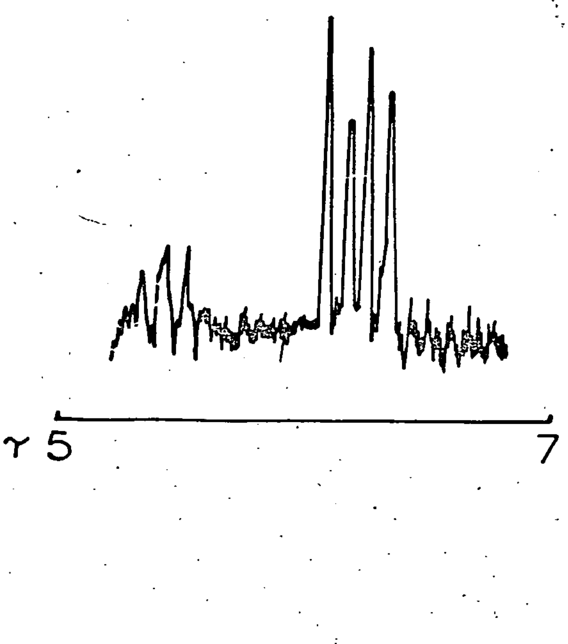


FIG. 16 NMR. SPECTRUM OF $(NSOC_3H_5ClBr)_3$



Shifts of similar species

		τ
a)	$-CH_2Br$	6•7
b)	$-CH_2Cl$	6•43
c)	$-CH_2OR$	6•6
d)	-CHCl	6•0
e)	-CHOR	6•37

The doublets must be due to species (a). (b) or (c) when R is the SN ring. (a) must be present, it exists in both isomers. The other groups most likely present are (b) and (e). The epichlorohydrin product has τ 5•44 for CH-O-R. This suggests that the same isomer had been produced as in the epichlorohydrin product.

The reaction of $(NSCl)_3$ with nitriles

Trithiazyl trichloride was warmed with excess nitrile to a temperature at which the former dissociates significantly to the green monomer in the hope that co-polymerisation of the two unsaturated entities C≡N and S≡N would occur. Two other modes of reaction were anticipated (i) condensation with CH (the nitriles PhCN, CCl_3CN and Bu^tCN were chosen to minimise this) (ii) addition across C≡N by SCl

e.g. $$RSCl + -C{\equiv}C- \longrightarrow -\underset{RS}{\overset{|}{C}}{=}\underset{Cl}{\overset{|}{C}}-$$ 24

$$PCl_5 + RC{\equiv}N \longrightarrow R\text{-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}\text{-}N{=}PCl_3 \qquad 114$$

The reaction of PhCN, CCl_3CN and Bu^tCN with trithiazyl trichloride produced orange crystalline solids which analyses to S_2N_2CClR where R is Ph, CCl_3 and Bu^t. The solids were insoluble in most organic solvents, polar or non-polar, but could be recrystallised from the parent nitrile, acetonitrile (p.137) or thionyl chloride. They decomposed when exposed to the atmosphere, slowly turning white, although they could be stored indefinitely under a nitrogen atmosphere without noticeable change. In the presence of water they decompose exothermically to give a black tar. They are extremely involatile, sublimation does not occur at 80°C under a reduced pressure of 0·001 mm.Hg. Their melting points are high, being in the region 210-240° (cf.$(NSCl)_3$ 91° and $(NSOCl)_3$ 135°). The mass spectra of these compounds show that in all three cases the chlorine is loosely bound, no parent peak is obtained but the most abundant fragment in the spectrum is that with m/e corresponding to $S_2N_2CR^+$. These properties suggest that (a) the chlorine is bound to sulphur, or to a carbon atom α to nitrogen[115] (accounting for the hydrolysis of $(NSCl)_3$).

(b) the SCl/CCl bond is highly polar, or even ionic which would be analogous with $S_3N_2Cl_2$ where X-ray analysis has shown the structure to be $S_3N_2Cl^+Cl^-$.[12]

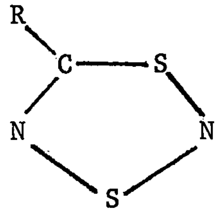
TABLE 6

Mass Spectra of S_2N_2CRCl (R = CCl_3, Bu^t, Ph)

S_2N_2CClPh			$S_2N_2CClBu^t$			$S_2N_2CClCCl_3$		
Fragment	m/e	Abundance	Fragment	m/e	Abundance	Fragment	m/e	Abundance
S_2N_2CPh	181	72	$S_2N_2C.C_4H_9$	161	64	$S_2N_2CCCl_3$	225 223 221	7 21 20
			$S_2N_2CC(CH)_2$	146	30			
						$S_2N_2C_2Cl_2$	190 188 186	20 73 100
PhCNS	135	47	C_4H_9CNS	115	10	CCl_3	121 119 117	10 10 4
			C_4H_8CS	100	10			
PhCN	103	90	C_4H_8CN	82	14			
PhC	89	4						
S_2N	78	100	S_2N	78	50	S_2N	78	29
Ph	77	57						
CS_2	76	53	CS_2	76	14	CS_2	76	29
			C_4H_8C	68	60			
			N_2S	60	6	N_2S	60	2
			C_4H_9C	57	100			
SN	46	22	SN	46	18	SN	46	29
			$(CH_3)_2C$	42	34			
HCl	38 36	7 19	HCl	38 36	8 8	HCl	38 36	14 36
			CH_3	15	8			

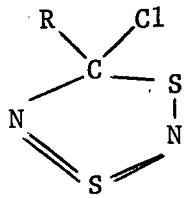
The organic group R is still bound to the carbon as the nitrile appears in the mass spectrum. S_2N and N_2S fragments also appear as do RCS and RNCS.

The most likely atomic skeleton which contains such fragments would be

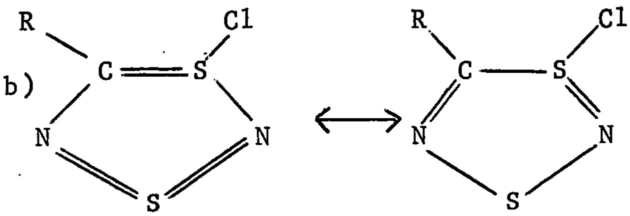


Chlorine could be attached to carbon or either sulphur giving a to c as possible structures, b and c being 'aromatic'

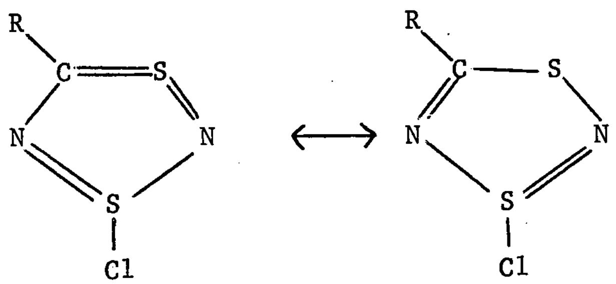
(a)



(b)



(c)



The similarities in infrared spectra of S_2N_2CClR (Table 7) indicate, (together with the mass spectra) the same ring structure for the different reactions.

These compounds do not react with olefins, epoxides or other nitriles(p137)in which by comparison with sulphenyl chlorides (p.39) and trithiazyl trichloride (p.120) the SCl should add across the unsaturated system. This militates against SCl. The main conflicting evidence for this structure comes from an $(NSCl)_3/C_2Cl_4$ reaction.[116] The product $S_2N_2C_2Cl_4$ is obtained from $(NSCl)_3$ and C_2Cl_4 by heating a solution of trithiazyl trichloride (8 g.) in tetrachloroethylene (50 ml.) to 60^o for 35 hrs., whereon an orange solid, $S_2N_2C_2Cl_4$, is slowly precipitated. The infrared spectrum is identical to that of $S_2N_2C_2Cl_4$ prepared from $(NSCl)_3/CCl_3CN$. It seems most unlikely that $Cl_2C{=}CCl_2$ after reaction with $(NSCl)_3$ could produce a fragment $Cl_3C\text{-}C{\lessdot}$ or even $Cl_3C-\overset{Cl}{\underset{|}{C}}-$

Structural evidence from infrared spectra

If the prepared compounds are dithiadiazoles, then some spectral similarity to 1,2,4-thiadiazoles (I), 1,2,5-thiadiazoles (II) and $S_3N_2Cl_2$ (III) is likely, particularly in the region for the ring stretching modes. Absorptions are compared in Table 7.

As can be seen from the table there is a marked similarity in the 900-1100 cm^{-1} region. Where the ν_{SN} mode usually appears, and a

Table 7

Infrared Spectra of S_2N_2CClR (R = CCl_3, Ph, Bu^t), 1,2,5-thiadiazole and thiodithiazyldichloride

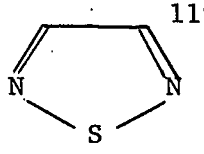
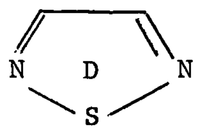
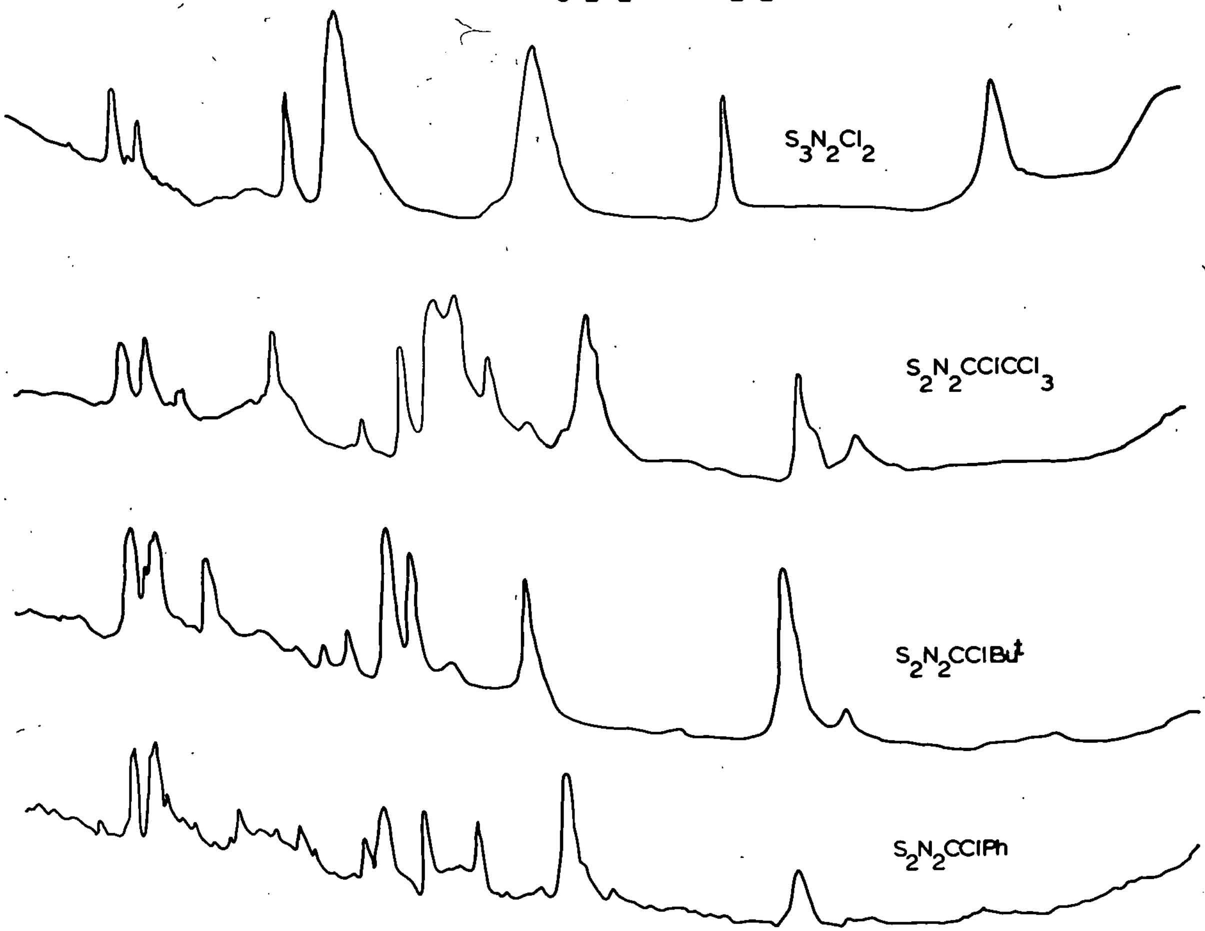
Compound	Absorption Frequency cm^{-1}							
 119	1377	1349 1245 1224	1043	892	838	802	769	515
 119	1408	1295	1181	866	844	751	654	502
$S_2N_2CClCCl_3$		1299	1052	856	814	794 760 723	675 669	542 535 515
$S_2N_2CClBu^t$	1369	1219	1096 1025 942	884	854	733		553 524
S_2N_2CClPh	1392	1105	1073 1028 921	893	842	748	702 690	549
$S_3N_2Cl_2$			1015 936			712		578 458

FIG. 17 INFRARED SPECTRA OF $S_3N_2Cl_2$ AND S_2N_2CClX



reasonable correspondence occurs through the spectrum from 1200 cm^{-1} to 500 cm^{-1}.

The i.r. of these compounds would be expected to show an absorption due to ν_{CN} around 1667 cm^{-1}, 6 μ. In some cases a weak absorption can be seen in this area, but the band is expected to be weak when involved in a delocalised system (cf. the C=C in an aromatic system; phenyl, also in this region is usually very weak). Structural evidence therefore favours b as this has the greater similarity with 1,2,5-thiadiazoles.

<u>Structural evidence from reactions of S_2N_2CClR</u>

(i) <u>Halogen exchange</u>. If the compounds are ionic, anion exchange is likely if it brings together the smallest cation and smallest anion. Exchange may still occur without this situation if the SCl is polar covalent (cf. 'halogen' exchange with $(NSOCl)_3$ and KF or KNCS). The absence of reaction with KF and KNCS (p.136) favours an ionic structure.

(ii) <u>Lewis acids</u>. No reaction occurs between $S_2N_2C_2Cl_4$ and either $FeCl_3$ or $TiCl_4$ in thionyl chloride indicating $S_2N_2C_2Cl_4$ is not a strong donor (cf. 1,2,5-thiadiazoles[113] and $S_3N_2Ph_2$.[117]) This indicates significant delocalisation of lone pairs on both sulphur and nitrogen.

(iii) <u>With $SbCl_5$</u>. The reaction with $SbCl_5$ of S_2N_2CClR (R = Ph, CCl_3 p.136) gave immediate precipitation of a white solid whose infrared spectrum was similar to that of the original material. Although turning orange at about 200° this solid had a melting point above 360° which again slightly favours an ionic nature.

Thus the experimental indication of the structure of compounds S_2N_2CClR is fairly convincing and favours b. Only an X-ray analysis can finally decide whether the chlorine is ionic or an extremely polar bond is present.

The reaction with other nitriles did not produce this type of product. In the above reactions the nitriles possessed no active α-hydrogens. When benzyl cyanide was used ($PhCH_2CN$) and air sensitive red oil was obtained and ammonium chloride was isolated. The reaction probably included chlorination of the α carbon atom. With 1-naphthonitrile there was practically no reaction under the conditions employed, a higher reaction temperature would probably result in the formation of a derivative, as there are no α hydrogens in 1-naphthonitrile it would be expected to be of the type formed with PhCN. However the reaction with bromocyanogen did not give the expected S_2N_2CClBr but the crystalline solid isolated in very small quantities only had the analyses: 3,39•5; N,60•2% which give an atomic ratio of S_2N_7!

The reaction of $(NSCl)_3$ with other strained or unsaturated systems

(a) With azobenzene

The reaction of $(NSCl)_3$ with azobenzene produced an orange crystalline solid whose infrared spectrum was very similar to that of azobenzene. The analysis showed a low chlorine content, the C:H:Cl ratio was 1:20:24, which showed a chlorine content of one for every four phenyl rings suggesting that the $(NSCl)_3$ acted as a mild chlorinating agent rather than the SCl adding across the N=N. The melting point of 83^o was higher than that of azobenzene (71^o) indicating a significant degree of chlorination (the presence of a very small amount of a chloroazobenzene would probably depress the m.p.). Nevertheless it is concluded that trithiazyl trichloride does not add across N=N under the conditions employed (refluxing carbon tetrachloride).

(b) With diphenylketiminolithium

Sulphenyl chlorides will react with diphenylketiminomagnesium bromide[82] with the precipitation of a mixed magnesium halide. In the reaction with diphenylketiminolithium and $(NSCl)_3$ a black solid was formed but no lithium salt could be isolated. Its infrared spectrum was complex and it would not grind easily with Nujol to give a mull; on exposure to air its physical appearance remained unchanged but its solubility in ether and benzene was considerably lowered. Its physical properties suggested that it was a polymeric material which polymerised further on exposure to the atmosphere so the reaction was not investigated further.

(c) With propylene sulphide

Alkylsulphenyl chlorides RSCl react with episulphides[87] with ring opening and the formation of disulphides so the reaction of $(NSCl)_3$ with propylene sulphide was investigated. An orange solid was isolated (m.p. ~ 80° with decomposition) whose analysis showed an atomic ratio $C_3H_5N_{5\cdot4}S_{4\cdot5}Cl_3$ and the infrared spectrum indicated ring breakdown by the lack of absorption in the region 1150 to 1010 cm^{-1}, absorption here is typical of one of the SN ring modes of all the SN ring compounds studied. The reaction can be compared to that of $(NSCl)_3$/ethylene oxide studied by G.G. Alange[110] where a compound of uncertain composition was obtained. The alkyl fragment was not initially halogenated and a mixture of ring opening and chlorination probably occurred. Similar situations have arisen in the reaction of sulphenyl chlorides with epoxides.[24]

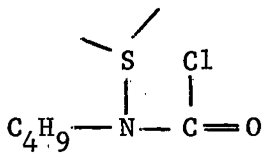
(d) With phenylisocyanate

In the reaction of trithiazyl trichloride with PhN=C=O a yellow solid was isolated which was identified as S_4N_3Cl, this immediately suggests chlorination of the organic compound had taken place. The remaining solid had a CH:N:S:Cl ratio of 18:14•5:4:1:2•75 suggesting that it was the expected mixture of chlorinated compound and sulphur nitrogen residues, so the investigation was discontinued.

(e) With t-butylisocyanate

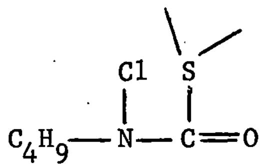
The reaction of $(NSCl)_3$ with t-butylisocyanate gave rise to a yellow solid the infrared spectrum of which contained a peak at 1090 cm^{-1} which could be assigned to ν_{SN}. The trithiazyl ring usually absorbs in this region and so this absorption is indicative of the ring remaining intact. The analyses suggested the empirical formula $NSCl.C_4H_9NCO$, but the compound was highly insoluble in hydrocarbons, ethers, chloroform and carbon tetrachloride so could not be recrystallised or subjected to cryoscopic or osmometric molecular weight measurements. It remained unchanged on exposure to the atmosphere.

The infrared absorptions at ~ 6μ are in the correct region for C=N but are strong (C=N absorptions are normally weak) and so are assigned to C=O which shows strong absorptions in this region.[105] The C=O group remaining infers addition could have occurred across the C=N. Addition across the C=N bond of RN=C=O is common in the reaction of aminoboranes and boron hydrides with isocyanates.[118] The product is therefore expected to be of the nature



(a)

or



(b)

In either of these cases the chlorine would be expected to be reactive and easily hydrolysed, but no reaction occurs on prolonged exposure to the atmosphere (24 hr.). General insolubility and steric protection would help to stabilise C(Cl)=O where the reactivity can be seen to decrease as molecular weight increases cf. acetyl and benzoyl chlorides.

The presence of a new band in the infrared spectrum - i.e. one that does not occur in either Bu^tNCO or $(NSCl)_3$ - which could tentatively be assigned to ν_{CS}. ν_{CCl}, ν_{NS} or ν_{NCl} would be slight evidence of the reaction having proceeded to give (a) or (b). ν_{CCl} and ν_{C-S} generally occur in the region 700-750 cm^{-1} and 550-700 cm^{-1}.[105] A new medium intensity band appeared at 733 cm^{-1} which could be assigned to ν_{CCl} or some deformation mode, although another new band was present at 561 cm^{-1}. As N-Cl is eliminated by its high reactivity and the fact that in other additions across N=C=O it is not formed (a) is suggested as the possible product.

Reactions of thiodithiazyldichloride

(a) With sulphuryl chloride

Trithiazyl trichloride has generally been prepared by the chlorination of S_4N_4 or $S_3N_2Cl_2$ with chlorine gas. Alange[110b] prepared it in high yield from the reaction of sulphuryl chloride and S_4N_4, the $(NSCl)_3$ so obtained closely resembling that prepared by Jolly and Maguire[29]. The reaction of $S_3N_2Cl_2$ was therefore investigated and trithiazyl trichloride was isolated in yields $>90\%$ (based on nitrogen). The sample was similar to that prepared from the sulphuryl chloride chlorination of S_4N_4 having a melting point of 90-1^{o}C. SO_2 gas was given off during the reaction. The side products would be SCl_2 or S_2Cl_2. As S_2Cl_2 reacts with $S_3N_2Cl_2$ to give S_4N_3Cl[111] and none of this compound was isolated. Therefore the other product of the reaction was probably SCl_2 which being volatile (b.p. 59^{o}) was removed under reduced pressure. The reaction can be summarised as follows:

$$3S_3N_2Cl_2 + 3SO_2Cl_2 \longrightarrow 2(NSCl)_3 + 3SCl_2 + 3SO_2$$

Sulphuryl chloride and thiodithiazyl dichloride now provide the easiest route to $(NSCl)_3$.

(b) With thionyl chloride

The reaction of trithiazyl trichloride with thionyl chloride resulted in the formation of two solids, one volatile which could be sublimed out of the reaction mixture and a second involatile one, these were identified as $(NSCl)_3$ and S_4N_3Cl respectively. Fractional distillation under reduced pressure of the liquid products indicated the presence of two liquids other than the solvent, $SOCl_2$, which were identified as SCl_2 and SO_2Cl_2. Only a very small quantity of gas, SO_2, was given off during the reaction, and the SO_2Cl_2 also was only in very small quantities. Possible reactions taking place in the mixture are

(i) $3S_3N_2Cl_2 + SOCl_2 \longrightarrow 2S_4N_3Cl + SO_2Cl_2$

(ii) $3S_3N_2Cl_2 + 3SO_2Cl_2 \longrightarrow 2(NSCl)_3 + 3SO_2 + 3SCl_2$

as a result of either (i) or (ii) the following side reactions could occur

(iii) $3S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2S_4N_3Cl + 3SCl_2$

(iv) $2SCl_2 + SO_2 \longrightarrow SO_2Cl_2 + S_2Cl_2$

(v) $3S_3N_2Cl_2 + 3SO_2Cl_2 \longrightarrow 2(NSCl)_3 + 3SO_2 + 3SCl_2$

all of which are known to occur at room temperature.

No S_2Cl_2 and only very little SO_2 was obtained, therefore any of these compounds formed must be consumed in reactions (III) and (IV) respectively. Adding 1 x (II), 3 x (III), 1 x (IV) gives

$$12S_3N_2Cl_2 + 2SOCl_2 \longrightarrow 2(NSCl)_3 + 6S_4N_3Cl + SO_2Cl_2 + 7SCl_2$$

The SO_2Cl_2 formed is likely to react as shown in (V).

The S_4N_3Cl was by far the most abundant solid (by weight) but an accurate mole proportion of $(NSCl)_3$ to S_4N_3Cl could not be obtained as the $(NSCl)_3$ tended to sublime throughout the fractionation apparatus so this method of establishing the validity of the overall reaction equation was abandoned. (Even with (V) occurring to a small degree the overall ratio $(NSCl)_3:S_4N_3Cl$ should still be near 1:3).

(c) With trichloroacetonitrile

Thiodithiazyldichloride is an ionic compound[12] containing the cation $S_3N_2Cl^+$ and a sulphur chlorine bond. Its reaction with nitriles was attempted for comparison with those of trithiazyl trichloride. $S_3N_2Cl_2$ reacts only slowly at room temperature with trichloroacetonitrile and a considerable quantity of unreacted but slightly contaminated starting material was recovered. However a small quantity of buff acicular crystals were isolated from the filtrate which analysed (C, N, S, Cl totalling 102%) to give an empirical formula $S_3N_5C_4Cl_9$. The mass spectral fragmentation pattern gave as its heaviest fragment a peak at 529 which showed a multiple chlorine isotope pattern typical of Cl_9. This is where $S_3N_5C_4Cl_9$ would be expected. The empirical formula suggests that it could comprise an $S_3N_3Cl_3$ unit and two CCl_3CN units. This is neither supported nor contradicted by the mass spectrum which contains the following fragments.

fragment	mass	abundance
SN	46	100
CS_2	76	63
S_2N	78	97
CCl_3	117	29
	119	31
	121	13
C_2Cl_3S	161	8
	163	6
	165	2
C_2Cl_4S	186	32
	188	23
	190	14
	192	7

fragment	mass	abundance
C_2Cl_4SN	200	32
	202	34
	204	14
	206	7
$C_2Cl_3S_2N_3$	235	36
	237	38
	239	15
$C_3Cl_8N_3S$	382	9
	384	10
	386	10
	388	9
	390	3
$S_3N_5C_4Cl_9$	529	8
	531	10
	533	8
	535	6

If the compound is of the type containing an $(NS)_3$ there must be an SCl bond remaining, provided the CN of the nitrile has not broken completely. Also the presence of a N-Cl or a C-Cl α to N should be easily hydrolysed or substituted by an organic group. Insufficient of this material was obtained for identification reactions although some has been sent away for X-ray analysis.

Reactions of $S_2N_2CClCCl_3$ and S_2N_2CClPh

(a) With metal salts

There was no reaction with potassium fluoride. If the compound $S_2N_2CClCCl_3$ is ionic this is to be expected on the basis of lattice energy considerations (p.127). With potassium thiocyanate this is not expected to be the case, but a complex product was formed whose infrared spectrum indicated ring breakdown (cf. $(NSOCl)_3$ and KNCS [42d]).

(b) With $SbCl_5$

The reaction of $SbCl_5$ with both $S_2N_2C_2Cl_4$ (p.127) and S_2N_2CClPh was investigated. A white solid was precipitated immediately on adding the $SbCl_5$ in both cases indicating complex formation ($S_2N_2CR^+$, $SbCl_6^-$ or an adduct containing donor N or S). The analysis of the $S_2N_2CClR/SbCl_5$ corresponded to a 1:1 compound. In the reaction with $S_2N_2C_2Cl_4$ the melting point of the product was greater than 360^o. This perhaps favours an ionic nature.

If the compounds are ionic there should be immediate formation of the $SbCl_6^-$ anion which being of larger ionic size could result in the immediate precipitation of $S_2N_2CR^+SbCl_6^-$. In both reactions the infrared spectra of the products were very similar to those of the starting materials S_2N_2CClR. If the complex were due to lone pair donation a greater change in infrared spectra would be expected than if the anion just changed from Cl^- to $SbCl_6^-$.

(c) Reaction with tetrachloroethylene and acetonitrile

Trithiazyl trichloride reacts with tetrachloroethylene to give a compound of empirical formula $S_2N_2C_2Cl_4$ whose infrared spectrum is extremely similar to that of $S_2N_2C_2Cl_4$ obtained from the reaction of CCl_3CN with $(NSCl)_3$.[116] The very minor differences are probably due to slight contamination. Acetonitrile (20^o) reacts with $(NSCl)_3$ to give a crude black mass probably due to chlorination as well as addition across the C≡N bond.[110a]

If the compounds S_2N_2CClR obtained from nitriles contain an active SCl similar to sulphenyl chlorides and $(NSCl)_3$ a reaction with C_2Cl_4 (and CH_3CN) is to be expected. S_2N_2CClPh did not react with C_2Cl_4 (120^{o}C) or CH_3CN (80^{o}C). However in the attempted reaction the S_2N_2CClPh was recrystallised. Therefore if SCl is present in these compounds it is remarkably less reactive than in sulphenyl chlorides. As a result these liquids can be used as solvents for further reaction, especially as S_2N_2CClR is practically insoluble in most of the common organic solvents.

(d) With diphenylacetylene, cyclohexene and epichlorohydrin

As alkyl sulphenyl chlorides react vigorously with acetylenes[24] it was decided to investigate the reaction of $S_2N_2C_2Cl_4$. No reaction occurred under the conditions employed (p.106) again suggesting that the SCl is not similar to that of trithiazyl trichloride or RSCl. Similarly there was no reaction between cyclohexene oxide and S_2N_2CClPh. However with epichlorohydrin, S_2N_2CClPh gave a low melting (45-6°) red solid which was very susceptible to hydrolysis. The infrared spectrum shows strong absorptions above 3100 cm^{-1} which are typical of ν_{NH} and a strong peak at 691 cm^{-1}. ν_{C-Cl} can occur in the region 680 to 750 cm^{-1} when more than one chlorine is attached to carbon,[105] the 691 cm^{-1} peak is in this region. It appears that hydrolysis and/or chlorination has therefore occurred - this would account for the ν_{NH}. Further investigations on this reaction were therefore discontinued.

(e) <u>Reaction of S_2N_2CClPh with phenyl lithium and diphenyl mercury</u>

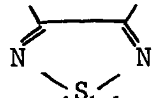
Phenyl lithium and diphenyl mercury have both been used in the formation of phenyl derivatives of sulphanuric halides. Phenyl lithium causes ring breakdown of $(NSOCl)_3$,[42d] diphenyl mercury gave $(NSO)_3ClPh_2$ in 58% yield.[55] In an attempt to stabilise the above compound by introducing a second phenyl group (to achieve further delocalisation of π electrons) both reactions were attempted.

Phenyl lithium reacted with S_2N_2CClPh but only extremely slowly at room temperature, a small amount of black oil being extracted from the unreacted starting material. With diphenyl mercury there was a very much faster reaction producing a highly soluble black material which tended to form an oil. By recrystallisation from absolute alcohol below 0°C (cf. $Ph_2N_2S_3$[117]) a small quantity of black crystals were obtained whose analyses approximated closely to those of $S_2N_2CPh_2$ (p.110). The infrared spectrum indicated that the sulphur-nitrogen skeleton of the molecule was unchanged in the reaction. However on standing at room temperature in the sunlight these decomposed to give diphenyl disulphide and a black tar. Therefore because of the reduced stability of the system and difficulty in isolation the $S_2N_2CPh_2$ was not investigated further.

Further possible reactions to stabilise or evaluate the system (S_2N_2CClR)

The reaction with lithium iodide would be worth investigation, the precipitation of LiCl being favourable from lattice energy considerations but the inherent stability to date of sulphur iodine compounds suggests that if S_2N_2CClPh contains covalent S-Cl, the product might be rather unstable. A stable product with similar i.r. to the chloride would favour an ionic structure. Substitution by NR has provided the majority of derivatives in the sulphanuric field and reactions may be worth investigating with amines and Me_3SiNR_2; there is however no reported reactiions between $(NSCl)_3$, S_4N_3Cl or $S_3N_2Cl_2$ and amines. The main danger in amine reactions is addition of NH across S=N (cf.RNSO[118])

(g) Comparison of S_2N_2CClX and 1,2,5-thiadiazoles[113]

Oxidation and reduction of 1,2,5-thiadiazoles is generally accompanied by ring breakdown even with mild reducing agents such as alcohols. They generally resist electrophilic substitution or the ring disintegrates: however their stability is high toward many reagents. They are inert to chlorination and nitration under various conditions and remain unchanged in the presence of refluxing benzoyl chloride and aluminium trichloride (a Friedel Crafts reaction). Nucleophilic substitution of chlorine in  however occurs readily. The ring has a pronounced electron-withdrawing effect and reactions which necessitate the aquisition of a positive charge in intermediate or transition states are rare, only occurring when electron-donating substituents are already present. If S_2N_2CClX is of a similar nature (tending to be electron-rich) it is unlikely that the ring provides the cation, i.e. going against all the previous arguments in favour of an ionic formulation! The unsubstituted 1,2,5-thiadiazole is highly reactive towards water as is S_2N_2CClX. Their infrared spectra are compared on p.125 The sulphur in thiadiazoles is unsubstituted so there can be little comparison between any sulphenyl chloride type reactions of S_2N_2CClX and those of chlorinated thiadiazoles.

If the compounds are similar in nature, oxidation of the sulphur to sulphur VI is unlikely to be successful without ring breakdown and quite severe conditions will be necessary for electrophile substitution. Thiadiazoles and their derivatives show a vast range of useful biological activity from antidiabetic and long acting antibacterial to local anti-inflammatory agents so there is the chance of a considerable future for a similar ring system..

Reactions of S_4N_4 and derivatives

When moving from the investigation of sulphanuric chemistry various reactions were investigated as possible starting points for further study.

The reactions to be discussed below were looked at at this time together with those of $(NSCl)_3$.

(a) <u>S_4N_4 and $CuCl_2.2H_2O$</u>

Fluck and Goehring[98] prepared a compound from the reaction of S_4N_4 and $CuCl_2.2H_2O$ in the presence of dimethyl formamide which they identified as $S_2N_2CuCl_2$ which was supposed to contain the five-membered S_2N_2Cu ring. It was attempted to repeat this reaction under the conditions reported, but the main product was copper sulphide together with a small quantity of material of uncertain composition whose analysis indicated a N:S:Cl ratio of 5:1:1.

(b) <u>"$S_6N_6Cl_4$"</u>

The chlorination of S_4N_4 with a rapid stream of chlorine gas gives rise to a yellow crystalline solid of empirical formula $S_3N_3Cl_2$, which is discussed by G.G. Alange.[25a] The reaction of this compound, $S_6N_6Cl_4$ with epichlorohydrin does not proceed in the same fashion as that of $(NSCl)_3$. A red oil is obtained together with S_4N_4, and the expected solid $S_6N_6(\text{O-CH}(CH_2Cl)CH_2Cl)$ could not be isolated. The oil shows similar properties to those formed in the reaction of $(NSCl)_3$ with butylene and ethylene oxides. The reaction was not investigated further as the formation of S_4N_4 suggested that the original system had disintegrated and/or chlorination of the epoxide had taken place, or it contains S_4N_4

APPENDIX

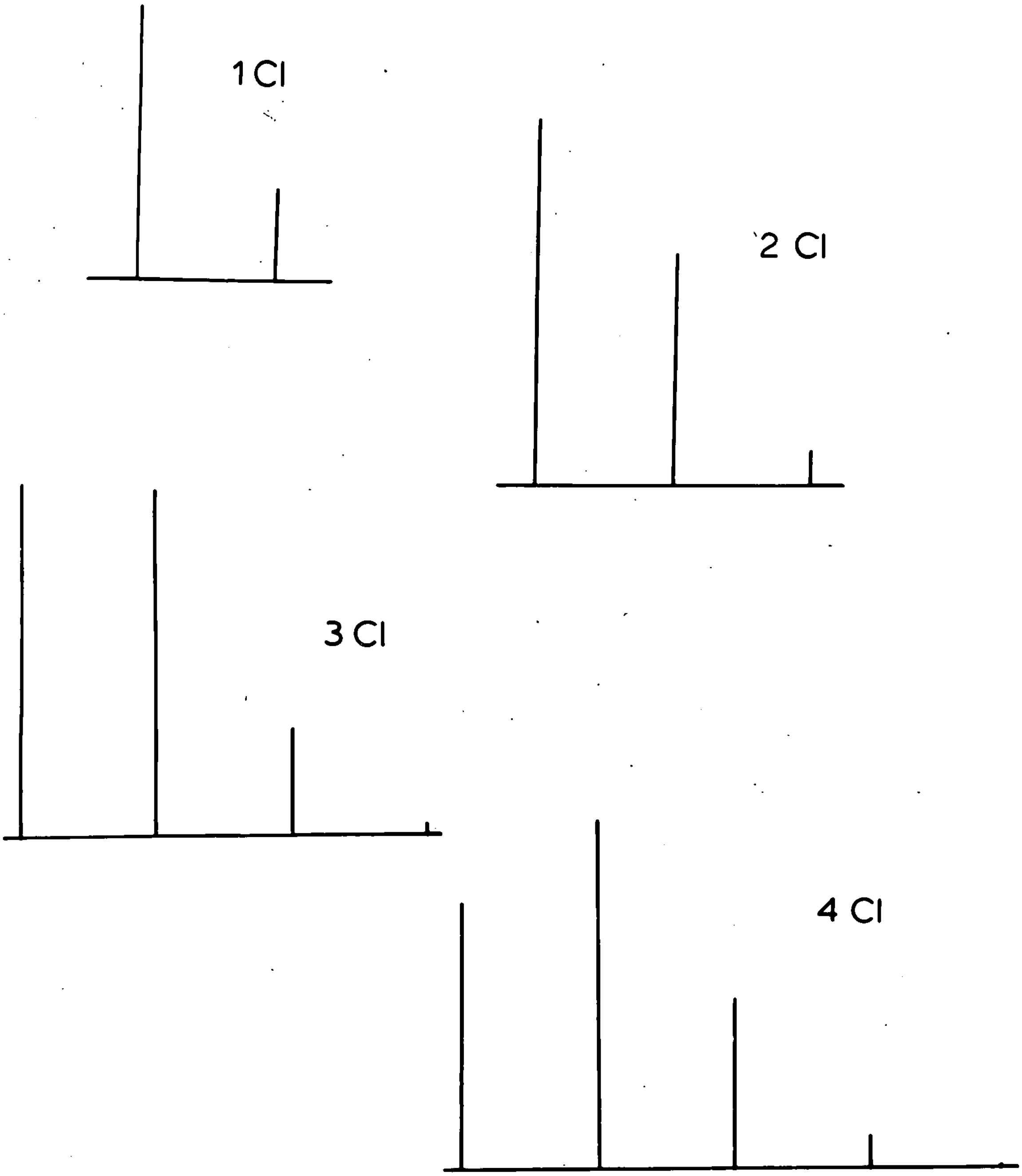
Mass Spectral Fragmentation Patterns

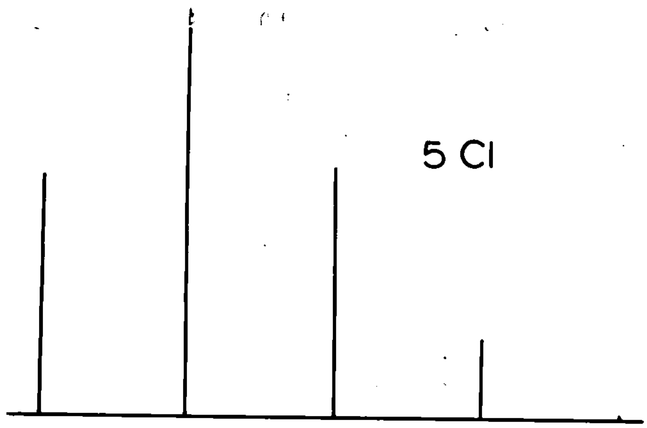
Mass Spectral Fragmentation Patterns

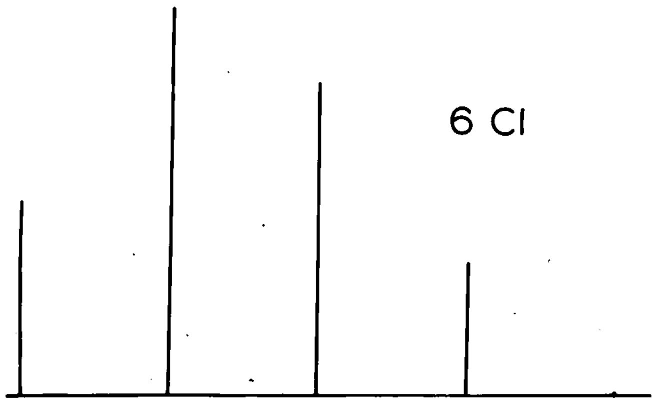
The mass spectrometer bombards the substance under investigation with an electron beam and records the damage as a spectrum of positive ion fragments and their relative abundances. The position of the fragment in the spectrum is based on the mass/charge ratio but as the charge is one in the vast majority of cases it can generally be taken as being based on mass. When an element has more than one naturally occurring isotope a pattern is observed in the spectrum; the relative abundances of a species containing only one atom of that element show the isotopic abundances of that element (all other elements in the species being monoisotopic). The P, P+1 and P+2 pattern for the parent peak of organic molecules containing H is well known. However when the isotope abundances are reasonably large typical patterns can be seen for varying numbers of these elements in fragments as well as the parent molecule ion. In the case of chlorine the number of atoms of chlorine in the fragment can often be seen at a glance by looking at the first peak of a fragment, P, at P+2, P+4 etc. and their relative abundances. This is particularly useful in the study of the mass spectra of sulphur-nitrogen-chlorine compounds as the isotopic abundances of other elements in the compounds is generally low.

In this appendix a) the isotopic splitting patterns for chlorine 1-8 in the absence of other elements are illustrated and b) the calculated patterns for some of the fragments occurring in the mass spectra of compounds, prepared or used in the work included in this thesis, are compared with the observed patterns.

Mass spectal isotope patterns for chlorine




5 Cl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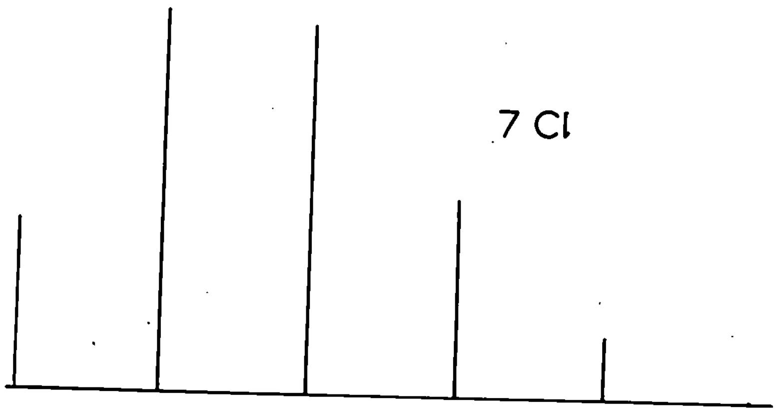
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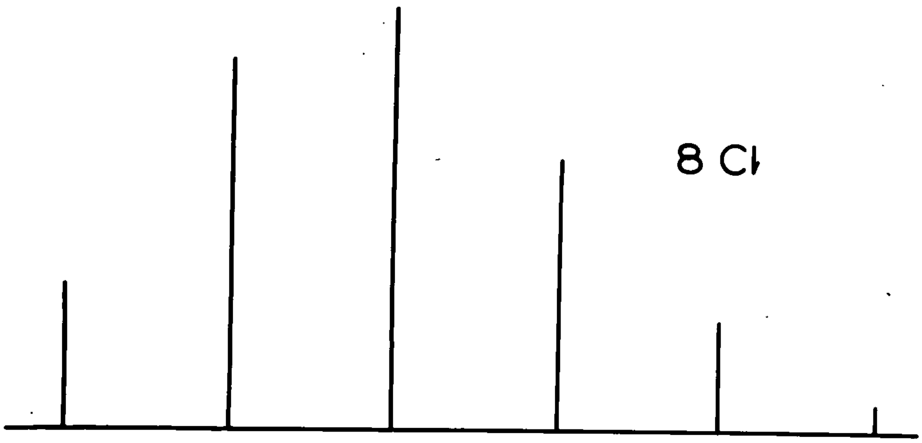
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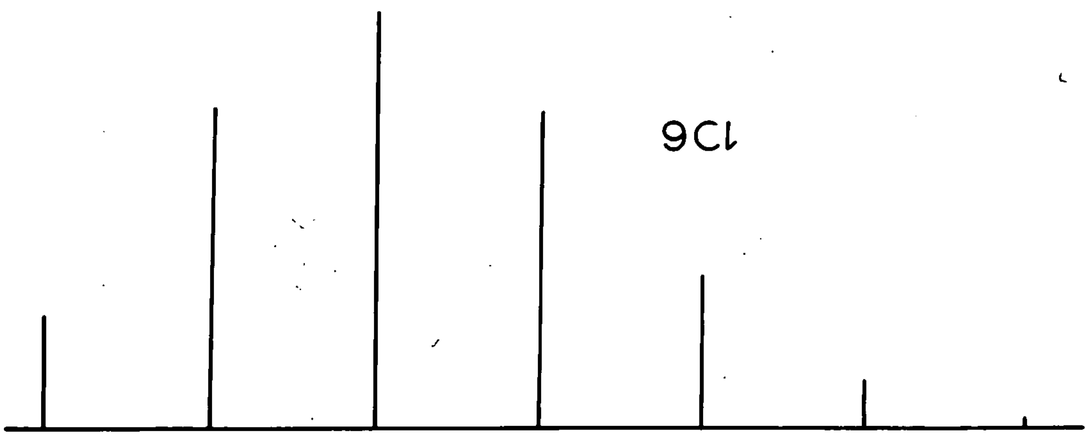
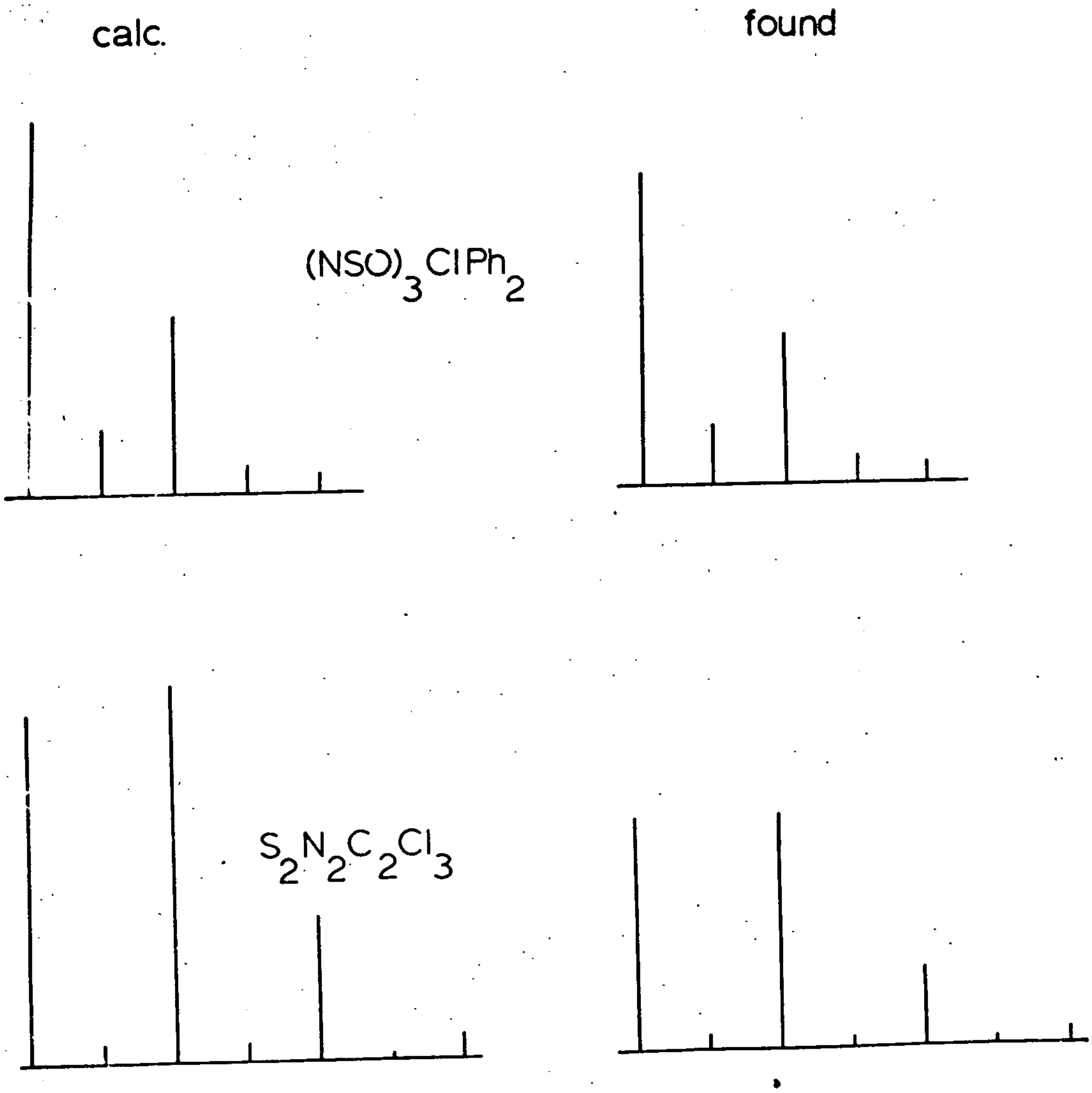
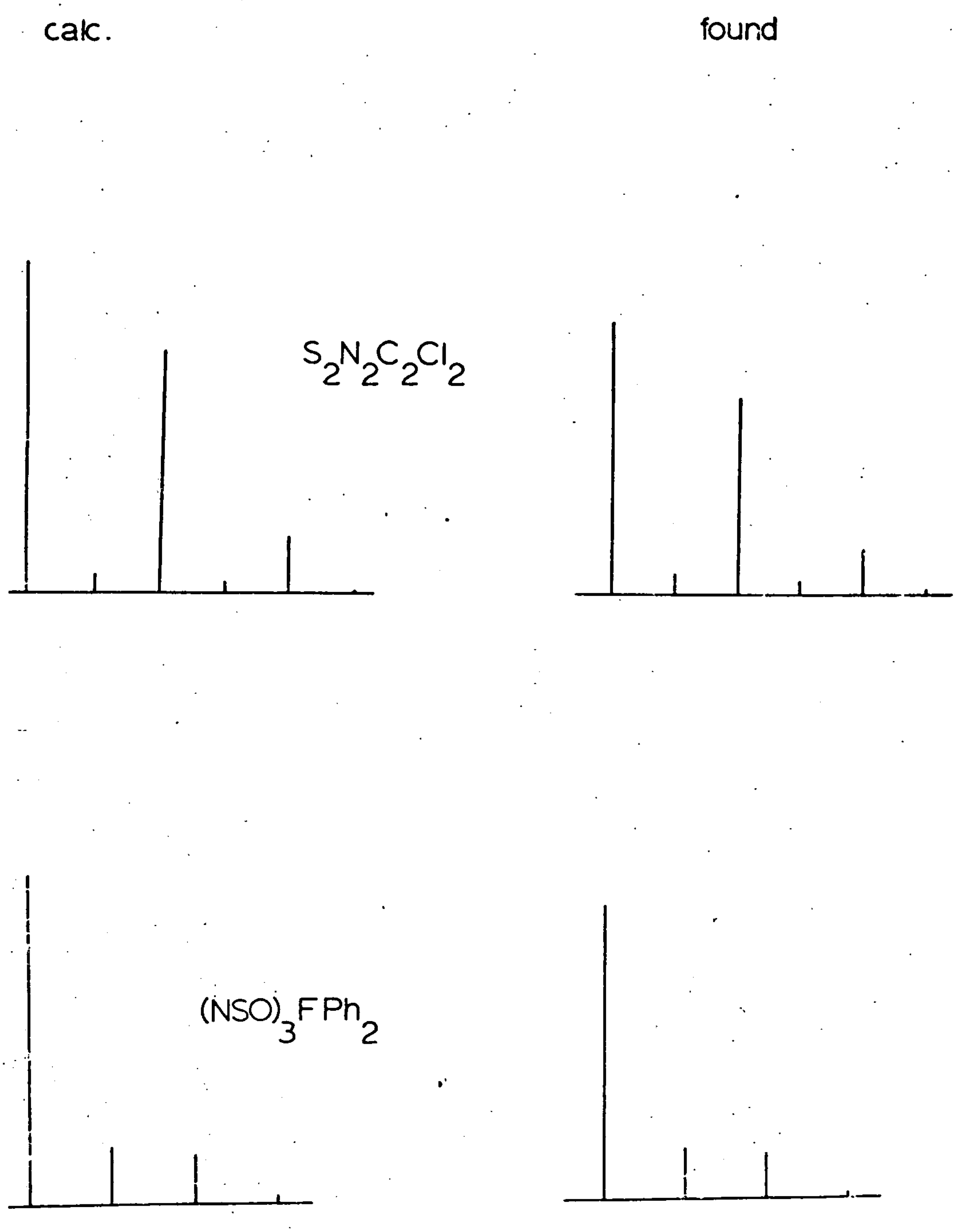

9Cl

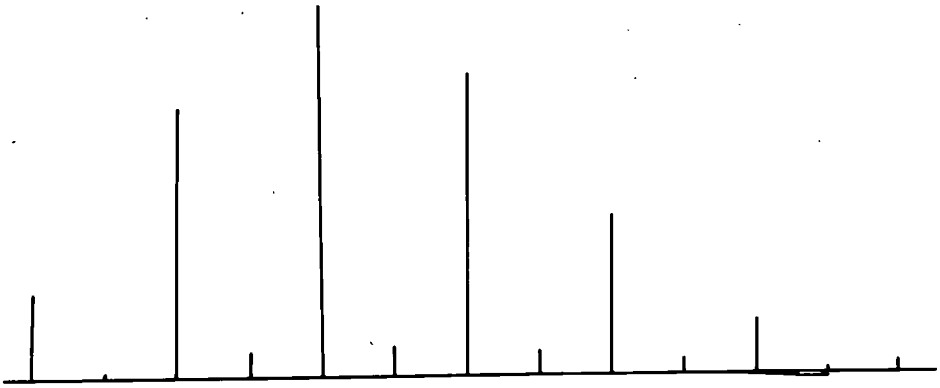
Comparison of the calculated & actual patterns for some fragments




calc.
found
$S_2N_2C_2Cl_2$
$(NSO)_3FPh_2$

$S_3N_5C_4Cl_9$

calc.



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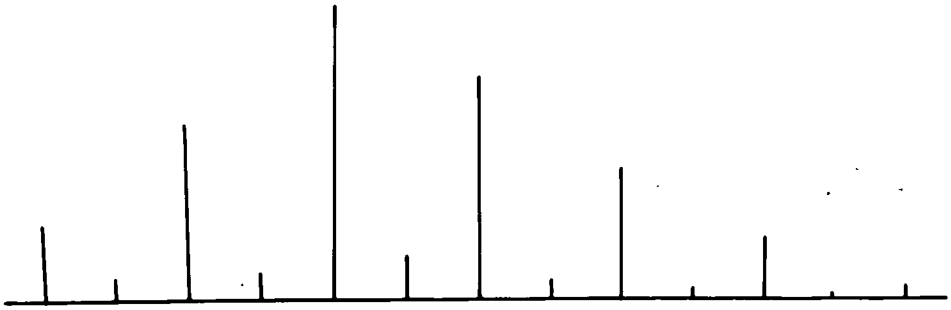

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