# Reactions of tetrathiotetraimide

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# REACTIONS OF TETRATHIOTETRAIMIDE

by

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# MEMORANDUM

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

## ABSTRACT

The aims of the work described in this thesis are to study the reactions of tetrathiotetraimide and to attempt to systematise its chemistry. Tetrathiotetraimide is one of the series of sulphur imides $S_x(NH)_{8-x}$ derived from octasulphur. The introduction describes the reported chemistry of all known imides derived from octasulphur up to the time of writing, and their behaviour is discussed in terms of seven reaction types.

(i) Addition reactions with organic substrates
(ii) Adduct formation with Lewis acids
(iii) Hydrogen substitution
(iv) Hydrogen abstraction
(v) Oxidation to thionylimides
(vi) Ring degradation
(vii) Ring contraction e.g. to $S_4N_3^+$ or $(NSCl)_3$

The behaviour of tetrathiotetraimide has been investigated with four types of compounds;

(i) metal halides (Lewis acids),
(ii) other compounds containing reactive halogen,
(iii) organometallic compounds, and
(iv) oxygen compounds (all containing the group $\diagdown O \diagup$).

Two new 1:1 adducts of tetrathiotetraimide with $AlBr_3$ and $AlCl_3$ are described, these are probably $\sigma$ adducts via donor nitrogen.

Ring contraction from the eight-membered $(SN)_4$ ring to (a) the seven-membered ring cation $S_4N_3^+$, and (b) the six-membered $(SN)_3$ ring by reaction with the halogens and several active halogen compounds is reported for the first time.

Finally, the preparation of a tetrathiotetraimidolithium derivative, and its use as a possible reaction route to $(SNX)_4$ derivatives, is discussed.

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# 1. TETRATHIOTETRAIMIDE

## General Properties

Tetrathiotetraimide is an air-stable, diamagnetic, colourless crystalline solid melting point 152°[1], 145°[2], 156° (this work). It is not wetted and not dissolved by water[1], is readily soluble in pyridine[1] and THF (this work), and slightly soluble in acetone[1,3], ethyl[1,3] and amyl[3] alcohols, ether[3], carbon disulphide[3] and piperidine[3].

## Structure

The structure has been determined by X-ray[4,5] and neutron diffraction[6] studies. The molecule has a puckered eight membered ring with alternate S and N atoms, identical SN bond lengths, and coplanar SNHS groupings, the i.r. spectrum[7] indicates NH rather than SH bonds (organic imides absorb at 3500-3220 $cm^{-1}$, thiols in 2600 $cm^{-1}$ region[8]). The SN distance, 1.674 ± 0.004 Å[4] indicates a bond order slightly greater than one[9], even though the formal bond order is one. It is now generally accepted that $(SNH)_4$, in common with $S_4N_4$ and other related SN ring systems contains a π-delocalised system of electrons[10,11] which may be thought of as being derived from π overlap of nitrogen lone pair electrons and empty sulphur d orbitals.

The structure of $(SNH)_4$ in the solid state is shown in Fig. 1.[4,6]

## Preparation

The preferred preparative route is by reduction of $S_4N_4$ in benzene solution by methanolic stannous chloride,[12] though reduction of $S_4N_4$ with dithionite has been reported (but without practical details)[1].

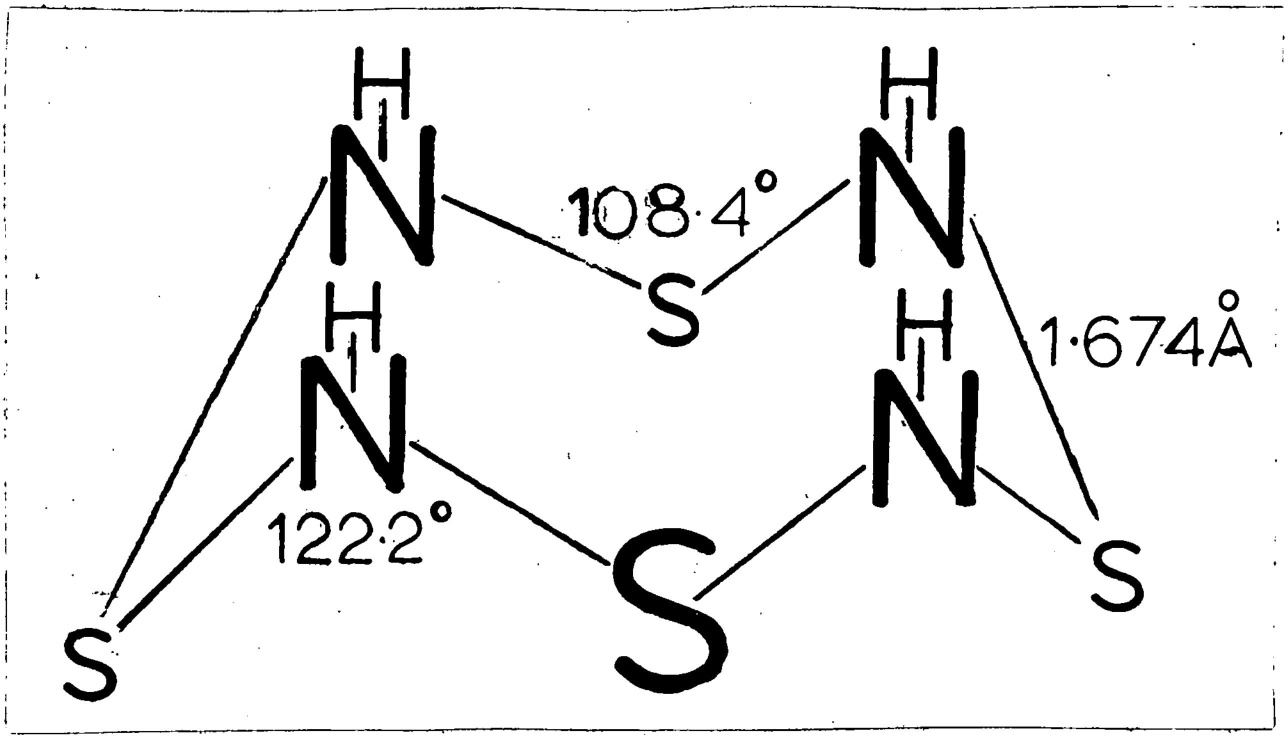


Fig. 1.

## Reactions

It has been found that $(SNH)_4$ undergoes seven types of reaction:

(1) Addition reactions with organic substrates

(2) Adduct formation with Lewis acids

(3) Hydrogen substitution

(4) Hydrogen abstraction

(5) Oxidation to tetrathionylimide

(6) Ring degradation

(7) A new type of reaction, ring contraction e.g. to $S_4N_3^+$ or $(NSCl)_3$, is described in this work.

These reactions can also be systematised according to the nature of the reactants (see p. 12 ).

## (1) Addition Reactions with Organic Substrates

There are remarkably few reported cases of organic derivatives of $(SNH)_4$. Two derivatives $(SNCONHPh)_4$[13] and $(SNCH_2OH)_4$[13,14] have been made by reaction with phenylisocyanate and formaldehyde. Hydrolysis of $(SNCONHPh)_4$ with hot hydrochloric acid yields NHPh.CO.NHPh, interpreted as evidence that the H atoms in $(SNH)_4$ are attached to the N atoms.[13] The hydroxy-methylene derivative $(SNCH_2OH)_4$ has been converted to esters $(SN.CH_2OCOR)_4$ by reacting with acyl chlorides RCOCl ($R = CH_3$, $pNO_2C_6H_4$)[13]. Both are crystalline solids; the acetyl derivative melting at 87.5°, and the p-nitrobenzoyl derivative at 212° with decomposition.

## (2) Adduct Formation with Lewis Acids

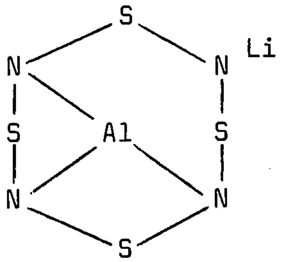
There are only two reported cases of $(SNH)_4$ adducts. Addition of $(SNH)_4$ to an ether solution of $TeBr_4$ yields an amorphous orange powder $(SNH)_4.TeBr_4$[15], stable in dry air, whose structure has not been determined. It seems to be the only reported case where a cyclic sulphur imide forms a stable adduct with a Lewis acid without simultaneous rearrangement or elimination. The reaction between $(SNH)_4$ and $AgNO_3$ in acetonitrile or acetone yields $(SNH)_4.2AgNO_3$[16] which may be a simple adduct, but is unstable, decomposing within a few hours, immediately with water (see p. 9).

Two new adducts are reported in this thesis. Both $AlBr_3$ and $AlCl_3$ react with $(SNH)_4$ in carbon disulphide to yield orange $(SNH)_4.AlBr_3$ and pale orange-yellow $(SNH)_4.AlCl_3$. These adducts are amorphous solids and have been characterised by elemental analysis and examination of i.r. spectra (see p.27). Reaction with $SnBr_4$ in ether (surprisingly) yields an $S_4N_4$ adduct, $2S_4N_4.SnBr_4$. This compound was identical to that produced from $S_4N_4$.[17]

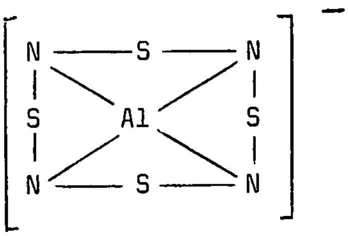
## (3) Hydrogen Substitution

There are five reported cases of hydrogen substitution involving retention of the $S_4N_4$ ring system. An acetyl derivative $(SNCOCH_3)_4$ has been reported,[3] by reaction with acetyl chloride in ethyl acetate, but we were unable to repeat this preparation (see p.31). We believe that this report[3] has entered the literature through an error in translation. Arnold[13] described the reaction between the hydroxy-methylene derivative $(SNCH_2OH)_4$, of $(SNH)_4$, and acetyl chloride in ethyl acetate solution containing a trace of potassium carbonate yielding the derivative $(SNCH_2OCOCH_3)_4$, mp 87.5°. Garcia-Fernandez however, refers[3] to the reaction between $(SNH)_4$ and acetyl chloride in ethyl acetate containing a trace of potassium carbonate to yield the derivative $(SNCOCH_3)_4$ mp 87.5°. The reference to $(SN.COCH_3)_4$ in a recent review[18] is probably also as a result of the same translation error.

Reactions with copper (11) salts in non-aqueous solvents[19] yield the covalent molecules $S_4N_4H_2(CuCl)_2$ and $S_4H_4H_2(CuNO_3)_2$ which presumably contain metal-nitrogen bonding, while $LiAlH_4$ in THF gives the explosive white solid $LiAl(S_4N_4)$ [20]. Careful hydrolysis of the latter compound with moist acetone results in formation of LiOH, $Al(OH)_3$ and $(SNH)_4$ indicating that the ring system is retained. M. Becke-Goehring suggests that the structure of this compound may be (I), or it may contain the complex anion (II).[21]



(I)



(II)

That $(SNH)_4$ can function as a Brønsted acid is shown by the reaction with $Ph_3CNa$ in ether-dioxane.[22] Two salts $(S_4N_4H_2)^{2-}Na^+_2$ (citron yellow) and $(S_4N_4)^{4-}Na^+_4$ (orange red) were isolated and proved much more unstable and reactive than $(SNH)_4$. Both formed unstable solutions in polar organic solvents and detonated or ignited with water. Evidently $Ph_3C^-$ is a strong enough base to ionise off and accept protons from the $(SNH)_4$ ring which acts as a very weak Brønsted acid. $S_7NH$ (see p. 14 ) is a non-conductor in pyridine [23], with which it hydrogen bonds[24], and is very soluble in this solvent. It seems likely that $(SNH)_4$, also very soluble in pyridine (see p. 1. ) may behave similarly, demonstrating that pyridine is not a strong enough base to remove protons from either of these imides.

We now report (see p. 40 ) that the n-butyl carbanion in n-butyl lithium is a strong enough base to remove protons from $(SNH)_4$. Measurement of butane evolved during the reaction suggested that the yellow solid obtained was predominantly $(S_4N_4)^{4-}Li^+_4$.

There are no reported cases of direct alkylation of $(SNH)_4$. Tetra-alkyl derivatives have been made indirectly in low yield (2% or less) by reacting sulphur dichloride $SCl_2$ with the corresponding primary amines (see Table 1).

| R | mp | Reference |
|---|---|---|
| $CH_3$ | 126° | 25 |
| $C_2H_5$ | 143° | 26 |
| $C_6H_5CH_2$ | 164° | 27 |
| $C_6H_5(CH_2)_2$ | 165.5° | 27 |

$(SNR)_4$

TABLE 1.

An unstable linear polymer $(SNCH_3)_x$ has also been reported[25] from the reaction between gaseous methylamine and sulphur dichloride in hexane. There is an apparent inconsistency in reports of $(SNC_2H_5)_4$. Lengfeld and Stieglitz[28] reported this compound as an oil (excellent analyses and molecular weight determination). Later workers[26], using identical reagents but very dilute solutions, obtained a sharp melting solid after chromatographic separation. The low melting point of the Lengfeld and Stieglitz product is probably due to the presence of impurities, possibly including a mixture of isomers.

As in $(NP)_4$ rings ($NPX_2$ tetramers), there are four ring conformations (crown, saddle, tub and chair)[29]. X-ray[4,5] and neutron diffraction[6] studies have shown that $(SNH)_4$ exists as the crown form in the solid state. It is significant that the SNS bond angle (122.2° [4]) is close to 120° hence there is only one hydrogen position, and no further isomers in the crown conformation. This could be as a result of complete nitrogen lone-pair delocalisation i.e. SN bond order 1.5 (SN bond length suggests SN bond order of 1.3 [9]), or because the lone pair (or at least the remaining lone pair character) is in a p-orbital. Thus, if the SNS angle is nearly 120° in $(SNC_2H_5)_4$, there will be four isomers (crown, saddle, tub and chair), but if the SNS angle is significantly less than 120° then each ethyl group could be axial or equatorial, (i.e. five conformational isomers in the crown form). Moreover, there may well be isolable conformational isomers based on other ring shapes.

## (4) Hydrogen Abstraction

There are two reported cases of hydrogen abstraction. Heating under vacuum at 110-135° produces $S_4N_4$ in over 95% yield[30] and heating with $(NSCl)_3$ in $CCl_4$ containing a trace of pyridine results in almost quantitative conversion to $S_4N_4$[31]. The proposed equation is:-

$$3(SNH)_4 + 4(NSCl)_3 \longrightarrow 6S_4N_4 + 12HCl$$

Reaction between $(SNH)_4$ and $(NSCl)_3$ in $CCl_4$ with pyridine absent results in formation of the red-brown adduct $S_4N_4.4HCl$, which reacts with a trace of water to give $S_4N_3Cl$,$NH_4Cl$ and $Cl_2$. The overall equation is

$$3(SNH)_4 + 4(NSCl)_3 \longrightarrow 3S_4N_4 + 3S_4N_3Cl + 3NH_4Cl + 3Cl_2$$

A further instance of hydrogen abstraction is reported in this thesis (see p.34). Reaction with N-bromosuccinimide (1:1 molar ratio) produced $S_4N_4$, and with excess N-bromosuccinimide (1:2 molar ratio) $S_4N_3Br$.

## (5) Oxidation to Tetrathionylimide

The air oxidation of $(SNH)_4$ at 110-120° yielding orange-red tetrathionylimide $(SONH)_4$ is reported by Fluck and Becke-Goehring.[32]

## (6) Ring Degradation

There are several reported cases of $(SNH)_4$ reacting with metal compounds in non-aqueous solvents to give metal thionitrosyls, $M_x(NS)_y$. A green/yellow powder $Hg_5(NS)_8$ results[33] from rapid (15 minutes) reaction with mercury (11) acetate in methanol (or pyridine) at low temperature. This compound is unstable forming HgS on exposure to air. Slow reaction between $(SNH)_4$ and a large excess of mercury (11) acetate in pyridine forms $Hg(NS)_2$.[33] $Hg_5(NS)_8$ is considered to be a molecular compound of $3Hg(NS)_2$ and $Hg_2(NS)_2$.[33] $Hg_5(NS)_8$ can be oxidised by thionyl chloride in $CS_2$ solution to thionyl dinitrosyl $(NS)_2SO$.[33] Reaction of $Hg_5(NS)_8$

with $S_2Cl_2$ gives tetrasulphur dinitride $S_4N_2$ (an unstable red oil) in 42% yield,[34] a reaction which throws light on the structure of $Hg_5(NS)_8$.

$$Hg_5(NS)_8 + 4S_2Cl_2 \longrightarrow 4S_4N_2 + 3HgCl_2 + Hg_2Cl_2$$

This is considered[21] to be evidence for the presence of $S_2N_2^{2-}$ ligands in $Hg_5(NS)_8$, reacting as shown

$$S_2N_2^{2-} + S_2Cl_2 \longrightarrow S_4N_2 + 2Cl^-$$

A third mercury compound $(Hg(NS))_x$ has been obtained as a yellow precipitate[35] by reaction between $(SNH)_4$ and mercury (1) nitrate in DMF at -70°. This compound is stable at room temperature and is acted on slowly by water and dilute acids. It is quickly decomposed by strong acids and bases.

Copper (1) chloride and silver nitrate in non-aqueous solvents yield black CuNS and red-brown AgNS respectively[19] (see p. 3 ). It has been suggested[19] that the reacting species in these reactions are HNS and $S(NH)_2$, the former yielding the nitrosyl and the latter serving as an oxidising agent. The derivatives of $(SNH)_4$ mentioned so far are insoluble in inert solvents, suggesting that they may be coordination polymers containing the ligands $S_4N_4^{4-}$, $S_2N_2^{2-}$ (see above) or $SN^-$ [21]. Reaction between AgNS and ethyl iodide yielded a yellow oil[19], similar to the yellow oil reported by Lengfeld and Stieglitz[28] as $(SNC_2H_5)_4$. (see p. 6 ). Goehring et al[19] interpreted this as evidence that the eight membered SN ring was retained in the silver compound. We believe that the structure of the silver compound may well be $(AgNS)_4$, giving on reaction a mixture (yellow oil) consisting mostly of $(SNC_2H_5)_4$ which would yield the pure derivative (solid) after chromatographic purification.

It has been reported[36] that treatment of $(SNH)_4$ in liquid ammonia with lead (11) acetate or iodide yields the compound $Pb(NS)_2.NH_3$. Later workers[16] were unable to repeat this preparation. Treatment of $(SNH)_4$ in liquid ammonia with potassamide $KNH_2$ results in formation of the compound $KNS.NH_2K$[16] which is immediately decomposed by moist air. It is however freely soluble in liquid ammonia as long as $(SNH)_4$ is present. Addition of lead iodide to such a solution precipitates a mixture of $Pb(NS)_2.NH_3$, PbNH and $PbN.PbI.NH_3$ indicating the presence of various nitrogen-containing anions.

Treatment of $(SNH)_4$ in pyridine with halo-substituted benzene sulphonyl chlorides yielded a series of thiodithiazyl compounds $R_2S_3N_2$ [37], the structures of which are unknown (see Table 2).

| R | Product | mp |
|---|---|---|
| Phenyl | No reaction | - |
| 3.4 dichlorobenzene | Deep red solution no satisfactory product | - |
| 2.4.5 trichlorobenzene | Red $(2.4.5.Cl_3C_6H_2)_2S_3N_2$ | 209°C (decomposition) |
| 2.5 dichlorobenzene | $(2.5Cl_2C_6H_3)_2S_3N_2$ | 200°C (decomposition) |
| 2.4.5 tribromobenzene | Orange-red $(2.4.5.Br_3C_6H_2)_2S_3N_2$ | 214°C |

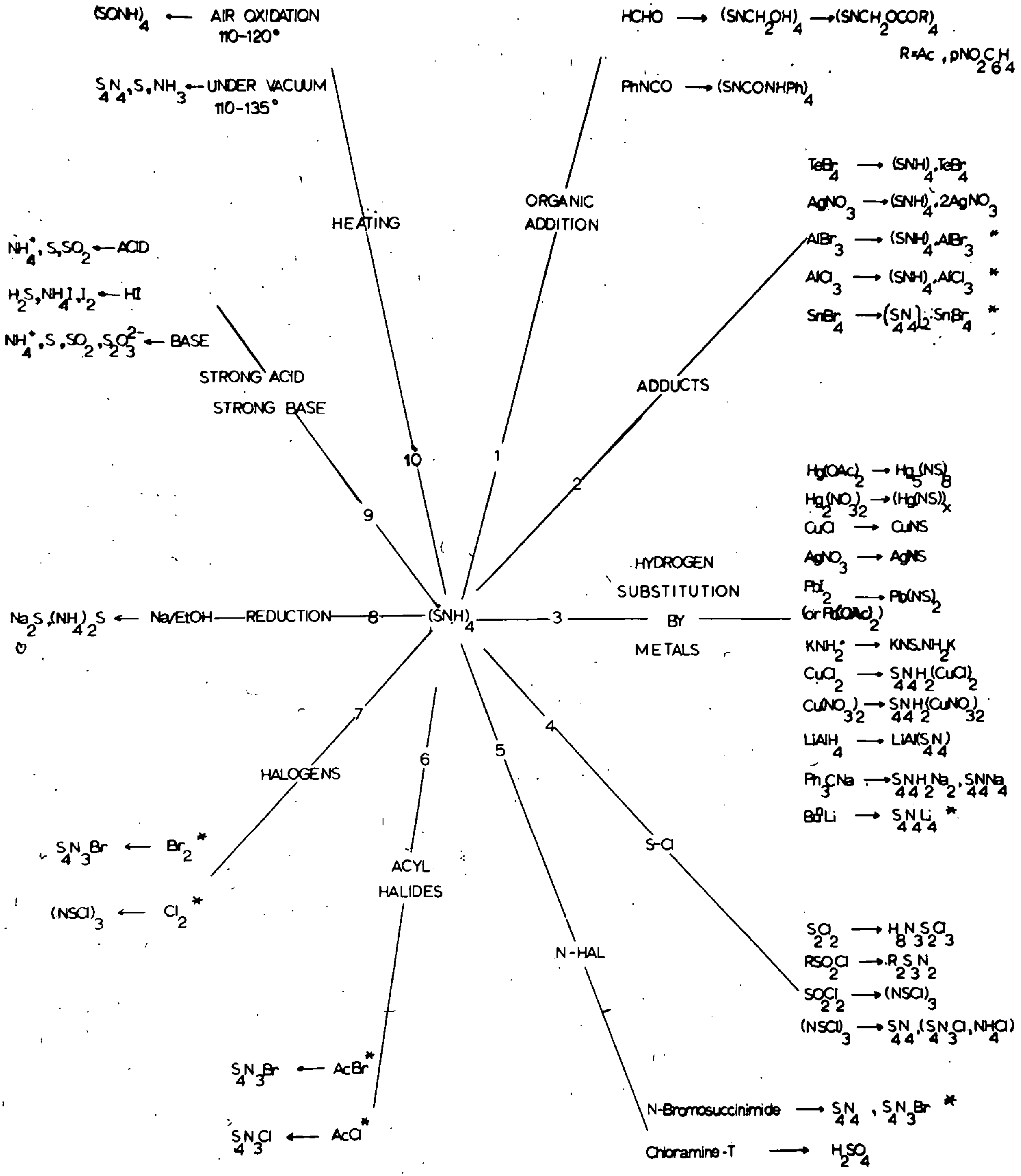
<u>REACTIONS BETWEEN $(SNH)_4$ AND $RSO_2Cl$</u> [37]

<u>TABLE 2</u>

$(SNH)_4$ reacts with $S_2Cl_2$ to give the compound $H_8N_3S_2Cl_3$.[13] This substance is described as a salt, having similar properties to $S_4N_3Cl$ (see ref. 84 ). Reaction of $(SNH)_4$ with Na/EtOH gives $(NH_4)_2S$ and $Na_2S$ [16], and with hydrogen iodide gives S, $I_2$ and $NH_3$ [38], or (according to Murthy [39]) $H_2S$, $NH_4I$ and $I_2$. Hydrolysis with strong acids gives $NH_4^+$, S and $SO_2$ [40], and strong bases result in the formation also of $S_2O_3^{2-}$ [40]. Oxidation of $(SNH)_4$ with chloramine -T in acidified aqueous dioxane also results in ring degradation (quantitative conversion of the sulphur to $H_2SO_4$)[41]. Oxidation without ring degradation is described on p. 8.

## 7. Ring Contraction

Ring contraction to $S_4N_3^+$ and $(NSCl)_3$ is described in this thesis. Treatment with bromine (see p. 33 ) or acetyl bromide (see p. 32 ) results in the formation of thiotrithiazyl bromide, $S_4N_3Br$, and ammonium bromide. Similarly acetyl chloride gives $S_4N_3Cl$ and $NH_4Cl$ (see p. 31 ). However, reaction with chlorine (see p. 38 ) or sulphuryl chloride (see p. 39 ) results in the formation of trithiazyltrichloride $(NSCl)_3$.



REACTIONS OF TETRATHIOTETRAIMIDE

(* THIS WORK)

Fig. 2.

## 2. Other Sulphur Imides Derived from Octasulphur.

Imides derived from octasulphur are discussed in a recent review[42], a brief summary of which is given here.

Imides contain the bivalent $>$NH group which can take the place of a divalent sulphur atom in the $S_8$ ring. Imide hydrogens are somewhat acidic, and are also labile towards sulphonation, acylation etc.

Up to 4 sulphur atoms in the $S_8$ ring have been replaced by $>$NH groups and all possible imide derivatives up to $(SNH)_4$ are known. Replacement of more than four sulphur atoms results in adjacent NH groups, and, although there is no reason why such compounds should not be preparable (e.g. from $N_2H_4$ and sulphur halides), none is known. However, it seems likely that if they could be made they would easily eliminate molecular nitrogen.

There are two general methods of making these imides. First, reduction of sulphur nitrides. The reduction of $S_4N_4$ with stannous chloride to give $(SNH)_4$ has already been described in this thesis and Garcia-Fernandez[2,43] has reduced tetrasulphur tetranitride and thiotrithiazyl chloride with hydrazine on silica gel to obtain heptasulphur imide $S_7NH$ in good yield, with smaller amounts of the di-, tri-, and tetraimides. The second general method is to react ammonia with a sulphur chloride in a polar solvent, generally DMF[44,45,46,47,48,49,50,51]. $S_7NH$ is produced in good yields by this method, along with the di- and triimides in much smaller quantities, separation being effected by chromatography on silica gel[52]. Similar yields of $S_7NH$ and of the diimides are obtained by adding a $CCl_4$ or $CS_2$ solution of $S_2Cl_2$ to aqueous ammonia[49,53,54]. The reaction of azides with chlorosulphanes in polar solvents to give these imides has also been reported.[55]

(i) Heptasulphur Imide $S_7NH$

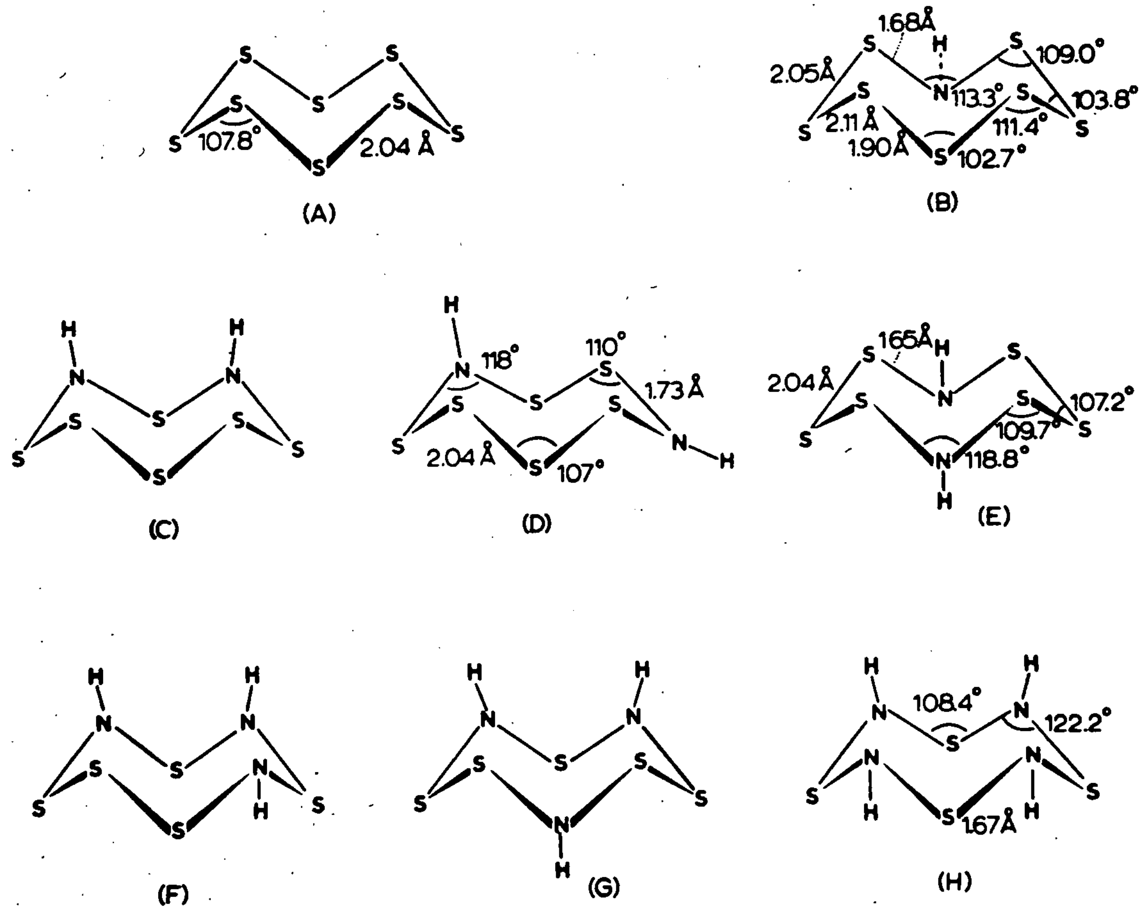
$S_7NH$ is a stable, almost colourless crystalline solid m.p. 113.5° insoluble in, and not affected by, water. It is readily soluble in most organic solvents[47] and is very soluble in pyridine to which, as the i.r. spectrum shows, it hydrogen bonds.[56] The S-N bond lengths correspond to a bond order of 1.3, suggesting some delocalisation of the nitrogen lone-pair.

(ii) The Hexasulphur Diimides, $S_6(NH)_2$.

All three isomers 1,3-, 1,4- and 1,5- hexasulphur diimide have been isolated[47, 50,51,57]. Their structures were deduced from X-ray diffraction studies[57,58], examination of i.r. spectra (showing splitting of the SN stretching frequency due to interaction between NH groups as they become closer)[47], and measurement of dipole moments which agreed with calculated values based on vector addition of contributions from the imide groups.[48] The hexasulphurdiimides are colourless, crystalline compounds, 'almost indefinitely stable' when pure, though the 1,4- isomer darkens superficially on exposure to daylight.[59]

(iii) The Pentasulphur Triimides $S_5(NH)_3$

These imides are present in very small quantities in the reaction product from $S_2Cl_2$ and ammonia in DMF, and can be isolated by chromatography.[48] There are two reported isomers; the 1,3,5- and 1,3,6- triimides, both



(A) (B) (C) (D) (E) (F) (G) (H)

Fig. 3.

Molecular structures of octasulphur and the imides derived from it, showing dimensions where known.

(A) $S_8$, rhombic,
(B) $S_7NH$,
(C) 1,3-$S_6(NH)_2$,
(D) 1,4-$S_6(NH)_2$,
(E) 1,5-$S_6(NH)_2$,
(F) 1,3,5-$S_5(NH)_3$,
(G) 1,3,6-$S_5(NH)_3$,
(H) $S_4(NH)_4$.

being crystalline solids. The former can also be prepared by hydrazine reduction of $S_4N_4$[2], and it seems likely that the 1,3,6- isomer could also be made in this way.[2] The structure of the 1,3,5- isomer has been determined by X-ray diffraction studies.[60]

## Reactions

The reactions of the imides $S_7NH$, $S_6(NH)_2$ and $S_5(NH)_3$ will be divided into reaction types so that similarities and differences in behaviour can be compared with those of $(SNH)_4$.

### (1) Addition Compounds with Organic Substrates

Like $(SNH)_4$ (p. 3.  ), $S_7NH$ forms a crystalline derivative $S_7NCH_2OH$ with formaldehyde.[61] There are no reported cases of this type of reaction for the other imides.

### (2) Adduct Formation with Lewis Acids

$(SNH)_4$ forms simple adducts with Lewis acids (see p. 3.   ) No reaction is known in which the other imides add on to a Lewis acid without simultaneous rearrangement or elimination. $S_7NH$ reacts with boron trihalides in $CS_2$ at low temperatures (below -40°) to give the compounds $S_7NBCl_2$ and $S_7NBBr_2$.[62] Sulphur trioxide gives a carmine red 1:1 compound with $S_7NH$, which by analogy with other reactions of $SO_3$ is probably a sulphonic acid $S_7NSO_3H$.[63,64]

### (3) Hydrogen Substitution

Unlike $(SNH)_4$, which has not been acylated (see p. 4.  ), $S_7NH$ and the hexasulphur diimides can be acylated by standard methods giving crystalline organic derivatives, those of $S_7NH$ being prepared in high yields.[65] (See Table 3).

## ACYL DERIVATIVES OF SULPHUR IMIDES

| | R | mp$^o$C | Ref. |
|---|---|---|---|
| $S_7NCOR$ | $CH_3$ | 104 | 65,66,67 |
| | $CH_2Cl$ | 110 | 65 |
| | $C_6H_5$ | 138 | 65 |
| | $CH_2C_6H_5$ | 110 | 65 |
| | $(CH_2)_7CH_3$ | Liquid | 65 |
| | $(CH_2)_{16}CH_3$ | 68 | 65 |
| | $CH = CHC_6H_5$ | 146 | 65 |
| | $o\text{-}ClC_6H_4$ | 92 | 65 |
| | $p\text{-}NO_2C_6H_4$ | 136 | 65 |
| $S_7NCO(CH_2)_2CONS_7$ | | 195 | 68 |
| $1,3\text{-}S_6N_2(COR)_2$ | $CH_3$ | 130 | 68 |
| | $C_6H_5$ | unstable | 68 |
| $1,4\text{-}S_6N_2(COR)_2$ | $CH_3$ | 77 | 68 |
| | $C_6H_5$ | 156 | 68 |
| $1,5\text{-}S_6N_2(COR)_2$ | $CH_3$ | 158 | 68 |
| | $C_6H_5$ | 183 | 68 |

TABLE 3

A trimethylsilyl derivative $S_7NSi(CH_3)_3$ has also been reported,[69] and $S_7NH$ forms methylene diamino derivatives of the type $S_7NCH_2NR_2$ (R = $CH_3$, $C_2H_5$, $C_4H_9$) with N-hydroxymethyl dialkylamines $R_2NCH_2OH$.[76] $S_7NH$ and $(SNH)_4$ give similar derivatives with N-hydroxymethylpiperidine.[76]

Mercury derivatives of $S_7NH$ have been prepared; $Hg(NS_7)_2$, nearly white, and $Hg_2(NS_7)_2$, yellow, by reaction with mercury (11) acetate in methanol[61] and mercury (1) nitrate in DMF[35] respectively (cf. p. 8. ). The structures of these compounds are unknown, but it is suggested that $Hg(NS_7)_2$, somewhat soluble in carbon disulphide, is covalent with the simple monomeric formula shown.[21]

The imides function as weak Brønsted acids if a strong enough base is available. The triphenylmethyl carbanion in $Ph_3CNa$ removes protons from both $S_7NH$ and $(SNH)_4$[22], the methyl carbanion in methyl magnesium iodide does the same with $S_7NH$ and 1,5-$S_6(NH)_2$,[51,70] and Olsen et. al. report that Na, $NaNH_2$, NaH, LiOH and ethyl lithium all deprotonate $S_7NH$.[71] The isomeric forms of $S_6(NH)_2$ behave similarly with ethyl lithium,[71] and the removal of protons from $(SNH)_4$ by n-butyl lithium is described in this thesis (p. 40 ).

There are no reports of "direct" i.e. single stage alkylation of these sulphur imides. Alkyl derivatives have been produced in two ways; firstly by reacting an alkyl halide with the lithium substituted imide (i.e. the imido anion),[71] and secondly by reacting primary amines with sulphur chlorides in inert solvents.[25,26,27,72.]

# ALKYL DERIVATIVES OF SULPHUR IMIDES

| | R | mp°C | Ref. |
|---|---|---|---|
| $S_7NR$ | $CH_3$ | Yellow oil | 71 |
| | $CH_2=CHCH_2$ | Yellow oil | 71 |
| | $C_6H_5CH_2$ | Yellow oil | 71 |
| | $C_2H_5$ | Yellow oil | 71 |
| | $(CH_3)_2CH$ | Yellow oil | 71 |
| $1,5-S_6(NR)_2$ | $CH_3$ | 77 | 72 |
| | $CH_3$ | 81.5-82 | 71 |
| $1,5S_6.NH.NR$ | $CH_3$ | 100.5-102 | 71 |
| $1,4S_6(NR)_2$ | $CH_3$ | 24.5-25.5 | 71 |
| $1,4S_6NH.NR$ | $CH_3$ | 51.5-53 | 71 |
| $1,3,5S_5(NR)_3$ | $CH_3$ | 45 | 25 |
| $1,3,6S_5(NR)_3$ | $CH_3$ | 55 | 25 |
| | $C_6H_5CH_2$ | 150 | 26 |
| | $C_6H_5(CH_2)_2$ | 89 | 26 |
| $(SNR)_4$ | $CH_3$ | 126 | 25 |
| | $C_2H_5$ | 143 | 26 |
| | $C_6H_5CH_2$ | 164 | 27 |
| | $C_6H_5(CH_2)_2$ | 165.5 | 27 |

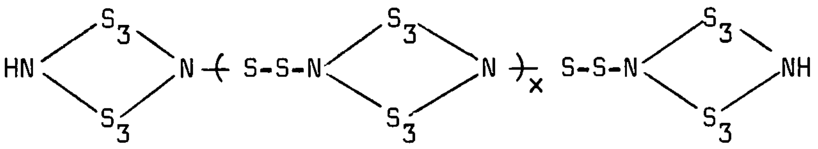
TABLE 4

Heal et. al. mention preliminary work on the reaction between $S_2Cl_2$ and aqueous methylamine yielding the methyl derivatives of $S_7NH$, all three hexasulphur diimides and at least one of the pentasulphur triimides.[73] (cf. reaction in hexane between gaseous methylamine and $SCl_2$ [25]).

An interesting difference in behaviour is observed in the reaction of these imides with disulphur dichloride. Arnold reported that $(SNH)_4$ gave a white salt $H_8N_3S_2Cl_3$ with properties similar to $S_4N_3Cl$ on reaction with $S_2Cl_2$.[13] The other imides, however, give a condensation reaction of form

$$>NH + Cl-S-S-Cl + HN< \xrightarrow[py]{CS_2} >N-S-S-N< + 2HCl$$

on reaction with $S_2Cl_2$ to give linear polymers. Thus $S_7NH$ gives $S_7N-S-S-NS_7$ (and $S_7N-S-NS_7$ by reaction with $SCl_2$).[74] A series of linear polymers of general formula



(x = 0,1,2,3)

has been isolated from the reaction with 1,5-hexasulphur diimide.[75] The 1,4-diimide gives optically active isomers, and the 1,3-diimide geometrical isomers based on $HNS_6N-SS-NS_6NH$.[75]

(4) Hydrogen Abstraction

The only reported cases of hydrogen abstraction from these imides are those already recorded for $(SNH)_4$ (see p. 7 )

(5) Oxidation to Thionylimides

The only reported case is that already described (see p.8) in which $(SNH)_4$ gives $(SONH)_4$ on air oxidation.[32]

### (6) Ring Degradation

Heptasulphur imide reacts readily with HI according to the equation[38]

$$S_7NH + 2HI \longrightarrow 7S + I_2 + NH_3$$

Tetrathiotetraimide reacts similarly (see p. 11 ). On reaction with $(NSCl)_3$, the $S_7NH$ ring is destroyed, sulphur being formed according to the equation[31]

$$4(NSCl)_3 + 12S_7NH \longrightarrow 6S_4N_4 + 12HCl + 72S$$

This reaction may be compared with that of $(SNH)_4$ in similar conditions where hydrogen abstraction occurs and the $S_4N_4$ ring is retained.[31] (see p. 7 ) Oxidation of heptasulphur imide, with chloramine-T in acidified aqueous dioxane also results in ring degradation (quantitative conversion of sulphur to $H_2SO_4$)[41]. Tetrathiotetraimide behaves similarly (see p. 11 )

### (7) Ring Contraction

The reactions of $(SNH)_4$ with chlorine, sulphuryl chloride, bromine, and acetyl bromide reported in this thesis are the only known examples of this reaction type.

# EXPERIMENTAL

## Handling Techniques

As many of the compounds dealt with were sensitive to moisture, operations were carried out in an atmosphere of dry nitrogen. Traces of water were removed from the nitrogen by passing through two traps cooled in liquid nitrogen. Operations which were impractical or inconvenient under counter-current nitrogen were carried out in a glove box.

## Infrared Spectra

Infrared spectra were recorded on Grubb-Parsons prism grating spectrometers; the Spectromaster and GS2A were used for the range 4000 - 400 $cm^{-1}$. Samples of solids were prepared as nujol mulls, liquids were examined as contact films, and gases were investigated in gas cells. The mull or liquid was supported between sodium chloride or potassium bromide plates as was appropriate. The following symbols are used to denote the relative intensities of i.r. absorptions: vs - very strong; s - strong; m - medium; w - weak; vw - very weak; sh - shoulder; and b - broad.

## Purification of Solvents

Hydrocarbons and Diethyl Ether were dried over excess sodium wire for at least 48 hours before use.

Tetrahydrofuran was stored over $LiAlH_4$ and distilled as required.

Carbon Tetrachloride was dried over $P_2O_5$ for at least 48 hours before use.

Chloroform was stored over molecular sieve 4A.

Pyridine was stored over NaOH and distilled on to fresh NaOH for use as required.

Carbon disulphide was stirred with mercury for 12 hours, distilled on to $P_2O_5$ and then distilled as required for use.

Ethyl Acetate technical grade was distilled before use.

## Preparation of Starting Materials

### Tetrathiotetraimide

The method used at first was that described by Brauer.[12] 20g. $S_4N_4$ dissolved in 600 ml. dry benzene were heated to $80^o$ in a 2 litre flask on an oil bath. A solution of 70g. $SnCl_2.2H_2O$ in 160 ml. methanol containing about 5% water was added all at once. The solution began to boil and did so vigorously for nearly an hour until it was colourless. The precipitate was suction filtered and washed with 2M HCl until no tin remained. Washing with alcohol removed last traces of colour and finally washing with ether gave shiny colourless crystals. Yield 12g. Recrystallisation if required, is from methanol. This preparation was less than satisfactory in four ways:

(i) addition of methanolic stannous chloride produced very vigorous boiling resulting in the reactants boiling out of a 2 litre flask,

(ii) it was not usually possible to add the stannous chloride solution "all at once" because of the vigorous reaction,

(iii) the solution did not go colourless as described but often retained an orange colour indicating unreacted $S_4N_4$,

(iv) recrystallisation from methanol resulted in the loss of most of the material and the product was often little better. A repeat preparation is preferable if poor analyses are obtained.

Accordingly a modified procedure, described here, was worked out. 10g. $S_4N_4$ in 300 ml. dry benzene was heated to 80° in a 5 litre flange top flask fitted with a wide neck condenser and stirrer. A solution of 35g. $SnCl_2.2H_2O$ in 80 ml. methanol containing 5% water was added all at once to the solution when reflux had just stopped and a further long necked condenser had been fitted to the flange top. Care should be exercised at this point for if the solution is refluxing vigorously bumping will occur, pushing the reactants out of the flask. When the exothermic reaction was completed, the solution was again heated to reflux, and, using the same procedure as before, a further 35g. $SnCl_2.2H_2O$ in 80 ml. methanol was added. The solution turned from yellow to almost white. The products were allowed to cool and then filtered through a sinter, washed with 100 ml. 2M HCl, then with 100 ml. ethanol and finally with 100 ml. ether to leave pale buff crystals. Melting point 156°. Yield 5g.

Manganese (11) and Iron (11) chlorides were refluxed with $SOCl_2$ for 24 hours and 2 hours respectively, and then dried in vacuo.

Aluminium bromide was purified by sublimation on to a water cooled cold-finger. The containing vessel was evacuated, then sealed and maintained at 80° for the sublimation.

Aluminium chloride was supplied by G. G. Alange.[17a]

Tin tetrabromide was distilled under vacuum.

Trimethylchlorosilane, Acetyl chloride and Acetyl bromide were distilled before use.

N-Bromodiphenylketimine was supplied by K. Farmery.[87a]

Hydrogen chloride prepared from $NH_4Cl$ (Voltoids) and concentrated sulphuric acid was dried by passage through a long (50 cm.) $P_2O_5$ tube.

Benzoyl and Sulphuryl chlorides were distilled before use.

Tetrachloroethylene was dried over $CaH_2$ and distilled before use.

Methyl Iodide, Iodobenzene and Acetic anhydride were distilled before use.

Ethylene oxide and Epichlorohydrin were supplied by G. G. Alange.[17b]

n-Butyl Lithium was standardised by the method of Watson and Eastham.[94] 1 mg. phenanthroline was added to 5 ml. of the $Bu^nLi$ solution in 20 ml. benzene, giving a rust red complex. The solution was titrated using *M* sec-butanol in xylene, a sharp disappearance of the colour taking place after addition of 1 mole equivalent of the titrant.

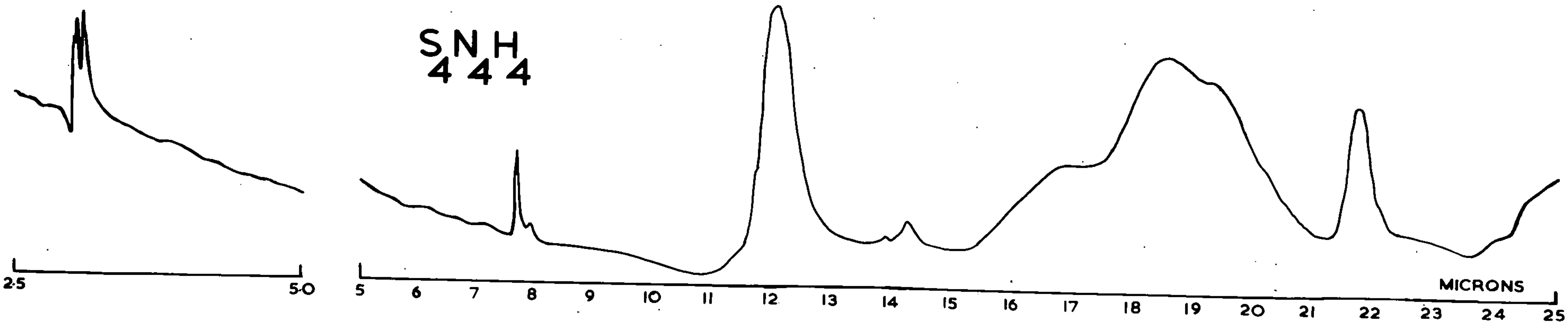

$S_4N_4H_4$
2·5
5·0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
MICRONS

Fig. 4.

## SECTION I

## METAL HALIDES

### Tetrathiotetraimide and Manganese Chloride

Precedure according to Goehring, Weiss and Zirker.[19] Tetrathiotetraimide (0.9 g., 4.8 m.mole) in pyridine (10 ml.) was added to anhydrous manganese chloride (4.2 g., 33 m.mole) suspended in pyridine (100 ml.) at 20°. The mixture was refluxed for 48 hours, the pyridine turning dark brown. The pyridine was evaporated under reduced pressure and the residual brown solid washed with water, ammonium hydroxide solution, acetone until washings colourless, and ether. The pale brown solid gave a weak i.r. spectrum showing no trace of SN absorption and was not investigated further.

### Tetrathiotetraimide and Iron (11) Chloride

Tetrathiotetraimide (0.15 g., 0.8 m.mole) in pyridine (5 ml.) was added to anhydrous iron (11) chloride (0.6 g., 4.7 m.mole) in pyridine (40 ml.) at 65°. The orange solution showed no change after 7 hours and was then heated under reflux for 48 hours, during which time the colour darkened. The pyridine was evaporated under reduced pressure and the residual black solid washed with water, ammonium hydroxide solution, acetone until washings colourless, and ether. The golden brown solid obtained was found, on analysis, to contain no sulphur and was not investigated further.

### Tetrathiotetraimide and Aluminium Bromide

Aluminium bromide (1.84 g., 6.9 m.mole) in carbon disulphide (20 ml.) was added to a stirred mixture of tetrathiotetraimide (1.30 g., 6.9 m.mole) and carbon disulphide (10 ml.) at -196° and the reaction mixture was allowed to warm to 20°. An orange flocculent solid precipitated from the orange solution, darkened and finally lightened to pale orange. After no further colour change was visible (4½ hours) the orange product was filtered, washed with carbon disulphide and dried _in vacuo_ (2.46 g., 78%). (Found: Br,53.7; S,27.6; $(SNH)_4.AlBr_3$ requires: Br,52.7; S,28.2). I.r. absorptions ($cm^{-1}$) at: 3174m, 1511w, 1404s, 1294w, 1126m, 852m, 824s, 539w, 459w.

## Tetrathiotetraimide and Aluminium Chloride

Tetrathiotetraimide (0.76 g., 4.0 m.mole) was added to aluminium chloride (0.53 g., 4.0 m.mole) under carbon disulphide (30 ml.) at -196°. The stirred mixture was allowed to warm to room temperature (20°) the solid quickly turned brown (solvent yellow) then slowly turned red and finally pale orange-yellow.

After further stirring (total 24 hours at 20°), the mixture was filtered, washed with carbon disulphide and dried _in vacuo_. (0.8 g., 62%) (Found: Al,8.7; N,16.9. $(SNH)_4.AlCl_3$ requires: Al,8.4; N,17.4). I.r. absorptions ($cm^{-1}$) at: 3247m, 3252m, 3200m, 1412s, 1295w, 1261w, 1143w, 975w, 935w, 823s, 741w.

## Tetrathiotetraimide and Tin Tetrabromide

Tin tetrabromide (3.3 ml., 10.9 g., 2.5 m.mole) was added to tetrathiotetraimide (0.47 g., 2.5 m.mole) under diethyl ether (30 ml.) at -196° and the stirred mixture was allowed to reach 20°. The solution and suspension slowly turned dark red. After 60 hours, the suspension was filtered, washed with diethyl ether and dried _in vacuo_. The dark red product turned yellow at 184° but did not melt below 300°. (Found: Br,59.7; S,50.86, 12.4, 11.76;

N,6.13, 17.69, 7.1). No serious attempt was made to solve the analytical problem posed by these erratic analyses since the i.r. spectrum corresponded exactly to that of $2S_4N_4.SnBr_4$ (prepared from $S_4N_4$ and $SnBr_4$[17]) with extra peaks corresponding to $NH_4Br$. There were no signs of absorptions due to $S_4N_4$ or $(SNH)_4$ in the i.r. spectrum of the dark red solid.

| Dark Red Solid | $2S_4N_4.SnBr_4$ | $NH_4Br$ |
|---|---|---|
| 3175 m | | 3175 s |
| 1724 vw | | 1700 m |
| 1403 s | | 1403 s |
| 1156 w | 1156 vw | 1156 w |
| 1041 vs | 1041 vs | |
| 961 vs | 961 vs | |
| 926 wsh | | 926 vw |
| 794 vs | 794 vs | |
| 725 w | 725 vw | 725 m |
| 671 m | 671 m | |
| 621 mb | 621 mb | |
| 563 w | 563 w | |
| 513 m | 513 m | |

<u>Absorptions ($cm^{-1}$)</u>

# SECTION II

## OTHER HALIDES

### Tetrathiotetraimide and Trimethylchlorosilane

Trimethylchlorosilane (4 ml., 29 m.mole) was added to tetrathiotetraimide (0.4 g., 2.1 m.mole) and refluxed for 9 hours. Excess trimethylchlorosilane was removed by evaporation under reduced pressure. The i.r. spectrum of the off-white solid obtained was identical to that of tetrathiotetraimide.

The reaction was repeated in pyridine. Tetrathiotetraimide (0.19 g., 1 m.mole) in pyridine (5 ml.) was added to trimethylchlorosilane (4 ml., 29 m.mole) in pyridine (10 ml.) and heated to reflux. After one hour the suspension was filtered to give a white solid and red solution which, on evaporation under reduced pressure, yielded a red-brown solid. The i.r. spectrum of the red solid showed traces of tetrasulphur tetranitride but no trace of trimethylsilyl peaks.[77]

I.r. absorptions shown by red solid ($cm^{-1}$): 1266w, 1163w, 1053w, 1005w, 926s, 800w, 752s, 728m, 699s, 685s, 610m, 551sh, 546s.

I.r. absorptions shown by trimethylchlorosilane ($cm^{-1}$): 2977s, 2912m, 1454w, 1415w, 1260s, 857s, 767m, 700w, 640m, 487m.

The i.r. spectrum of the white solid was identical to that of pyridine hydrochloride[78]; again there were no signs of trimethylsilyl absorptions. This reaction was not studied further.

## Tetrathiotetraimide and Acetyl Chloride

### (1) Procedure according to Garcia-Fernandez.[3]

Acetyl chloride (1.5 ml., 21 m.mole) was added to tetrathiotetraimide (0.76 g., 4 m.mole) and potassium carbonate (1.25 g., 9 m.mole) under ethyl acetate (30 ml.). At 20° the mixture was stirred for 16 hours, during which time the ethyl acetate turned orange, and was then filtered. A white solid (A) remained on the sinter and evaporation of the filtrate under reduced pressure gave a red-brown solid (B). The i.r. spectra of the white and red-brown solids indicated (A) unreacted tetrathiotetraimide and (B) a mixture of tetrathiotetraimide and tetrasulphur tetranitride respectively.

The reaction was repeated in absence of potassium carbonate (2) in ether, and (3) using excess acetyl chloride and no other solvent.

(2) Acetyl chloride (2.0 ml., 28 m.mole) was added to a stirred mixture of tetrathiotetraimide (0.38 g., 2 m.mole) and diethyl ether (30 ml.) at 20°. The ether turned pale yellow within 3 hours and orange within 24 hours. After 120 hours, the solid had turned yellow and as no further change occurred, the mixture was filtered after 150 hours. Evaporation of the filtrate under reduced pressure gave a dark oil which was not investigated further. The i.r. spectrum of the yellow solid indicated

the presence of both unreacted tetrathiotetraimide and thiotrithiazyl chloride.

(3) Acetyl chloride (20 ml., 280 m.mole) was added to tetrathiotetraimide (0.5 g., 2.65 m.mole) and the stirred suspension heated under reflux. The acetyl chloride quickly turned yellow, orange and finally yellow. After 24 hours the yellow suspension was filtered. A pale yellow solid remained on the sinter. The filtrate was evaporated under reduced pressure to give a small quantity of yellow-brown solid which was not investigated further. Analysis and the i.r. spectrum of the insoluble yellow solid, by far the major product, indicated a 1:1 mixture of thiotrithiazyl and ammonium chlorides. (Found: N,21.1; Cl,25.9. 1:1 mixture of $S_4N_3Cl$ and $NH_4Cl$ requires N,21.6; Cl,27.4).
I.r. absorptions ($cm^{-1}$) occurred at: 3125sb, 1754w, 1403s, 1299w, 1166m, 1129vw, 1005s, 787w, 775w, 725w, 683s, 645vw, 610vw, 565s, 474sh, 467vs, 453s.

### Tetrathiotetraimide and Acetyl Bromide

Acetyl bromide (3.0 ml., 5.0 g., 40 m.mole) was added to tetrathiotetraimide (0.94 g., 5 m.mole) under diethyl ether (30 ml.) at -196°. The stirred mixture rapidly turned brown as it warmed to room temperature (20°) and gradually changed to give an orange-red solution and yellow precipitate. The mixture was stirred (12 hours, 20°) and filtered. The yellow solid was washed with ether until washings were colourless, and dried *in vacuo*. Analyses and the i.r. spectrum indicated a 1:1 mixture of thiotrithiazyl bromide and ammonium bromide; the latter was removed by washing with 98% formic acid. Water was found to be much less efficient for leaching out the ammonium salt. (Found: N,16.85; S,52.7. $S_4N_3Br$

requires N,16.8; S,51.3).

The filtrate was examined using vapour pressure chromatography, (retention times being expressed as distances (cm.) on chart paper from injection of sample) comparing observed retention times with retention times given by pure liquids.

| Pure Liquid | Retention time (cm.) |
|---|---|
| Ether | 4.05 |
| Acetyl bromide | 6.4 |
| Acetic acid | 8.7 |
| Diacetyl | 6.05 |
| <u>Sample</u> | |
| Retention time (cm.) | Source |
| 4.05 | Ether |
| 6.4 | Acetyl bromide |
| 7.6 | Unknown |

Instrument: Pye 104 Chromatograph

Column length: 10 ft.

Column temperature: 90°

Static phase: 10% Apiezon L on celite

Volume of sample: 1 μ litre

Further work to identify the substance responsible for the peak at 7.6 cm. was not carried out.

<u>Tetrathiotetraimide and Bromine</u>

Bromine (2.0 ml., 5.9 g., 36 m.mole) in chloroform (20 ml.) was added to tetrathiotetraimide (0.94 g., 5 m.mole) under chloroform (40 ml.) at -196°. The reactants were allowed to warm to 20° and stirred for 24 hours. The deep yellow solid (dark red solution) was filtered and pumped dry. Analyses and the i.r. spectrum corresponded to a 1:1 mixture of $S_4N_3Br$ and $NH_4Br$. The latter could be removed by repeated washing with

98% formic acid. I.r. absorptions ($cm^{-1}$) at: 1156s, 995s, 719w, 676w, 559w.

Tetrathiotetraimide and N-Bromosuccinimide

(a) Stoichiometry 1:1

Tetrathiotetraimide (0.94 g., 5 m.mole) dissolved in tetrahydrofuran (20 ml.) was added to N-bromosuccinimide (0.89 g., 5 m.mole) in tetrahydrofuran (20 ml.) at -196°. A red suspension, quickly turning yellow, was obtained as the stirred mixture warmed to room temperature (20°). After 20 minutes at 20° the mixture was filtered and the filtrate evaporated under reduced pressure. The dark brown residue was extracted with ether and the extract on recrystallisation from hexane yielded succinimide (insoluble) and tetrasulphur tetranitride. Both products were identified from their i.r. spectra.

(b) Stoichiometry 1:2

N-Bromosuccinimide (4.27 g., 24 m.mole) in tetrahydrofuran (50 ml.) was added to tetrathiotetraimide (2.2 g., 12 m.mole) in tetrahydrofuran (40 ml.) at -196°. A red suspension, quickly turning yellow, was obtained as the stirred mixture warmed to room temperature (20°). After 20 minutes at 20° the mixture was filtered. Evaporation of the filtrate under reduced pressure yielded a small quantity of dark brown residue, which on extraction with ether and recrystallisation from hexane, gave tetrasulphur tetranitride, identified by its i.r. spectrum. The i.r. spectrum of the insoluble yellow solid, the major product, indicated a mixture of thiotrithiazyl and ammonium bromides.

## Tetrathiotetraimide and N-Bromodiphenylketimine

N-Bromodiphenylketimine (0.78 g., 3 m.mole) in tetrahydrofuran (8.5 ml.) was added to tetrathiotetraimide (0.57 g., 3 m.mole) in tetrahydrofuran (15 ml.) at -196°. The mixture was allowed to warm up becoming a bright yellow suspension while still well below 0°. No further change was observed on warming to room temperature (20°) and the suspension was filtered (20 minutes reaction time at 20°) to give a white solid on the sinter and a red/green filtrate. Evaporation of the filtrate under reduced pressure yielded a red solid which would not mull and was not investigated further.

The i.r. spectrum of the white solid contained absorptions due to tetrathiotetraimide and also absorptions very closely resembling those of diphenylketimine hydrobromide.

Absorptions ($cm^{-1}$)

| White Solid | $Ph_2CNH_2Br$ | $(SNH)_4$ |
|---|---|---|
| 3306 (sh) | | 3306 (sh) |
| 3289 (m) | | 3289 (s) |
| 3226 (m) | | 3226 (s) |
| 3125 (s) | 3125 (s) | |
| 2920 (s) | 2900 (s) | |
| 2857 (s) | | |
| 2778 (m) | 2778 (m) | |
| 2667 (w) | 2667 (w) | |
| 2516 (vw) | 2516 (vw) | |
| 1923 (vw) | 1923 (vw) | |
| 1842 (vw) | 1842 (vw) | |
| 1736 (w) | 1736 (w) | |
| 1653 (vs) | 1653 (vs) | |
| 1600 (s) | 1600 (s) | |
| 1458 (vs) | 1460 (s) | |
| 1380 (vs) | 1380 (s) | |
| 1328 (vw) | 1325 (w) | |

| | | |
|---|---|---|
| 1299 (m) | 1300 (m) | 1299 (m) |
| 1190 (w) | 1193 (w) | |
| 1163 (s) | 1167 (s) | |
| 1139 (s) | 1139 (s) | |
| 1075 (vw) | 1075 (vw) | |
| 1031 (w) | 1031 (w) | |
| 1010 (vw) | 1010 (vw) | |
| 1000 (m) | 1000 (m) | |
| 982 (vw) | 982 (vw) | |
| 943 (w) | 943 (w) | |
| 910 (vs) | 910 (vs) | |
| 870 (m) | 870 (m) | |
| 851 (msh) | 851 (w) | 851 (sh) |
| | 830 (w) | |
| 826 (vs) | 811 (vw) | 826 (vs) |
| 797 (vs) | 797 (vs) | |
| 758 (m) | 758 (m) | |
| 726 (s) | 726 (s) | |
| 703 (vs) | 703 (vs) | |
| 696 (sh) | 696 (sh) | 699 (vw) |
| 639 (w) | 639 (s) | |
| 614 (s) | 614 (s) | |
| 565 (s) | 565 (s) | |
| 540 (b) | | 540 (b) |
| 459 (w) | | 459 (s) |
| 446 (w) | 446 (w) | |

The reaction was repeated in toluene. N-Bromodiphenylketimine (1.04 g., 4 m.mole) in toluene (10 ml.) was added to tetrathiotetraimide (0.75 g., 4 m.mole) under toluene (15 ml.) at -196$^{0}$ and the stirred mixture allowed to warm to room temperature (20$^{0}$). The toluene turned brown within 20 minutes and red within 1 hour, much creamy solid being present. After one further hour, the suspension was filtered leaving a white solid on the sinter. On evaporation of the filtrate under reduced pressure yellow crystals formed, which, after drying in vacuo, were identified by the i.r. spectrum as tetrasulphur tetranitride. The i.r. spectrum of the white solid was identical to that of the white solid obtained in the first reaction, save that those peaks corresponding to tetrathiotetraimide were much stronger. The white solid was washed three times with tetrahydrofuran (10 ml.), to remove tetrathiotetraimide. The i.r. spectrum of the solid washed out of the white solid indicated a mixture of tetrasulphur tetranitride and tetrathiotetraimide. The i.r. spectrum of the white solid was now identical to that obtained from reaction in tetrahydrofuran i.e. strongly resembling the i.r. spectrum of $Ph_2CNH_2Br$. Analysis indicated the absence of sulphur in this solid which was not investigated further.

Tetrathiotetraimide and Benzoyl Chloride

Benzoyl chloride (1.5 ml., 13 m.mole) was added to tetrathiotetraimide (0.5 g., 2.65 m.mole) under ether (20 ml.) at $-196^{0}$. The stirred suspension was allowed to reach room temperature. After 1½ hours no apparent change had taken place, so pyridine (1 ml., 12.4 m.mole) was added as an acid scavenger. Within 30 minutes the ether was pale yellow and did not change during a further 4½ hours. The suspension was filtered to give a white solid (A) and a yellow filtrate. Evaporation of the filtrate under reduced pressure gave a small quantity of yellow solid and yellow oil which were not investigated further. The i.r. spectrum of the white solid (A) indicated unreacted tetrathiotetraimide.

## Tetrathiotetraimide and Hydrogen Chloride

Hydrogen chloride, dried by passage through a long $P_2O_5$ tube, was passed into tetrathiotetraimide (0.45 g., 2.39 m.mole) suspended in chloroform (20 ml.). The chloroform turned yellow and the colour intensified to orange within 40 minutes. The suspension was filtered to give a pale solid (A) and a red solution. Evaporation of the filtrate under reduced pressure gave a very small quantity of yellow orange crystals and a dark brown solid. The latter was not investigated further. The yellow orange crystals were identified as thiotrithiazyl chloride by i.r. spectrum. The white insoluble solid (A) was similarly identified as a mixture of ammonium chloride and unreacted tetrathiotetraimide.

## Tetrathiotetraimide and Chlorine

Chlorine was bubbled through a suspension of tetrathiotetraimide (1.0 g.) in carbon tetrachloride (60 ml.) at $20^{\circ}$. Heat was evolved and the suspension immediately turned orange-brown. As the reaction proceeded the solution became clearer and paler. After no further colour change, the suspension was filtered; the insoluble off-white solid (mostly ammonium chloride) was discarded. The filtrate was evaporated under reduced pressure to give golden yellow crystals, which were recrystallised from carbon tetrachloride (0.53 g., 30 % based on $(SNH)_4$). Melting point ($77^{\circ}$) and i.r. spectrum were the same as for $(NSCl)_3$ prepared from tetrasulphur tetranitride or thiodithiazyl dichloride and chlorine.[79]

### Tetrathiotetraimide and Sulphuryl Chloride

Sulphuryl chloride (5 ml., 8.35 g., 60 m.mole) was added to tetrathiotetraimide (1.5 g., 8 m.mole) and carbon tetrachloride (30 ml.) at -196°, and the stirred mixture warmed to 20°. The suspension quickly darkened and gas was evolved. After no further colour change (2 hours) the clear orange-red solution was separated from pale pink solid (ammonium chloride), evaporated under reduced pressure and the residue recrystallised from carbon tetrachloride to give yellow crystals (0.9 g., 35 % based on $(SNH)_4$). (Found: N,17.6; S,39.0. $(NSCl)_{\underline{x}}$ requires N,17.2; S,39.3). The i.r. spectrum was the same as that of the previous product.

### Tetrathiotetraimide and Tetrachloroethylene

Tetrathiotetraimide (0.5 g., 2.65 m.mole) was refluxed with tetrachloroethylene (20 ml., 195.7 m.mole) for 3 hours. At first a creamy flocculent suspension formed, the colour of the tetrachloroethylene changing to orange then red during the reaction. The solution was allowed to reach room temperature (20°) and was then filtered. Some orange needles (A) remained on the sinter and the filtrate on evaporation under reduced pressure yielded an orange-yellow solid (B). Both solids (A) and (B) were identified by i.r. spectrum as tetrasulphur tetranitride. No trace of absorptions due to C-Cl (850-550 $cm^{-1}$)[80] could be found and the reaction was not studied further.

# SECTION III

# ORGANOMETALLICS

## Tetrathiotetraimide and Trimethylaluminium

Trimethylaluminium ( 1 ml., 10.4 m.mole) was added to tetrathiotetraimide (0.94 g., 5 m.mole) under toluene (30 ml.) at -196°. On warming to room temperature (20°) with stirring, methane, identified by i.r. spectrum was evolved and a clear orange solution formed. After 2 hours an orange-yellow solid precipitated and the suspension was filtered after a further 1 hour. Hexane (30 ml.) was added to the filtrate precipitating more orange-yellow solid and the solvent decanted. The i.r. spectrum of the orange-yellow solid included absorptions in both the NH (3300-3200 $cm^{-1}$)[7] and SN (680-930 $cm^{-1}$)[9] stretching regions. (Found: C,25.05; H,3.24; S,43.6). It was concluded that substitution was incomplete and the reaction was not investigated further.

## Tetrathiotetraimide and n-Butyl Lithium

A solution (2.33m, 2.0 ml., 4.66 m.mole) of n-butyl lithium in hexane was added to tetrathiotetraimide (0.19 g., 1.0 m.mole) in tetrahydrofuran (4.5 ml.) at -196° in a tube fitted with a break seal and constriction. When the hexane had solidified, the tube was evacuated, sealed at the constriction and allowed to stand (20°, 90 hours); the colour gradually changed from pale yellow to red, then to yellow, blue and yellow. The tube was opened to a vacuum line via the break-seal and the volume of butane evolved was measured (3.7 m.mole) using a Töpler pump. The yellow insoluble solid was presumed to be predominantly $(SNLi)_4$.

## Tetrathiotetraimidolithium and Methyl Iodide

Methyl iodide (1 ml., 2.3 g., 16 m.mole) was added to a cooled (-196°) mixture of $(SNLi)_4$ and n-hexane, prepared as above from tetrathiotetraimide (0.47 g., 2.5 m.mole) and n-butyl lithium (10 m.mole) in hexane. An orange suspension formed on warming to room temperature which turned yellow in 2 hours. The suspension was filtered and the filtrate evaporated under reduced pressure to yield a red tar which was not studied further.

## Tetrathiotetraimidolithium and Trimethylchlorosilane

Trimethylchlorosilane (3 ml., 21.6 m.mole) was added to $(SNLi)_4$, prepared from tetrathiotetraimide (0.94 g., 5 m.mole) and n-butyl lithium (21 m.mole), in hexane at -196°. The stirred mixture was allowed to warm to room temperature 20°, forming a deep red solution. After 3 hours the solution clouded and after 48 hours hexane (6 ml.) was added to precipitate lithium chloride. The suspension was filtered and the filtrate evaporated under reduced pressure to give an orange semi-solid which was dissolved in benzene, filtered, and the benzene removed by evaporation under reduced pressure to yield a deep red, purgent smelling liquid. Analysis and i.r. spectrum indicated that this liquid was probably mostly the tetratrimethylsilyl derivative of $(SNH)_4$. I.r. spectrum absorptions at $(cm^{-1})$; 2959s, 2933sh, 2857m, 1460w, 1408w, 1379w, 1250s, 1185m, 1093w, 877sh, 844s, 796w, 757m, 690w, 633w.

Trimethylchlorosilane(77) shows i.r. absorptions at (cm$^{-1}$); 2977s, 2912m, 1454w, 1260s, 857s, 767m, 700w, 640m, 487m. (Found: C,30.5; H,5.36. Required for $(SNSi(CH_3)_3)_4$: C,30.3; H,7.56).

### Tetrathiotetraimidolithium and Acetyl Bromide

Acetyl bromide (1.5 ml., 21 m.mole) was added to $(SNLi)_4$, prepared from tetrathiotetraimide (0.5 g., 2.65 m.mole) a slight excess of n-butyl lithium (15 m.mole), in THF/hexane at -70°. The yellow suspension became a dark red solution and some gas was evolved as reactants warmed to room temperature (20°). After 4 hours in a low temperature bath (-100°) a little light coloured precipitate had formed which was filtered off. After removing 80% of the solvent by evaporation under reduced pressure hexane (10 ml.) was added, but no solid was precipitated. Continued evaporation under reduced pressure gave an oily red liquid, insoluble in both ether and heptane, and finally a red tar which was not investigated further.

### Tetrathiotetraimidolithium and Iodobenzene

Iodobenzene (2.9 ml., 26 m.mole) was added to $(SNLi)_4$ (prepared from $(SNH)_4$ (0.94 g., 5 m.mole) and n-butyl lithium (21.3 m.mole) in THF/hexane) at 20°C. The yellow suspension darkened to a medium brown which did not change during 96 hours stirring at 20°. The suspension was filtered to give a pale brown solid and dark red/brown filtrate. The filtrate was evaporated under reduced pressure yielding a red tar which was not investigated further.

### Tetrathiotetraimidolithium and Chlorine

Chlorine was bubbled into $(SNLi)_4$ (prepared from $(SNH)_4$ (0.94 g., 5 m.mole) and n-butyl lithium (21 m.mole) in THF/hexane) suspended in carbon tetrachloride (40 ml.) at $-23^{0}$. After 5 minutes vigorous reaction the suspension was filtered to give a white solid and yellow filtrate. Evaporation of the filtrate under reduced pressure gave a red tar which was not investigated further.

# SECTION IV

# OXYGEN COMPOUNDS

## Tetrathiotetraimide and Acetic Anhydride

Acetic anhydride (1.5 ml., 16 m.mole) was added to tetrathiotetraimide (0.5 g., 2.65 m.mole) under ether at 20° and stirred for 2 hours. There being no visible sign of reaction the ether was removed by evaporation under reduced pressure and more acetic anhydride (15 ml., 160 m.mole) was added. The reactants were heated at 125° under reflux until, after 75 minutes a clear dark red solution formed. The solution was filtered and evaporated under reduced pressure to give an orange solid. A red semi-solid collected in the cold trap. The i.r. spectrum of the orange solid indicated tetrasulphur tetranitride and the reaction was not investigated further.

## Tetrathiotetraimide and Ethylene Oxide

Ethylene oxide (10 ml., 200 m.mole) was added to tetrathiotetraimide (0.94 g., 5 m.mole) at -78°. On warming to 0°C the liquid turned faintly yellow and showed no further change after 150 hours at low temperatures (between -30° and -46°). The suspension was filtered leaving a white solid on the sinter, identified by i.r. spectrum as tetrathiotetraimide. The yellow filtrate was evaporated under reduced pressure to yield a white solid, identified by i.r. spectrum as tetrathiotetraimide.

### Tetrathiotetraimide and Epichlorohydrin

Epichlorohydrin (7 ml. 90 m.mole) was stirred with tetrathiotetraimide (0.15 g., 0.80 m.mole) for 1 hour with no apparent reaction. On heating to reflux (120°) the solid dissolved and gave an orange solution. After 1 hour the solution was allowed to cool to room temperature (20°) a white solid crystallising out. The solid was filtered off, washed with ether and identified by i.r. spectrum as tetrathiotetraimide. Evaporation of the filtrate under reduced pressure yielded a tarry solid which would not mull.

The reaction was repeated, refluxing for 48 hours. The resulting dark solution yielded a dark tar which was not investigated further.

## DISCUSSION

### 1. METAL HALIDES

Following the procedure of Goehring et. al.[19] reactions were attempted between $(SNH)_4$ and manganese (11), and iron (11), chlorides. In the first case examination of the i.r. spectrum of the product showed no sign of SN absorption, and in the second case the product isolated did not contain sulphur. These reactions were not studied further.

Reaction between $(SNH)_4$ and the strong Lewis acids $AlBr_3$, $AlCl_3$ and $SnBr_4$ gave products of two types. The aluminium halides gave amorphous solids analysing as the 1:1 adducts $(SNH)_4.AlBr_3$ (orange) and $(SNH)_4.AlCl_3$ (pale orange-yellow). The near i.r. spectra of these compounds were closely similar to that of the parent imide (i.e. NH absorptions at 3330 - 3170 $cm^{-1}$, and SN stretching frequency at 825 $cm^{-1}$), and so they are probably $\sigma$ adducts via donor nitrogen as in the $S_4N_4$ adducts of boron trifluoride and antimony pentachloride.[81] With tin tetrabromide the only insoluble (and major) product was a dark red solid whose i.r. spectrum was identical to that of $2S_4N_4.SnBr_4$ (prepared from $S_4N_4$ and $SnBr_4$ in hexane[17]) contaminated with a little $NH_4Br$. No further work was carried out on this reaction.

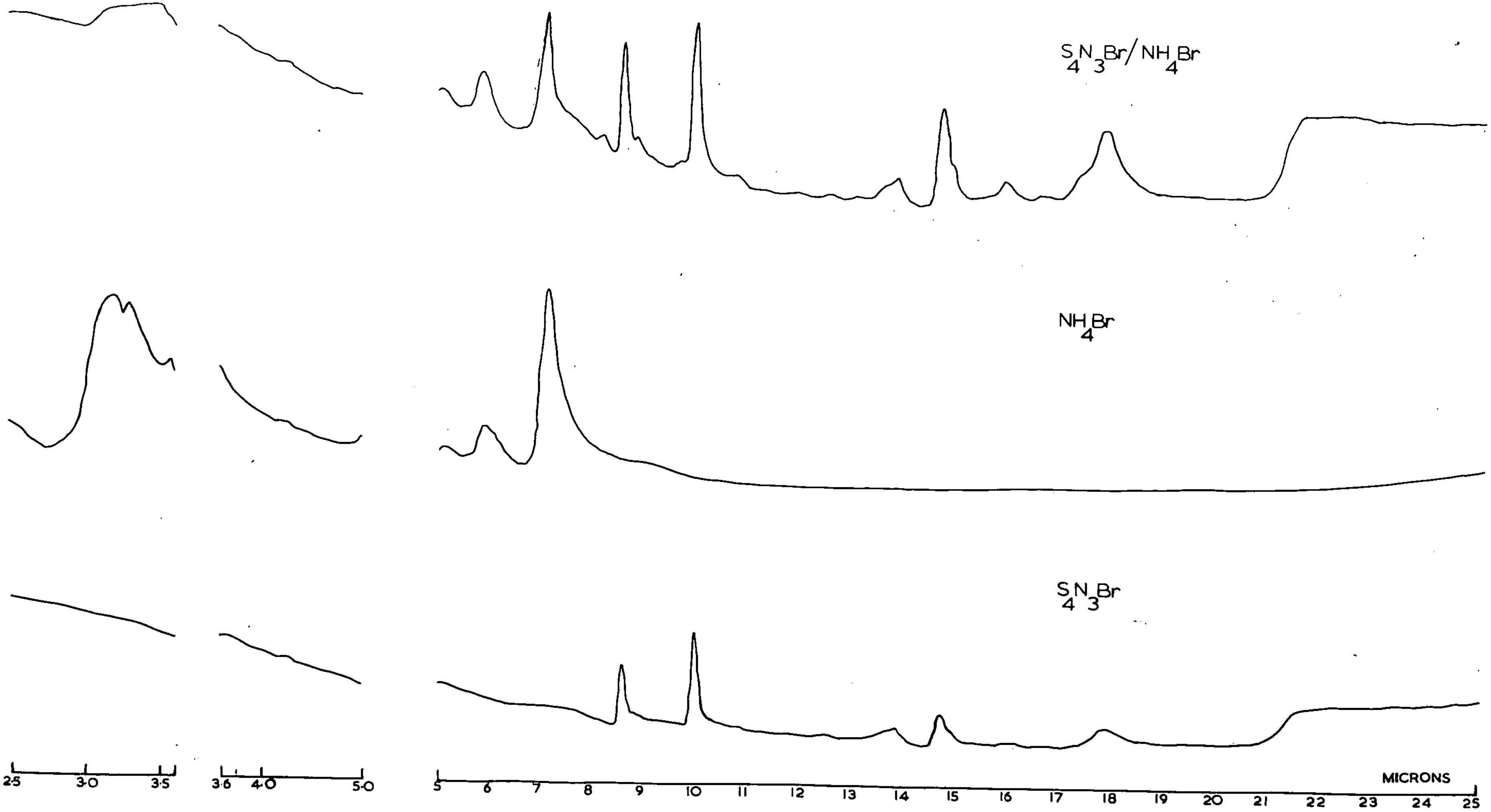
## 2. OTHER HALIDES

### Trimethylchlorosilane

In attempting to make derivatives of the type $(SNX)_4$ tetrathiotetraimide was treated with trimethylchlorosilane. The two substances did not react when heated under reflux for 9 hours; so the reaction was repeated in pyridine (which would act as a dehydrohalogenating agent). After refluxing for 1 hour a white solid was filtered off and the filtrate evaporated under reduced pressure to give a red brown residue. The i.r. spectra of the two solids obtained from this reaction showed no trace of trimethylsilyl peaks. The spectrum of the red brown solid indicated the presence of $S_4N_4$; and the i.r. spectrum of the white solid was identical to that of pyridine hydrochloride.[78] Although this reaction was not studied further, it is suggested that $R_3Si$ derivatives could perhaps be prepared under milder conditions (e.g. lower temperature and/or shorter reaction time).

### Acetyl Chloride

Garcia-Fernandez[3] reported an acetyl derivative of $(SNH)_4$ prepared by reacting $(SNH)_4$ with acetyl chloride in ethyl acetate containing a trace of potassium carbonate. This work was repeated but the only products isolated were tetrathiotetraimide and tetrasulphur tetranitride (identified from their i.r. spectra). This matter has already been discussed in the Introduction (see p. 4 ), the explanation offered is that this report has entered the literature through a mistranslation of work reported by Arnold.[13] Refluxing


$S_4N_3Br/NH_4Br$
$NH_4Br$
$S_4N_3Br$
2·5
3·0
3·5
3·6
4·0
5·0
5
6
7
8
9
10
11
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MICRONS

Fig. 5.

acetyl chloride and $(SNH)_4$ did however react. A yellow solid was obtained which was identified by i.r. spectrum and analysis as a 1:1 mixture of $S_4N_3Cl$ and $NH_4Cl$. Thiotrithiazyl chloride $S_4N_3^+Cl^-$ is a well established compound, the structure of the $S_4N_3^+$ cation having been determined by X-ray diffraction studies as a nearly planar seven-membered ring.[82,83]

Acetyl Bromide

Similarly $(SNH)_4$ and acetyl bromide reacted at room temperature (20°) to give a yellow solid characterised by analysis and i.r. spectrum as a 1:1 mixture of thiotrithiazyl and ammonium bromides. 98% formic acid was found to be much more efficient than water at washing out the ammonium salt. Unlike $S_4N_3Cl$ which is rapidly hydrolysed by atmospheric moisture (golden yellow crystals turn black)[84], $S_4N_3Br$ is air stable. This may be due to the stabilising effect of the larger $Br^-$ (i.e. less repulsive interaction between neighbouring $S_4N_3^+$ ions in the crystal lattice).

On account of the complexity of some of the reactions of $(SNH)_4$ with halides it was decided to investigate the behaviour of the imide with the simplest possible halogen compounds, i.e. the halogens themselves.

Bromine

Analysis and the i.r. spectrum of the yellow solid obtained from the reaction with bromine (in $CCl_4$) indicated a 1:1 mixture of thiotrithiazyl and ammonium bromides. (The latter could again be removed by washing with 98% formic acid). This reaction can be explained according to the equation:

$$S_4N_4H_4 \quad + \quad Br_2 \quad \longrightarrow \quad S_4N_3Br \quad + \quad NH_4Br$$

Such a simple equation is not possible for the reactions with the acetyl halides. One possible equation would be:

$$S_4N_4H_4 \quad + \quad 2CH_3COBr \quad \longrightarrow \quad S_4N_3Br + NH_4Br + (CH_3CO)_2$$

Unfortunately no trace of diacetyl could be found when the volatile products of the reaction were examined by vapour phase chromatography. The retention times, expressed as distances on the recording chart after injection of the sample, compared with those of known pure compounds, are given below.

| Retention Time cm. | Source |
|---|---|
| 6.05 | Diacetyl |
| 6.4 | Acetyl bromide |
| 7.6 | Unknown |
| 8.7 | Acetic acid |

More work is necessary to discover the identity of the substance giving a retention time corresponding to 7.6 cm. (e.g. mass spectra after chromatographic separation).

As the reaction between $(SNH)_4$ and bromine, giving $S_4N_3Br$ and $NH_4Br$, could be expressed by a simple equation it was decided to investigate reactions between $(SNH)_4$ and other compounds of type X-Br. $S_4N_3$ salts can be formed in two ways:

(i) $S_4N_4H_4 + XBr \longrightarrow S_4N_3X + NH_4Br$

(ii) $S_4N_4H_4 + XBr \longrightarrow S_4N_3Br + NH_4X$

Since there is no evidence to date for a predominantly covalent thiotrithiazyl compound, the formation of a stable $S_4N_3X$ salt according to (i), would be favoured by a large group X with high electronegativity (cf. $SO_3F$, $SO_3Cl$ [85] $N(SO_2Cl)_2$ salts [86]). Pairing of $NH_4^+$ with the smaller anion ($Br^-$) also maximises the lattice energy of the ammonium salt.

N-Bromosuccinimide and N-bromodiphenylketimine were selected as two suitable "active N-halogen compounds."

N-Bromosuccinimide

Tetrathiotetraimide and N-bromosuccinimide (1:1 molar ratio) reacted rapidly in THF to give a yellow suspension. The yellow solid was filtered off and the filtrate evaporated under reduced pressure to give a dark brown residue which was extracted with ether. Tetrasulphur tetranitride and succinimide (insoluble) were obtained on recrystallisation of the extract from hexane (both compounds identified from i.r. spectra). The yellow solid was similarly identified as a mixture of ammonium and thiotrithiazyl bromides. Apparently elimination of hydrogen bromide had occurred between $(SNH)_4$ and N-bromosuccinimide to give $S_4N_4$, HBr and succinimide, perhaps according to the equation:

$$(SNH)_4 + 2C_4H_4O_2NBr \longrightarrow S_4N_4 + 2HBr + 2C_4H_4O_2NH$$

(It does however seem unlikely that such a simple equation could accurately express the undoubtedly complex nature of this reaction.) The production of some $S_4N_3Br$ and $NH_4Br$ is similarly difficult to explain (unless there was some simultaneous formation of disuccinimide $(C_4H_4O_2N)_2$). When the reaction was repeated using tetrathiotetraimide and N-bromosuccinimide in a molar ratio 1:2 a yellow suspension was again produced. A yellow solid was filtered off and the filtrate on evaporation under reduced pressure yielded a small quantity of dark brown residue. This residue was extracted with ether, and the extract recrystallised from hexane to give $S_4N_4$ (identified from its i.r. spectrum). The insoluble yellow solid, the major product, was identified from its i.r. spectrum as a mixture of thiotrithiazyl and ammonium bromides. Some elimination of HBr (formation of $S_4N_4$) had obviously taken place, but the major reaction seems to be similar to the reaction of $(SNH)_4$ with acetyl bromide i.e. ring contraction to $S_4N_3Br$ and formation of $NH_4Br$.

N-Bromodiphenylketimine

Tetrathiotetraimide and N-bromodiphenylketimine (in 1:1 molar ratio) reacted rapidly in THF, (as did $(SNH)_4$ and N-bromosuccinimide) to give a yellow suspension. After 20 minutes at 20° the mixture was filtered to give a white solid. The red/green filtrate on evaporation under reduced pressure gave a red residue which would not mull and was not investigated further. Examination of the i.r. spectrum of the white solid revealed peaks characteristic of $(SNH)_4$ and, with one change in intensity of absorption at $15.64\mu$, of diphenylketimine hydrobromide. There were no absorptions due to $NH_4^+$, so reactions of types (i) and (ii) could be discounted. Since N-bromodiphenylketimine has a tendency to deprotonate THF, to give diphenylketimine hydrobromide,[87] it was decided to repeat the reaction in another solvent.

Keeping the molar ratio 1:1 the reaction was repeated in toluene, stirring a solution of N-bromodiphenylketimine with a suspension of $(SNH)_4$. The reaction was naturally much slower under these conditions, and after two hours the mixture was filtered to give a white solid and red filtrate. Evaporation of the filtrate under reduced pressure yielded yellow crystalline $S_4N_4$ (identified from i.r. spectrum). The i.r. spectrum of the white solid was identical to that of the white solid obtained from the reaction in THF, save that those peaks corresponding to $(SNH)_4$ were much stronger. (This was to be expected since the $(SNH)_4$ was not in solution initially and reaction would proceed more slowly.) Washing with THF removed both $(SNH)_4$ and $S_4N_4$, (detected by examination of i.r. spectra). The i.r. spectrum of the residue was identical to that of the white solid obtained from the initial reaction in THF, i.e. the spectrum differed from that of $Ph_2CNH_2Br$ in one respect only, change in intensity of the peak at 15.64μ. Apparently $Ph_2CNBr$ had deprotonated tetrathiotetraimide forming $Ph_2CNH_2Br$ and $S_4N_4$ (a similar deprotonation is observed when diphenylphosphine reacts with $Me_2NCl$ to give tetraphenyldiphosphine and $Me_2NH_2Cl$.[88]). As this reaction gave no new compound it was not studied further.

Before going on to discuss the reaction of tetrathiotetraimide and chlorine (as mentioned earlier page 49 ) it is convenient to mention here two further reactions; those of $(SNH)_4$ with benzoyl chloride and hydrogen chloride.

## Benzoyl Chloride

Because acetyl chloride reacted with $(SNH)_4$ it was decided to investigate the analogous reaction with benzoyl chloride. Benzoyl chloride was stirred with an ether suspension of tetrathiotetraimide for 1½ hours, no apparent change taking place. Pyridine was then added, (to act as a dehydrohalogenating agent) and the ether turned yellow within 30 minutes. After a further 4½ hours, the mixture was filtered to give a white solid which was identified from its i.r. spectrum as unreacted $(SNH)_4$, and a yellow filtrate. Evaporation of the filtrate under reduced pressure gave a small quantity of yellow solid and yellow oil which were not studied further. In view of the lesser reactivity of benzoyl chloride towards "active hydrogen atoms", as compared with acetyl chloride,[89] more vigorous conditions should perhaps be chosen (e.g. refluxing for several hours) in any future re-examination of this reaction. Addition of pyridine to the reaction mixture was carried out to create conditions analogous to those normally employed in the Schotten-Baumann reaction for benzoylation of an "active hydrogen" containing compound.

## Hydrogen Chloride

Hydrogen chloride, dried by passage through a long $P_2O_5$ tube, was passed into a suspension of $(SNH)_4$ in chloroform. After 40 minutes the mixture was filtered leaving a white solid on the filter. The i.r. spectrum of this material indicated a mixture of $NH_4Cl$ and unreacted $(SNH)_4$. Evaporation of the filtrate under reduced pressure yielded yellow orange crystals, (identified as $S_4N_3Cl$ from i.r. spectrum), and a dark brown solid which was not investigated further. Hydrogen chloride, chosen because it was a "simple" halide, thus reacted in an analogous way to the acetyl halides. Again it is not possible to represent the reaction by a simple, reasonable, equation. The simplest equation would be

$$S_4N_4H_4 + 2HCl \longrightarrow S_4N_3Cl + NH_4Cl + H_2$$

which is however unlikely.

Thus; bromine, acetyl chloride, acetyl bromide, N-bromosuccinimide and hydrogen chloride all react with $(SNH)_4$ under suitable conditions causing ring contraction from the 8-membered $(SN)_4$ ring to the 7-membered ring cation $S_4N_3^+$. The only reaction which can be reasonably expressed by a simple equation is that between $(SNH)_4$ and $Br_2$.

i.e. $$S_4N_4H_4 + Br_2 \longrightarrow S_4N_3Br + NH_4Br.$$

Chlorine

Chlorine reacted exothermically with $(SNH)_4$ in $CCl_4$ suspension which turned a dark orange brown. Ammonium chloride (identified from its i.r. spectrum) was filtered off and the filtrate yielded a yellow crystalline solid, identified from its melting point and i.r. spectrum as trithiazyl-trichloride $(NSCl)_3$. This product was identical to that prepared from tetrasulphur tetranitride, or thiodithiazyl dichloride, $S_3N_2Cl_2$, and chlorine.[79] This reaction resulting in ring contraction from $(SN)_4$ to $(SN)_3$ can be represented by the simple equation,

$$3S_4N_4H_4 + 12Cl_2 \longrightarrow 4N_3S_3Cl_3 + 12HCl$$

Since $SO_2Cl_2$ converts $S_4N_4$ and $S_3N_2Cl_2$ to purer products than chlorine[90] it was decided to study the reaction of $(SNH)_4$ with sulphuryl chloride.

## Sulphuryl Chloride

A suspension of $(SNH)_4$ in $CCl_4$ was treated with $SO_2Cl_2$. Ammonium chloride, identified from i.r. spectrum, was filtered off and the filtrate yielded yellow crystals analysing as $(NSCl)_3$. The i.r. spectrum of this product and that of the recrystallised product from $Cl_2/(SNH)_4$ were identical. This reaction can also be represented by a simple equation

$$3S_4N_4H_4 + 12SO_2Cl_2 \longrightarrow 4N_3S_3Cl_3 + 12SO_2 + 12HCl$$

Somewhat interesting behaviour was observed when this solid was either transferred under dry, oxygen-free nitrogen or exposed to a vacuum. Opening of a vessel containing $(NSCl)_3$ in a glove box, (or under counter current nitrogen), or evacuating the vessel resulted in the solid turning green. On standing the yellow colour returned. Explanation of such behaviour is necessarily speculative. Two possibilities are that the yellow crystalline $(NSCl)_3$ may have dissociated to green NSCl (adsorbed on the solid trimer) or it may have contained an impurity which reacted with a trace of water to produce a reactive green compound, which with more water gave a colourless product. However, development of the green colour on evacuating the containing vessel indicates that the first explanation is more likely to be correct. Patton proposes that the green colour is due to an $(NSCl)_3$ excited state.[91]

### Tetrachloroethylene

The possibility of an addition reaction with $C_2Cl_4$ (or deprotonation followed by copolymerization) was investigated. Refluxing $(SNH)_4$ with $C_2Cl_4$ yielded only tetrasulphur tetranitride, identified from i.r. spectrum. No traces of absorptions due to C-Cl could be found in this product and the reaction was not studied further.

## ORGANOMETALLICS

### Trimethylaluminium

Trimethylaluminium and $(SNH)_4$ reacted at room temperature giving methane, identified from i.r. spectrum, and an orange-yellow solid. The i.r. spectrum of the solid showed absorptions in both the NH and SN stretching ranges, but analytical figures did not give any sensible empirical formula.

Conclusions: (i) substitution was incomplete, and

(ii) a simpler organometallic compound should be used.

Accordingly, no further work was carried out using trimethylaluminium and n-butyl lithium was selected as a suitable reagent.

### n-Butyl Lithium

A sealed tube reaction between $(SNH)_4$ in THF and n-butyl lithium in hexane, in 1:4 molar ratio, was carried out to determine the extent of hydrogen substitution (metallation). Measurement of the volume of butane evolved, identified from i.r. spectrum, indicated that all four hydrogen atoms could be removed by the n-butyl carbanion (1m.mole $(SNH)_4$ gave 3.7 m.mole $C_4H_{10}$). The yellow solid obtained was presumed to be predominantly $(SNLi)_4$, formed according to the equation

$$S_4N_4H_4 + 4Bu^nLi \longrightarrow S_4N_4Li_4 + 4Bu^nH$$

During the reaction the colour changed from yellow to red, then yellow, blue and finally yellow. It is believed that the appearance of the four colours was due to successive stages in the substitution. These may be compared with colours of other $S_4N_4H_x$ anions obtained by reaction of $S_4N_4$ with sodium,[93] and $(SNH)_4$ with triphenylmethylsodium.[22] (See Table 5.).

| $S_4N_4$ + Na [93] | $S_4N_4H_4$ + $Ph_3\bar{C}Na$ [22]<br>(solid compounds) | $S_4N_4H_4$ + $Bu^nLi$ |
|---|---|---|
| $S_4N_4^-$ (red) | | $S_4N_4H_3^-$ (red) |
| $S_4N_4^{2-}$ (deep blue) | $S_4N_4H_2Na_2$ (lemon yellow) | $S_4N_4H_2^{2-}$ (yellow) |
| $S_4N_4^{3-}$ (green) | | $S_4N_4H^{3-}$ (blue) |
| $S_4N_4^{4-}$ (yellow green) | $S_4N_4Na_4$ (orange red) | $S_4N_4^{4-}$ (yellow)<br>$S_4N_4Li_4$ (yellow) |

COLOURS OF $S_4N_4H_x$ ANIONS

TABLE 5.

## Tetrathiotetraimidolithium

A possible route to $(SNX)_4$ derivatives was by reaction of the tetraimidolithium derivative with a halide, and elimination of the lithium halide. Treatment of $(SNLi)_4$ with methyl iodide, iodobenzene, acetyl bromide and chlorine gave red tars which were not studied further.

Trimethylchlorosilane and $(SNLi)_4$ gave a deep red, pungent smelling liquid which analysed fairly closely as $(SNSi(CH_3)_3)_4$. The i.r. spectrum of this liquid contained absorptions characteristic of trimethylsilyl groups, and it is likely that this liquid was mostly the tetratrimethylsilyl derivative of $(SNH)_4$. Owing to the unpleasant and viscous nature of the product this reaction was not studied further. Purification and conclusive characterisation of the product would be more convenient using a higher molecular weight chlorosilane e.g. $Ph_3SiCl$, which would possibly yield a solid derivative.

## OXYGEN COMPOUNDS

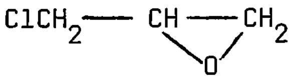
### Acetic Anhydride

Acetylation of $(SNH)_4$ using acetic anhydride was investigated. There were no visible signs of reaction when tetrathiotetraimide was stirred with acetic anhydride at 20°, however, on heating to reflux a clear dark red solution resulted from which $S_4N_4$, identified by i.r. spectrum, was obtained. The reaction was not studied further.

### Ethylene Oxide

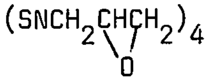
Possible opening of the epoxide ring and rearrangement with the imide hydrogen of $(SNH)_4$ to give a derivative $(SNCH_2CH_2OH)_4$ was explored. Ethylene oxide and $(SNH)_4$ were kept together at temperatures below -30° for 150 hours. The i.r. spectra of the two white solids obtained from the reaction mixture indicated unreacted tetrathiotetraimide. This reaction was not studied further.

### Epichlorohydrin



Two possible reactions giving $(SNX)_4$ derivatives are

(i) opening of the epoxy ring and rearrangement to form $(SNOCH_2CH_2CH_2Cl)_4$

(ii) elimination of HCl and formation of  $(SNCH_2CHCH_2)_4$

(cf. Brintzinger et. al.[92] report the reaction between carbazole and $ClCH_2SCl$ to give $C_{12}H_8N\text{-}CH_2S\text{-}NC_{12}H_8$).

$(SNH)_4$ and epichlorohydrin did not appear to react at 20°, and gave a dark tar after refluxing. This reaction was not studied further.

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