New routes to sulphur-nitrogen compounds

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NEW ROUTES TO SULPHUR-NITROGEN COMPOUNDS

by

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in the University of Durham.

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The sobering influence of other members of the laboratory is appreciatively acknowledged.

Memorandum

The work described in this thesis was carried out in the University of Durham between September 1969 and September 1970. It has not been submitted for any other degree, and is the original work of the author except where acknowledged by reference.

"Naso suspendis adunco Ignotus"

- Horace, Satires I.vi,5

(on old infrared spectra)

"....dabit deus his quoque finem."

- Virgil, Aeneid i,199.

Abstract

Several reactions have been investigated in the search for new routes to cyclic sulphur-nitrogen compounds. Pyridine -1- oxide and trithiazyl trichloride were found to rearrange (after initial adduct formation) to form a compound bearing some resemblance to the pyridine adduct of sulphanuric chloride.

This work has also established that barium and sodium trisulphimide salts are potential starting materials both for sulphanuric (six - membered) rings and for rings with exocyclic functional groups containing sulphur (probably O.SO.Cl). It is also possible that plumbic acetate may be an acceptable oxidising agent for the preparation of sulphur (Vl) systems, as witnessed by its reaction with thiodithiazyl dichloride. However, mercuric oxide has proved of no value in this role under the conditions employed in this work.

The effort to achieve sulphur-nitrogen-carbon systems was partly devoted to the reaction between potassium thiocyanate and trithiazyl trichloride, but mainly to the preparation of air-and moisture-stable derivatives of the suspected dithiadiazoles. Apparent success has been achieved using diphenylketiminolithium.

It can be concluded from this work that several new routes might be obtainable after further research, though the most potentially useful, and practicable work appears to be that connected with the dithiadiazoles.

CONTENTS

Reaction between Pyridine -1- Oxide and Trithiazyl Trichloride

Experimental

MERCURIC OXIDE AND TRITHIAZYL TRICHLORIDE

REACTIONS OF TETRATHIONYLIMIDE

REACTIONS OF THIODITHIAZYL DICHLORIDE WITH PLUMBIC OXIDE AND ACETATE

Discussion

ii. Thiodithiazyl dichloride and plumbic acetate

Page

PREPARATION & REACTIONS OF TRISULPHIMIDE SALTS

Introduction

Experimental

Discussion

INTRODUCTION

The aim of this research was to devise new or improved synthetic routes to cyclic sulphur-nitrogen compounds. Such compounds can be grouped into four broad classifications, namely;

(a) Molecules or cations containing only sulphur and nitrogen in the ring.

(b) The cyclic sulphur imides[1] containing -NR-, built on sulphur II (e.g. $S_x(NH)_{n-x}$ where n = 8 or 6) or sulphur IV (e.g. (OSNH)y, where y = 3 or 4).

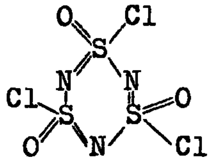
(c) Sulphur VI systems containing -NR- or nitrogen doubly bound to sulphur. In this very wide class can be placed sulphimide polymers derived from the hypothetical monomeric sulphimide, $HNSO_2$, and the sulphanuric halides of general formula (NSOX)n.

(d) Rings containing a third element, e.g. carbon, in addition to sulphur and nitrogen.

In the following investigations, compounds of group (a) were used as starting materials only; no attempts were made to find new methods for their preparation.

In group (b), $(OSNH)_4$ was studied only briefly. Several compounds of groups (c) and (d) were investigated because of their possibly wide applicability:-

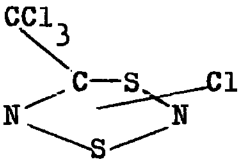
The sulphanuric halides, $(NSOX)_m$, can be related electronically to the cyclic phosphonitrilic compounds (NSOF is isoelectronic with NPF_2), and their chemistry is becoming as important and interesting as that of this latter class. The simplest, and as yet most important member of the sulphanuric compounds, trimeric sulphanuric chloride (I) is preparable in satisfactory yield by only one method [2,3], the pyrolysis of trichlorophosphazosulphonyl chloride, $Cl_3P = NSO_2Cl$,



(I)

obtained after reaction between sulphamic acid and phosphorus pentachloride. This method yields a mixture of geometrical isomers in addition to compounds containing sulphur, nitrogen, and phosphorus. Besides the theoretical aspects of interest in sulphanuric chloride (to be expected by analogy with phosphonitrilic systems), considerable importance derives from its potential in the field of pesticides. More convenient routes to the compound are therefore desirable.

Biological activity also inspires interest in compounds of group (d), which are represented by the delocalised molecules II and III[4], suspected dithiadiazoles whose structures have not yet been fully elucidated.



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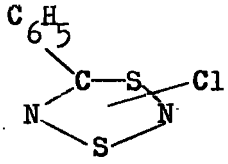

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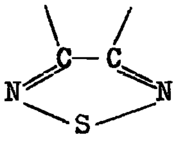
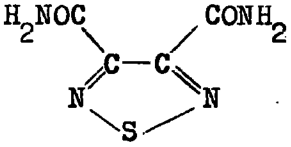


(IV)

II and III have similar structures to the 1,2,5 - thiadiazoles[5] (IV), of which numerous carbon-substituted derivatives can be prepared. Many of these compounds have been proved to possess valuable chemotherapeutic properties[5] (for instance, the compound (V) is used to combat diabetes), and consequently the relative ease of obtaining



(V)

compounds (III) and (IV), whose ring nuclei differ at only one position from that of the 1,2,5 - thiadiazoles, confers a high potential importance upon them. However, although their preparations have now been established[4], their moisture sensitivity, probably conferred by chlorine, has retarded the development of their chemistry.

These points concerning compounds of groups (c) and (d), therefore, provided the motivation for the various projects which comprise the research described in the following pages, namely:-

Possible routes to Sulphanuric Chloride (or other rings containing Sulphur VI)

i) Reaction of trithiazyl trichloride and pyridine -1- oxide.
ii) Reaction of trithiazyl trichloride and mercuric oxide.
iii) Reaction of thiodithiazyl dichloride and (a) Plumbic oxide,
  (b) Plumbic acetate.
iv) Reaction of tetrameric thionyl imide $(OSNH)_4$, with (a) chlorine,
  (b) sulphuryl chloride.
v) Trisulphimide salts and (a) Phosphorus pentachloride,
  (b) Thionyl Chloride.

Attempts to prepare compounds containing carbon, sulphur and nitrogen

vi) Reaction of trithiazyl trichloride and potassium thiocyanate.

vii) Reaction of trithiazyl trichloride and tetrachloroethylene.

viii) Attempts to prepare derivatives of the compounds $S_2N_2CClCCl_3$, $S_2N_2CClC_6H_5$.

The aim of projects vi) and vii) was to find new sulphur - nitrogen - carbon systems, whereas project viii) was undertaken with the aim of obtaining air - and moisture-stable derivatives of the suspected dithiadiazoles already prepared[4].

The overall objective of this research was to decide which of the projects i) - viii) were most suitable for further study.

EXPERIMENTAL (GENERAL)

Handling Techniques

Most of the compounds involved in this work were sensitive to moisture, so that reactions and manipulations were generally carried out in an atmosphere of dry nitrogen. This was supplied to previously evacuated systems by leads from a tube flushed with nitrogen dried by passage through two liquid nitrogen traps. Tasks which could not be carried out under counter-current nitrogen were performed in a glove box.

Infrared spectra

These were recorded on a Spectromaster prism grating spectrometer over the range 4000-400 cm^{-1}, solids being examined as nujol or hexachlorobutadiene mulls, liquids as contact films between potassium Bromide plates, and gases in gas cells. The relative intensities of i.r. absorptions are denoted by the following symbols:

vs - very strong; s - strong; m - medium; w - weak; vw - very weak; sh - shoulder; b - broad.

Mass spectra

These were obtained from an A.E.I. MS9 mass spectrometer, the sample being mounted on an inert support and being introduced by means of a direct insertion probe. The accelerating potential used was 8kv, 70 eV. The source temperature in all cases was 180-200°C.

Purification of Solvents

Hydrocarbons and diethyl ether were dried for at least one week over sodium wire before use.

Carbon tetrachloride was dried over P_4O_{10} for a similar period.

Chloroform was stored over molecular sieve 5A which had been oven dried at 90°C. for at least two days.

Pyridine was distilled from and onto fresh NaOH before use.

Sulphur dichloride was purified[6] by fractionation on a column, the middle fraction (b.p.50-62°) being collected and refractioned, boiling at 60°. Two drops of phosphorus trichloride were placed in both the receiver and the flask containing starting material to reduce contamination by chlorine or disulphur dichloride.

Thionyl chloride in 250ml.aliquots was purified by slow[7], dropwise addition of triphenylphosphite (40 ml), the thionyl chloride being well stirred. This was followed by fractionation up a 30cm. column (diam.1.5 cm.) packed with glass helices, the receiver being protected by a phosphorus pentoxide drying tube. The first few mls. of distillate were discarded, and approximately 60% recovery was achieved. Thionyl chloride is a highly corrosive liquid, necessitating immediate cleaning of syringes after use.

Purification procedures for other compounds are mentioned at the appropriate points in the text.

Analyses

Samples whose sulphur and/or chlorine contents were to be determined were analysed using a procedure devised by Mr. R. Coult[8]. For sulphur, the Budesinsky method[9] is modified, the sample being housed in a gelatine capsule and ignited in an oxygen atmosphere after measuring appropriate weights. Conversion to sulphate is achieved using a few ml. dilute hydrogen peroxide solution previously placed in the combustion vessel, and after condensation of vapours is complete, this solution is made up to 100 mls. Titration with standard barium perchlorate solution in the presence of acetone then gives an estimate of the sulphur content.

To estimate chlorine content, samples of the solution obtained above are titrated potentiometrically against N/100 $AgNO_3$ using Ag/AgCl electrode in acetone medium.

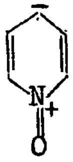
Carbon, hydrogen, nitrogen, and sometimes chlorine analyses were obtained using a Perkin Elmer 240 Elemental Analyser.

REACTION BETWEEN PYRIDINE -1- OXIDE AND TRITHIAZYL TRICHLORIDE

INTRODUCTION

Little attention was given to the chemistry of pyridine -1- oxide until the measurement of its dipole moment, when Linton[10] discovered that the difference between the dipole moments of pyridine and its oxide was less than half that separating the dipole moments of trimethylamine and its N-oxide. Linton concluded that the pyridine N-oxide molecule could reverse its polarisation, and that canonical


I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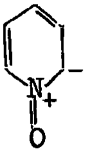
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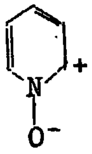

V

forms II and III made a significant contribution to the overall resonance hybrid . This hybrid is also composed of forms IV and V[11], so that in pyridine -1- oxide the nucleus may be electron-rich or electron-deficient. Consequently either electrophilic or nucleophilic attack may be undergone under appropriate conditions.

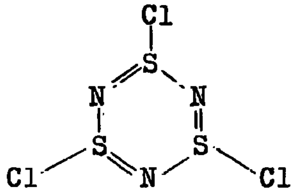
The properties of pyridine -1- oxide as a ligand have since been investigated by several groups,[12,13,14] always in the form of complexes with metals. Reedijk[14] concluded that pyridine -1- oxide can act as a strongly co-ordinating ligand whose position is low in the spectrochemical and nephelauxetic series.

Trithiazyl trichloride (VI) exists as a ring with a chain configuration, nitrogen atoms being below the sulphur, and chlorines being axial.[15,16] One chlorine differs from the other two[17], possibly due to the arrangement in the unit cell, and each atom of the ring contributes one electron to the π-system, evidence for which comes from the equal bond lengths.

This consists either of nitrogen pπ- sulphur dπ overlap causing delocalisation over the entire ring[18], or over three-centre S-N-S bonds[19].

The only adduct of trithiazyl trichloride forms with sulphur trioxide acting as a Lewis acid[20] (it is also capable of acting as a Lewis base[21]).

The aim of reacting pyridine -1- oxide and trithiazyl trichloride was to form a sulphanuric type molecule via rearrangement of the initially formed addition product, as in VII, thereby going from sulphur (IV) to sulphur (VI). Such a rearrangement can be compared with that found by Koenig and Wieczorek[22] in the reaction between pyridine -1- oxide and trichloroacetic anhydride in acetonitrile solution, which is summarized below:



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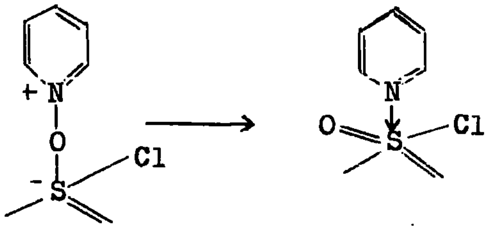

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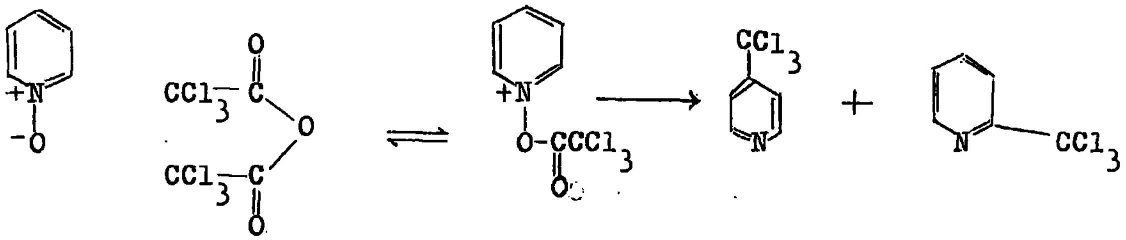
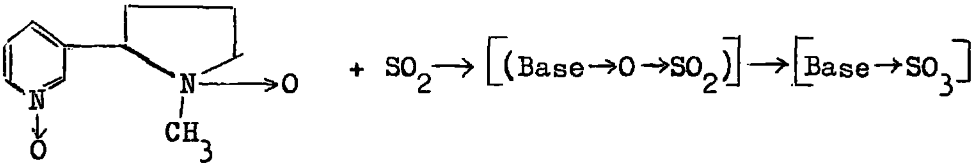


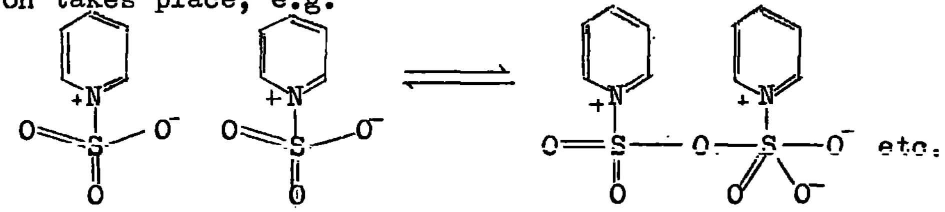
and other products.

The oxygen of the pyridine -1- oxide, after attacking a carbonyl group, remains with that group as the pyridine nucleus is removed. However, closer analogies can be drawn to the desired rearrangement from the reported cases of deoxygenation of aromatic N-oxides by sulphur-containing molecules. For instance, Taylor and Boyer[23] detected two stages in their reaction of nicotine -1,1'-dioxide in aqueous solution with sulphur dioxide, which they report as



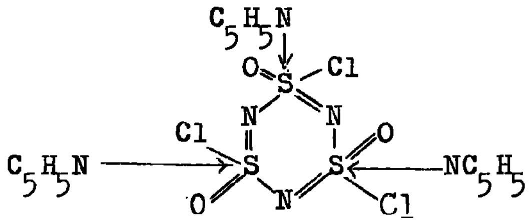
Daniker[24] reacted pyridine -1- oxide and sulphur dioxide, and also reported formation of a base-sulphur trioxide complex, though he did not comment on any intermediate stage. In his work on the deoxygenation of 4-substituted pyridine -1- oxides by dimethylsulphoxide, Traynelis[25] proposes a mechanism which, to account for dimeric species in the product mixture, invokes homolysis of the nitrogen-oxygen bond. However, this cannot be invoked as the sole, or even major mechanism in such deoxygenations, since Biffin[26] et al, performing the reaction with unsubstituted pyridine -1- oxide under different conditions, report almost quantitative formation of dimethylsulphone. Furthermore, Koenig[22] discounts the possibility of homolysis in the deoxygenation he reports.

The work of Moore suggests[27] that interchange between N-O-Sand N-S=O - containing molecules may occur in the reverse direction. Recrystallisation from nitromethane of the compound $C_5H_5NSO_3$ obtained on reacting pyridine and sulphur trioxide yields a compound of the same composition, but with a more complex i.r. spectrum, containing broader absorptions in some regions. One could interpret this as initial formation of a nitrogen-sulphur link followed by rearrangement to a nitrogen-oxygen-sulphur link. However, in view of the evidence quoted above, and the similarity in general pattern of the spectra, a more likely explanation (suggested by Moore) is that some polymerisation takes place, e.g.



In summary, therefore, it seems reasonable to anticipate formation of an oxygen-sulphur link, and subsequent rearrangement on reacting pyridine -1- oxide and trithiazyl trichloride. Complications might be anticipated should chloride ion be displaced during the reaction, since the pyridine -1- oxide ring is susceptible to nucleophilic attack and indeed undergoes it in the reaction with trichloroacetic anhydride[15]. Heal and Kane[28], basing their results on conductivity measurements, found that pyridine was sufficiently nucleophilic to displace chloride ion from disulphur dichloride in acetonitrile solution. However, they discovered K($\sim 10^4$) to be low, i.e. pyridine displaced chloride ion from sulphur (II) only with difficulty. Hence it seems reasonable to anticipate no such interference in the case of sulphur (IV).

It is also possible that the reaction may proceed no further after initial combination of pyridine -1- oxide and trithiazyl trichloride; Moore also attempted the formation of a sulphanuric chloride adduct with pyridine, and obtained a compound $(C_5H_5N)_3(NSOCl)_3$. However, the high co-ordination number of sulphur should this compound have the simple adduct structure VIII suggests that the possibility of a nitrogen-oxygen-sulphur link should be considered as an alternative.



(VIII)

Bearing in mind these points, work was carried out on the pyridine -1- oxide/trithiazyl trichloride system, and supplemented by the reactions between sulphur dichloride and pyridine*, and thionyl chloride and pyridine, in the hope that these similar, though simpler systems might assist the interpretation of results.

EXPERIMENTAL

Preparation and purification of reagents

(i) Trithiazyl trichloride

Two main methods are available. Schroeder and Glemser[29] passed chlorine through an inert solvent containing a suspension of tetrasulphur tetranitride. Jolly and Maguire[30] reported the action of chlorine on thiodithiazyl dichloride, $S_3N_2Cl_2$.

In this work, each method was adapted by use of sulphuryl chloride as a chlorinating agent:-

(a) Use of thiodithiazyl dichloride- -preparation of $S_3N_2Cl_2$.

This method was developed from that of Jolly et al[31] by Banister et al[32]. Ammonium chloride (200 gm.) and sulphur (40 gm.) were intimately mixed and placed in a 700 ml. straight-sided flange flask, to which a long air condenser fitted with a calcium chloride drying tube was attached. The whole was purged with nitrogen, and disulphur dichloride (200 ml.) added. The temperature was raised to 140-150°C., and after 24 hours, orange-brown crystals of $S_3N_2Cl_2$ began to form in the condenser (shielded from the heat by an asbestos sheet.)

The mass of deposited crystals was thickened by gradual reduction of reaction temperature, which lowered the reflux level. Total recovery of $S_3N_2Cl_2$ was 35.4 gm: $4S_2Cl_2 + 2NH_4Cl \longrightarrow S_3N_2Cl_2 + 8\ HCl + 5S$

i.e. 200 ml. (336 gm.) S_2Cl_2 should yield 195 gm. $S_3N_2Cl_2$,

i.e. yield = 30%.

The trithiazyl trichloride, obtained by stirring $S_3N_2Cl_2$ in sulphuryl chloride was less pure than that due to the more convenient alternative procedure:-[32]

(b) Reaction of Tetrasulphur Tetranitride and Sulphuryl Chloride.

Tetrasulphur tetranitride (5 gm.) was slurried in an excess of sulphuryl chloride (25 ml.) in one limb of a Schlenk. After about 24 hours, evolution of sulphur dioxide ceased, and a red solution remained above the yellow trithiazyl trichloride.

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

Sulphuryl chloride was removed in vacuo, and the crude product recrystallised from carbon tetrachloride.

A dark green colour develops reversibly in the solution on heating above 50°C, and also on removing the last traces of solvent at the vacuum pump. It has been suggested[33] that this is due to formation of monomeric thiazyl chloride, NSCl, which may be adsorbed on the surface of the $S_3N_3Cl_3$.

The yield from this reaction is virtually quantitative.

ii) Pyridine -1- oxide

The methods of Mosher [34a] and Payne[34b] were tried, but found to be time consuming and to provide low yields compared to the reported values.

Superior results were obtained by Ochiai's method[11], which was finally adopted. Pyridine -1- oxide was obtained as a white solid, stable in air, but extremely hygroscopic.

Reaction of $(NSCl)_3$ and C_5H_5NO

(a) Using solid reagents

Trithiazyl trichloride (1.79 gm.) and pyridine -1- oxide (2.08 gm.) suspended in dry carbon tetrachloride were mixed in stoichiometric ratio in one limb of a Schlenk. An immediate soft green colouration was observed, and on stirring, small amounts of mobile, reddish orange oil were produced. As the amount of this oil grew, the solution colour changed to dark orange over about four hours.

After 21 hours, a dark brown, semi-solid lump had formed beneath a yellow liquid. It reacted violently and exothermically with water. Because of its unmanageability, and likely contamination by unreacted starting materials, the semi-solid was not investigated further.

(b) Using reagents in solution

A solution of pyridine -1- oxide (2.09 gm.) in carbon tetrachloride (100 mls.) was syringed into a flask containing a transparent green solution of trithiazyl trichloride (1.76 gm.) in carbon tetrachloride (70 mls.) stirred magnetically at room temperature. A soft, translucent green colour immediately replaced the transparent green and after less than thirty minutes, particles of a flocculent, pale yellow solid were observed. The amount of this solid gradually increased, and after 2 - 3 hours its texture began to change to that of an oily, orange solid. This also happened to such solid as had collected on the walls of the flask above the liquid surface.

Twenty two hours after commencement of reaction the solution had become yellow, and the orange oil had become dark red, but still mobile.

Stirring for longer periods (up to eight days) produced a viscous, very dark oil and a brown solution. It was found that both the oil and the yellow solid absorbed silicone grease avidly, therefore in later runs, glass joints were sealed using teflon sleeves.

It was possible to separate the yellow solid by filtration in the early stages of the reaction, and after its removal only small amounts of oil still formed. It was stable when stored under dry nitrogen, and did not convert to the oil on stirring in pure carbon tetrachloride. It proved possible to compare peaks in the i.r. spectrum of the solid with the spectra of trithiazyl trichloride and pyridine -1- oxide.

Absorptions (cm^{-1}) TABLE I

Yellow Solid	Pyridine -1- oxide	Trithiazyl Trichloride	Yellow Solid	Pyridine -1- oxide	Trithiazyl Trichloride
2740 (mb)			952(sh)	977 (m)	
2151 (s)					
1615 (m)	1597(m)		823 (s)	840 (s)	
1538 -					
1515 (m)			797 (s)	826 (s)	800 (m)
1470(ssh)			770 (s)	799 (s)	
1331 (m)			721 (sh)	766 (s)	
1299 (m)			686 (sh)	681 (s)	700 (m)
1262 (s)	1258 (vs)		668 (s)	678 (s)	
1203 (m)	1204 (ms)		639 (w)	636 (w)	
1189 (m)	1171 (s)		608 (w)		621 (w)
1149 (m)	1147 (ms)		554 (w)	544 (s)	
1099 (s)	1100 (s)		537 (w)	521 (ms)	515 (m)
1071 (s)	1071 (s)		484 (ms)		
1052 (s)			483 (ms)		
1026 (s)			450 (m)	463 (s)	
1017 (s)	1003 (vs)	1016 (s)			

NOTE: The region 1120-1000 cm^{-1} contained several absorptions, not all of which were accurately determinable due to merging of the bands. The infrared spectrum of a sample taken from a different reaction mixture was identical.

A sample of the red oil was withdrawn by syringe after 24 hours, and its i.r. spectrum examined as a contact film between KBr plates. This film was used to follow the changes in the spectrum with time. The absorptions are shown in Table II below:

Growth peaks are signified by two symbols :- "g" shows those which grow approximately 20% over 47 hours, "G" shows those which grow 100% over 47 hours. "n" shows that these peaks are new (i.e. have no counterpart in the solid's spectrum). Shrinkage peaks are marked "shr", and peaks with constant intensities marked "c".

TABLE II

Absorption (cm^{-1})	Type of Absorption	Initial Strength	Absorption (cm^{-1})	Type of Absorption	Initial Strength
3154	g	s	952	c	sh,b
2597	g	s,b	808	c	sh
2096	c	w	796	c	s
1605	G	m	775	shr	s,sh
1527	shr	w	751	gn	s
1468	c	s	676	gn	s
1397	c	s	669	shr	s
1337	g	m	607	g	m
1256	c	s	583	g	w
1190	g	s,sh	557	g	w
1155	g	s	552	shr	w
1087	g	s	543	c	w
1043	c	vs	525	g	w
1019	c	s	506	c	w
1000	c	s	490-485	shr	w
			461	c	w

No two sets of analysis figures agreed, e.g.:-

	Atomic Ratios
C,39.66; H,3.84; N, 18.49; S, 15.17; Cl,27.9 (Yellow Solid)	$C_{7}H_{8}N_{5.5}SCl_{1.7}$
C,38 ; H,3.85; N, 13.04; S, 7.9; Cl,17.1 (Yellow Solid)	$C_{12.7}H_{15.4}N_{3.9}SCl_{1.9}$
C,26.98; H,2.3 ; N,13.71 ; S,23.2; Cl,30.9 (Oil)	$C_{3.1}H_{3.2}N_{1.4}SCl_{1.2}$

The weight of oil produced was found to be 86.5% of the total weight of starting materials, and no reactants were found to remain on evaporation of the carbon tetrachloride after removal of the oil.

A small amount of the oil was transferred to a 100ml. flask, concentrated aqueous sodiumhydroxide solution was added, and the system evacuated. Heat was applied (up to 50°C) and a distillate collected in a small cup at the base of a carbon dioxide /acetone cold finger). Infrared spectrum showed this distillate to be pyridine.

Reaction of Sulphur dichloride and Pyridine -1- Oxide

An excess of sulphur dichloride in carbon tetrachloride solution was syringed into a stirred solution of pyridine -1- oxide (2.5 gm.) in carbon tetrachloride (130 ml.) at room temperature. A gas was evolved, and identified by its infrared spectrum as sulphur dioxide, and a yellow liquid containing yellow solid particles was observed. By the time solvent had been removed at the pump, a yellow oil remained. Its i.r. spectrum showed bands at 3030 (s), 2857-2220 (s), 2008 (m), 1621 (s), 1538 (m), 1493 (s), 1466 (m), 1379 (w), 1355 (sh), 1340 (vs), 1316 (m), 1261 (m), 1202 (w), 1168 (w), 1127 (vs), 1109 (vs), 1081 (s), 1060 (s), 1023 (m), 1006 (m), 968 (m), 785 (s), 756 (vs), 734 (vs), 610 (s), 592 (w), 552 (vs), 521 (vs), 498 (cm^{-1}) (vs).

No change in the spectrum was observed as the oil aged. Analyses showed C,32.35; H,3.1; N,6.48; Cl,33.4; S, absent. These figures give atomic ratios $C_{5.9}H_{6.7}NCl_2O_{3.3}$.

Reaction of Thionyl chloride and Pyridine

(a) At room temperature.

Pyridine (5 ml.) was syringed into a stirred solution of thionyl chloride (3 ml, approximate stoichiometric equivalent for one to one reaction ratio) in carbon tetrachloride. The solution immediately became cloudy, and a gas, identified by its i.r. spectrum as sulphur dioxide, was evolved. On evaporation under vacuum, a pale yellow solid remained, and gave an i.r. spectrum with peaks at 1626 (w), 1603 (m), 1517 (m), 1258 (m), 1064 (sh), 1043 (s), 1021 (sh), 1000 (sh), 941 (m), 798 (s), 750 (s), 678 (s), 639 (sh), 607 (s), 591 (m), 568 (w), 559 (w), 530 cm^{-1} (w).

The solid gave the analyses

C,51.2; H,4.71, N,11.28; Cl, 49; S absent i.e.a total greater than 100 %, which indicates that this solid is a product of decomposition.

After leaving overnight in the glove box, the solid decomposed to a brown, oily liquid.

(b) At -78°C.

Pyridine (5 ml.) in toluene (20 ml.) and thionyl chloride(3 ml.) in toluene (25 ml.) were placed in separate flasks connected by a glass tube, and cooled in an acetone/carbon dioxide bath at -78°C.. The reagents were mixed by tipping the pyridine solution through the glass tube into the thionyl chloride.

Immediately, sulphur dioxide was evolved, and a white cloudiness developed in the solution. The cooling bath was removed to allow slow attainment of room temperature. The white solid gradually assumed a yellow colour, and proceeded to form a bright orange flocculent solid in a green solution. Forty-five minutes after bath removal, coagulation began, and after six hours the colour of both solid and liquid phases had reverted to yellow. Attempts to recrystallise the solid from benzene, ether and thionyl chloride were unsuccessful, so the experiment was repeated and the solid isolated whilst still white. Its i.r. spectrum showed peaks at 3390 (m), 1626 (sh), 1607 (s), 1522 (s), 1330 (sh), 1318 (m), 1250 (s), 1198 (s), 1163 (s), 1082 (s), 1054 (s) 1014 (s) 1004 (s), 944 (m) 870 (m) 797 (s), 752 (vs), 681 (vs), 609 cm^{-1} (vs)

Analyses showed C,43.48; H,4.51; N,6.19; Cl 31.26; S absent
C,47.33; H,4.9; N,8.25; Cl,44.93%, S absent (second reaction)
The first set indicates atomic ratios $C_{8.4}H_{10}NO_2Cl_2$
The second gives $C_{6.5}H_8NCl_2$.

The white solid was stable for several days under nitrogen, but eventually discoloured.

Preparation of 1-chloropyridinium chloride

This was undertaken on the suspicion that the product of the pyridine/thionyl chloride reaction was 1-chloropyridinium chloride, and Williams' method[35] was used. On mixing pyridine (3 gm.) in carbon tetrachloride (50 ml.) with a saturated solution of chlorine in carbon tetrachloride, a white solid was immediately precipitated. On attempting to remove solvent at the vacuum pump, decomposition to a yellowish solid began. The dissimilarity of this compound to the pyridine/thionyl chloride product made further investigation unnecessary.

DISCUSSION

In order to clarify the arguments which follow, this discussion of the pyridine -1- oxide/trithiazyl trichloride reaction is laid out in sections as follows:-

(i) Nature of solid

(ii) Relation between solid and oil and nature of oil

This section considers the molecular ratio of pyridine to sulphur-nitrogen compound in both solid and oil, and the electronic influences operating on the pyridine nucleus (whether similar to pyridine coordinating to a proton or to a metal).

This section concludes that the oil contains a compound with a six-membered sulphur-nitrogen ring to which pyridine and oxygen are attached, and is formed as the result of an intramolecular rearrangement.

(iii) Comparison of oil with pyridine adduct of sulphanuric chloride

By considering the difference between these two substances, more detailed suggestions concerning the nature of the oil are made.

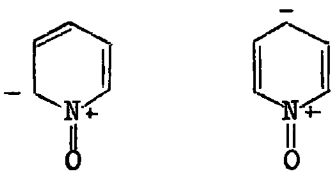
(iv) Summary of arguments

(v) Discussion of pyridine -1- oxide/sulphur dichloride and pyridine/thionyl dichloride reactions

(i) Nature of Solid

Spectral evidence alone indicates that the yellow solid obtained initially has characteristics of a pyridine -1- oxide/trithiazyl trichloride adduct. Table I (p.16) shows that the main features of both reagents can be detected in the solid's infrared spectrum at the same or slightly shifted frequencies.

The N-O stretch is not observable, but in general it undergoes a comparatively large shift in pyridine -1- oxide adducts.[36,37,38] Its absence supports the conclusion that the site of donation is the oxygen (as in the reaction between pyridine -1- oxide and iodine[36]). The shoulder at $952cm^{-1}$ may correspond to the γC-H out-of-plane bending vibration found at $887cm^{-1}$ in the free base, and reported at $935cm^{-1}$ for pyridine -1- oxide adducts of metal perchlorates.[39,40] This would represent an unexpectedly large shift; if correct it indicates C-H bond strengthening due to oxygen coordination. This can be explained[39] by the reduction in the contribution of the resonance forms shown below on coordination.



Other peaks, reported as characteristic of pyridine -1- oxide adducts with metal perchlorates and halides,[40,41] can also be detected at slightly different wavelengths in the yellow solid's spectrum, viz:-

Absorptions (cm^{-1})

C_5H_5NO (solid)	Range quoted, various adducts	Yellow Solid	Mode
463 s	455-468 s or vs	450 m	Ringskeletal
840 s	829-842 s or vs	823 s	NO bend
686 s	664-678 s or vs	668 s	
1470s	1471-1479 vs	1460 s	Ring def.
634 w	639-641 w	639 w	Ringskeletal

All of these peaks with the exception of that at $1460cm^{-1}$ disappear in the i.r. spectrum of the oil, indicating loss, by reaction or decomposition, of the pyridine -1- oxide adduct character.

That free pyridine is obtained after hydrolysis of the oil suggests that chloride ion has not been displaced during the reaction, since pyridine -1- oxide, being susceptible to nucleophilic attack[37], would undergo chlorination of the ring. However, it is possible that some chloride ion displacement might partially effect this, leaving some free pyridine to be recovered on hydrolysis.

It seems, then, that a solid pyridine -1- oxide/trithiazyl trichloride adduct was obtained. Unfortunately, analyses did not even show whether a 1:1, 2:1, or 3:1 adduct had been formed. They do not agree with the indications of the i.r. spectrum that the sulphur-nitrogen ring has been retained, and are thus to be considered as of little help. This analytical problem, especially in the presence of sulphur and halogen together, has been encountered in many sulphur-nitrogen compounds, and remains to be solved. However, the reproducibility of the infrared spectrum suggests that the solid is not a mixture, but a single compound.

(ii) a. <u>Relation between solid and oil</u>

It is apparent that the oil forms from the solid, and not independently, from the reduction in its amount after removal of the yellow solid. That any oil then forms at all suggests the formation of yellow solid to be gradual. However, the oil formation may be due to an ability of the solid to dissolve in carbon tetrachloride, then producing a less soluble oil. The oil's infrared spectrum absorbs in all areas occupied by the solid (though the intensities differ so that it does not exhibit the solid's similarity to pyridine -1- oxide) up to 36 hours after commencement of reaction (see fig. I). After this, certain regions where the solid absorbs (770,537,484 and 450cm^{-1}) become very largely unpopulated for its decomposition product.

Four relationships between solid and oil are possible:-

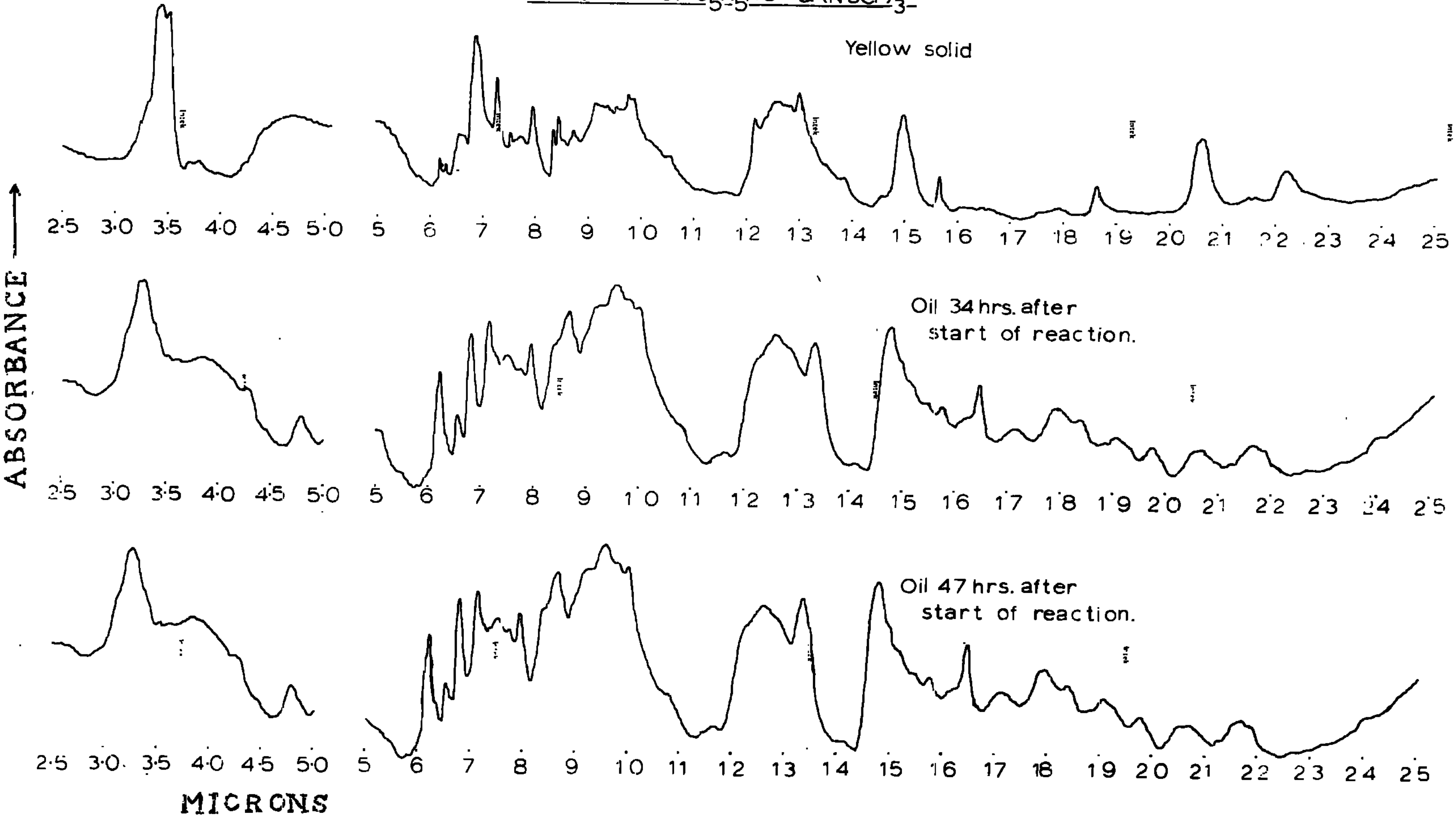
1. Solid ⟶ oil
2. Solid + solvent (as reactant or catalyst) → oil.
3. Solid + original reagent ⟶ oil.
4. Solid + other product ⟶ oil.

1) may be discounted because of the stability of the dry, isolated solid. Of course, if decomposition were thermodynamically possible, it might well not occur in the solid phase, where there are no molecular collisions, but require the presence of carbon tetrachloride. However, the stability under dry carbon tetrachloride rules out 2).

Reaction of the solid with unconsumed reagent (pyridine -1- oxide

Fig.1

REACTION of C_5H_5NO & $(NSCl)_3$



or trithiazyl trichloride) as in 3) is possible, and so is 4.). Unfortunately, their credibility cannot be further assessed without knowledge of the content of the filtrate after the removal of the yellow solid.

The solid does exhibit characteristics of a pyridine -1- oxide adduct, suggesting that 3) may produce initially only a 1:1 or 2:1 pyridine -1- oxide/trithiazyl trichloride adduct. Further addition or substitution on the sulphur-nitrogen ring and any accompanying rearrangement could produce the gradually changing oil.

(ii) b. Nature of initial oil

1. Stoichiometric Composition

The absence of initial reactants in the solution left after removal of the initial oil indicates that the oil's composition is close to $(C_5H_5NO.NSCl)n$, i.e. the stoichiometry of the reactants. This may, however, be modified due to the undetected loss of volatile products (eg. sulphur dichloride, sulphur dioxide, or hydrogen chloride).

2. Mechanism of decomposition of initial oil.

Spectral and colour changes in the oil still occur after its removal from the reaction system, and are therefore due to spontaneous decomposition (e.g. internal rearrangement). They are not due to either the solvent or to other reagents in solution.

It is still unknown whether these changes differ in detail from those occurring during the *in situ* decomposition of the oil, although they are visibly the same.

3. Nature of pyridine nucleus in oil

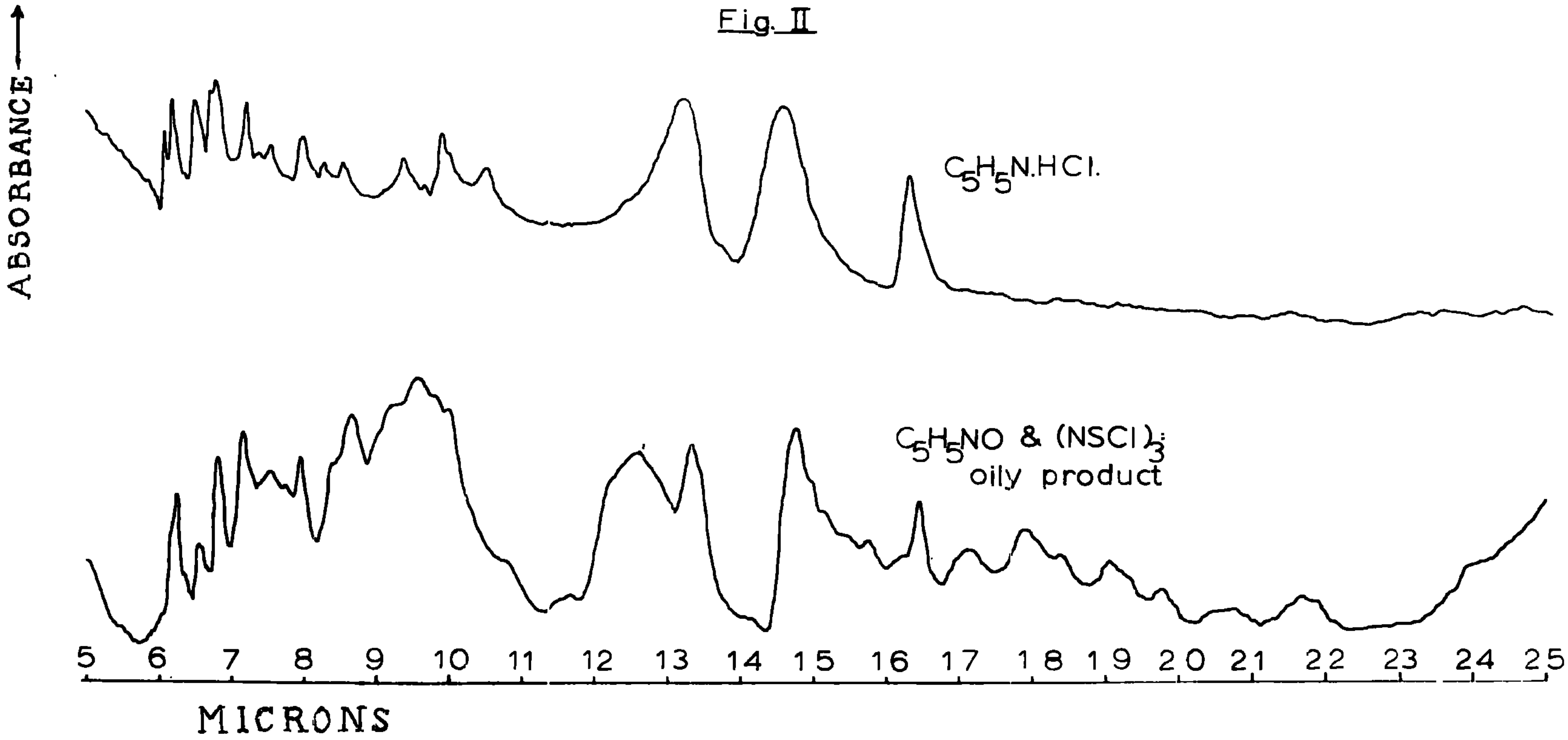
For various addition compounds of pyridine, the degree of outflow of electronic charge from the ring has been investigated.[42,43] Gill[42] investigated pyridinium compounds, where there is a large charge outflow (e.g. $C5H5NH^+Cl^-$ and $C_5H_5N^+CH_3Cl^-$), and reported characteristic infrared absorptions for such pyridine rings at 3200, 2800, 1640, 1530, 1327, and $1250cm^{-1}$, and Spinner[43] also reported pyridinium C-H bending vibrations at 680 and $750cm^{-1}$. Bands at similar frequencies to all these quoted can be found in the infrared spectrum of the oil (see Table II), and the correlation is made more obvious by comparison of this spectrum with that of pyridine hydrochloride[44] (see Fig. II).

Pyridine compounds where the charge outflow from the ring is weaker (Gill[42] describes such pyridine nuclei as "coordinated") show different infrared spectra; bands at 625 and $420cm^{-1}$, and also a weak band at 1235-$1250cm^{-1}$, are characteristic (e.g. for pyridine-halogen complexes). Such absorptions are not found in the infrared spectrum of the oil (the absorption at $1256\ cm^{-1}$ - see Table II - is strong).

It seems, therefore, that the i.r. spectrum of the oil shows indications of a large outflow of electronic charge from the pyridine ring.

A notable difference in the i.r. spectra of the yellow solid and the oil is the latter's absorption at $2597cm^{-1}$. This frequency is too

Fig. II


ABSORBANCE
C5H5N.HCl.
C5H5NO & (NSCl)3: oily product
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MICRONS

low for an ordinary C-H bond, and suggests that hydrogen bonding obtains, i.e. in going from solid to oil, the position of the pyridine α-proton with respect to oxygen has altered considerably. This, together with the change from pyridine -1- oxide adduct to pyridinium type compound evidenced by infrared spectra, suggests that a rearrangement of the type (IX) has occurred:-

a. Solid b. Initial Oil

(IX)

In case a) the hydrogen bonding will be weak if present at all; intramolecular hydrogen bonding could take place only with oxygen or chlorine, neither of which will have pronounced residual negative charge in (IXa). Intermolecular hydrogen bonding could occur, but would also be weak. These weak forces would not account for the indistinct absorption exhibited by the yellow solid at 2740 cm^{-1} (a shift of 260cm^{-1} compared with C-H absorption at 3000cm^{-1} for the parent base); the presence of moisture during preparation of the mull may provide an explanation. We cannot explain the strong absorption at 2151cm^{-1} in the solid, or the smaller peak at 2096cm^{-1} in the oil (which does not alter its intensity with time).

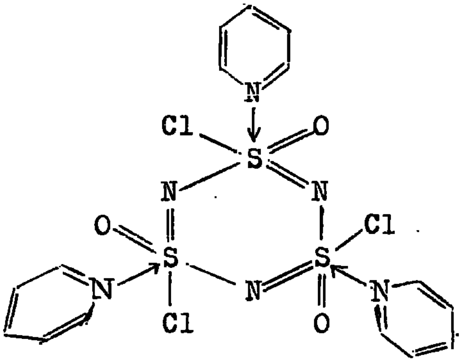
Further confirmation or otherwise of rearrangement (IX) might be anticipated from changes in the sulphur-oxygen and sulphur-nitrogen infrared absorption regions in solid and oil. The S=O region (1250-$1110 cm^{-1}$)[44] contains strong absorptions in the oil (see TableII), but the only absorptions in the i.r. spectrum of the solid can be seen from Table I to be due to vibrations of the ring in pyridine -1-oxide. The i.r. absorption region for the sulphur-oxygen single bond (840-$770 cm^{-1}$) is well populated in each case.

This suggests the formation of a sulphur-oxygen double bond, which may be accompanied by the formation of a pyridine-sulphur link.

The sulphur-nitrogen regions are more heavily populated for the oil than for the solid; in the low-frequency region, a peak appears at $751 cm^{-1}$ in the oil, and is not observed in the solid. This may be due to a new sulphur-nitrogen link. In the sulphur-nitrogen double bond absorption region (1110-$1000 cm^{-1}$) the absorptions of the oil are more intense than those of the solid (especially $1043 cm^{-1}$ - an absorption which is not due to the pyridinium nucleus.). This indicates an increase in the magnitude of the S=N dipole due to interaction between the π - systems of the pyridine and the sulphur-nitrogen rings. This is consistent with the heavy outflow of charge from the pyridine ring proposed earlier.

The bond distance, r_{SN}, corresponding to the sulphur-nitrogen absorption at $751 cm^{-1}$, can be calculated[45] from the equation $r_{SN} = 0.0483 (\mu SN) + 1.099$. Thus if the absorption at $751 cm^{-1}$ is due to a localised vibration, r_{SN} is close to 1.74 Å (the bond length in heptasulphurimide is (1.73Å),[45] and in $H_3\overset{+}{N}.SO_3^-$, (1.76Å), and indicates the pyridine nitrogen-sulphur link to be close to a single bond.

It therefore appears that, by a rearrangement process, the pyridine -1- oxide/trithiazyl trichloride reaction has produced a six membered sulphur-nitrogen ring with pyridine-sulphur and oxygen-sulphur links. Comparison with the pyridine adduct of sulphanuric chloride (X) is now undertaken.



(X)

(iii) Comparison of oil and pyridine adduct of sulphanuric chloride

These two substances differ in the ways detailed below. The differences are attributed to the relative amounts of different isomers in the compounds; the nature of these isomers, and their effects on the course of the formation reaction are then discussed:

By reacting stoichiometrically equivalent quantities of sulphanuric chloride and pyridine, both in toluene solution, Moore[46] obtained a viscous oil whose formula (from analyses) was $3C_5H_5N.(NSOCl)_3$. This oil contains predominantly complexed pyridine[47], the heavy build-up of electronic charge around sulphur being dispersed towards the more electronegative oxygen and chlorine nuclei.

The i.r. spectrum of this oil corresponds well with the oil from the pyridine -1- oxide/trithiazyl trichloride reaction over the range 4000-400cm^{-1}, but exhibits several absorptions that the latter compound does not:

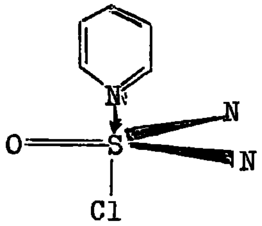
a. 1337cm^{-1} and 1307cm^{-1}, intense. Because of the dependence of infrared absorption intensities on rate of change of dipole moment,[48] this may indicate a more polar S=O bond, or merely a greater S=O content.

b. 658 vs, 569 vs, 529 vs, 523cm^{-1} vs; in a region where the oil from the pyridine -1- oxide reaction has only moderate absorptions.

Both these compounds result from reactions which are complex and slow, and the viscosity of each oil suggests extensive intermolecular forces such as hydrogen bonding. These may well interfere with the reaction rate, imposing kinetic control over the reaction's course. Furthermore, it is unlikely that interference will be similar in each case. Hence if isomers of differing stabilities exist, their relative amounts could well differ in the product mixtures from each reaction.

Nature of isomers of oil from pyridine -1- oxide/trithiazyl trichloride reaction

If the rearrangement (IX) has occurred at all three ring sulphur atoms in the oil, then each sulphur is five-coordinate, and will have a trigonal bipyramidal arrangement of bond angles (XI).



(XI)

The π -system of the ring will confer a bond order greater than one on the ring sulphur-nitrogen bonds; the sulphur-oxygen bond (in the ring plane, being the most electron-repelling species attached to sulphur) will have a bond order approaching two. Hence electron density in the ring plane about sulphur is fairly evenly distributed, so that the bond angles will be close to 120°, and the ring will approach planarity.

Two isomers would then result, one having all pyridine nuclei above the sulphur-nitrogen ring (cis isomer), and the other (trans) having one below. This ideal case may be modified if the ring only approaches, but does not fully achieve, planarity.

It is also possible that rearrangement may not occur at all three sulphurs, so that one or two sulphurs in the ring may be sulphur (with donor pyridine -1- oxide) (IV) in some product molecules. The increased donation to the sulphur-nitrogen π-system as rearrangement at one sulphur proceeds will reduce the tendency of the others to increase their electron acceptance. Yet another possible mechanistic source of isomers is ionisation of chloride during formation of solid or oil.

The gradual disappearance of certain of the solid's absorptions as the oil ages (p.24) suggests that extensive retention of donor pyridine oxide does not occur, though examination of the oil's spectrum shows that these peaks could have shrunk to merge with the background.

Effects of differing isomeric compositions in the oils

The infrared spectra of both the oil derived from the pyridine -1- oxide adduct (for the purposes of this discussion, "oil A"), and Moore's oil (B) contain absorptions indicating hydrogen bonding, which is probably between the α-proton on pyridine and the oxygen of the S=O group (see IX b). This electrostatic interaction, requiring some charge distribution between the oxygen and hydrogen, reduces the residual negative charge on oxygen, and hence the magnitude of the SO dipole. Thus not only should the S=O i.r. absorption frequency be reduced, but the intensity should diminish also.

Consequently, although the low S=O i.r. absorption intensity in A compared to B could be due to incomplete rearrangement of the pyridine -1- oxide adduct,it could also be explained if full rearrangement occurred, by stronger hydrogen bonding in A. This does occur, the C-H absorption showing greater weakening in A (frequency 2597cm^{-1} (frequency 2597cm^{-1}) than in B (frequency 2617cm^{-1})[44].

This stronger hydrogen bonding could also be due to a different isomeric composition for the oils A and B, hydrogen bonding being better accommodated in the mixture found in A.

This would limit the freedom of some or all of the S=O vibration modes more stringently in A than in B; if vibrations (e.g. bending) occurring in the region 660-520cm^{-1} were severely curtailed, the weaker infrared activity in this region for A (compared to B) could be explained. This could also be due to a reduction in the sulphur - chlorine dipole.

Course of Reaction after isomer production

Different isomeric forms of the product will decompose at different rates, probably by attack of chlorine on the C-H bonds of the pyridine rings, the distance between chlorine and pyridine units, as well as the acidity of hydrogens on pyridine, being dependent on the isomer(s). It is possible that some isomers produced in the pyridine -1- oxide reaction decompose more rapidly than the completion of rearrangement occurs, so that the formation of a product molecule such as (X) is never fully accomplished.

(iv) Summary of Arguments

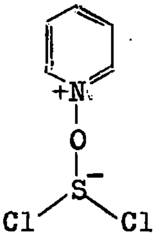
It has been proposed that initially a 1:1 or 2:1 solid pyridine -1- oxide/trithiazyl trichloride adduct forms, with no or incomplete displacement of chloride ion. This is followed by a rearrangement as in (IX), either after or during linking of a third pyridine nucleus to the sulphur-nitrogen ring. This results in a mixture of isomeric products which differs from that produced by the pyridine/ sulphanuric chloride reaction. The consequent difference in hydrogen bond strength may explain the spectral differences between the two mixtures.

However, it ought to be stressed that the preceding explanation fits experimental observation, and has not been firmly established. More data (especially analytical) is required to do this. A first step could be made, however, by reacting pyridine -1- oxide and trithiazyl trichloride in a) a 1:1 ratio , b) a 2:1 ratio , to check the theory advanced to explain the yellow solid's formation.

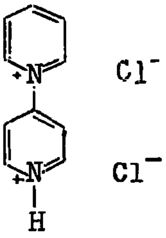
(v) Pyridine -1- oxide & Sulphur dichloride, Pyridine & Thionyl Chloride

Analyses show that the reaction products from a) sulphur dichloride/pyridine -1- oxide and b) thionyl chloride/pyridine contain no sulphur, and hence their spectra do not help in discussing the trithiazyl trichloride reaction product. The product from a) has an i.r. spectrum identical with pyridine hydrochloride,[44] except for bands at 1307, 791, and centred around 513cm^{-1}. Product b) also resembles pyridine hydrochloride, the only major difference being the band at 797cm^{-1}.

Whatever the nature of these products, these results show that sulphur (II), and sulphur (IV) in thionyl chloride, cannot (under the conditions described) form donor-acceptor adducts with pyridine -1- oxide and pyridine respectively. In case a) loss of chloride ion from intermediate (XII) is insufficient to dissipate the charge build-up on sulphur, hence a second pyridine -1- oxide molecule attacks, and sulphur dioxide forms. Displaced chloride ion could attack both coordinated and free pyridine -1- oxide at ring sites, thus affecting the analyses.

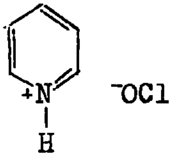


(XII)



(XIII)

The results of b) seem to depend very much on conditions. Moore[49] obtained only traces of a white precipitate on performing the reaction in carbon tetrachloride at 0°C. and later warming, and identified this precipitate as pyridine hydrochloride. However, reacting neat thionyl chloride and pyridine [50,51] at -20°C. produces 1-(4-pyridyl) pyridinium chloride hydrochloride (XIII). The infrared spectrum also resembles that of the compound analysing as C_5H_5NOCl (XIV) obtained by Moore[52a] on pyrolysis of the pyridine/ sulphuryl chloride adduct;



(XIV)

However, the thionyl chloride/pyridine product exhibits a higher spectral background and extra absorptions at 1082, 1014, and 797cm^{-1}.

It is possible that pyridine hydrochloride and also molecules

(XIII) and (XIV) are all present in the white compound obtained at -78°C. The most important point is that a stable compound with sulphur (IV) is not formed. It appears, since sulphur (IV) under these conditions cannot form a donor/acceptor complex with pyridine (cf $Me_3N.SOCl_2$, which is also unstable)[52b], that the π - system of trithiazyl trichloride must play an important part in stabilising the initial pyridine -1- oxide/trithiazyl trichloride adduct.

In conclusion, it seems that reaction of sulphur (IV) in trithiazyl trichloride with pyridine -1- oxide initially forms a simple adduct. Subsequently, this rearranges (entirely or in part) to produce a mixture of isomers of an adduct of a sulphur (VI) system similar to sulphanuric chloride.

Confirmation of these proposals requires further work, withheld in this case due to time limitations. However, it would appear that a route to sulphur (VI)-nitrogen ring systems could eventually result.

REACTION OF TRITHIAZYL TRICHLORIDE AND MERCURIC OXIDE

INTRODUCTION

The structural similarity between trithiazyl trichloride and sulphanuric chloride, in which the sulphur lone pair is replaced by oxygen, inspired an attempt at direct oxidation of trithiazyl trichloride to the sulphanuric compound.

The use of chromyl chloride, CrO_2Cl_2, as an oxidant has been reported.[53] It is capable of forming stable compounds with one, two, or three molecules of a donor such as triphenylphosphine, acetone, THF, and hydrogen sulphide.[54] An analogy to the desired oxidation ($S(IV) \longrightarrow S(VI)$) is the reaction with dimethylsulphoxide to yield an unstable adduct which, on hydrolysis, gives dimethylsulphone.

The preparation of chromyl chloride is not difficult,[55] but disadvantages arise from the expense, and the possibility that sulphur-nitrogen-chromium compounds may form. Vanadium pentoxide has also been used[56], as a catalyst in the hydrogen peroxide oxidation of sulphides to sulphoxides, but again, expense is the drawback. The same applies to argentic oxide, whose use as an oxidising agent is nevertheless well proved.[57]

A similar oxidant which might not give too serious side reactions is mercuric oxide, HgO. If one delves far enough back into antiquity, use as such,[58] especially with sulphur compounds, can be found.

Mercuric oxide is thermally unstable, and decomposes into its elements at 300°C. It was used by Bunsen[59] to convert metal sulphides to oxides, and by Vogel[60] to form sulphuric acid from sulphurous acid. Hammick[61] was able to convert sulphur dioxide to sulphur trioxide, and this was followed[62] by the reaction with disulphur dichloride to yield sulphur dioxide. Furthermore, sulphuryl chloride can be obtained by the action of mercuric oxide on thionyl chloride.[63]

EXPERIMENTAL

An excess of red mercuric oxide (general purpose reagent, Hopkins & Williams Ltd.) and trithiazyl trichloride were mixed in the same flask, dry carbon tetrachloride then being added as a solvent. Overnight stirring at room temperature left heavy black deposits on the side of the reaction flask, which also held a red solution. Immediately after decantation and evaporation, both a yellow and an orange-red solid were observed. After one hour, however, only the orange-red colour was noticeable, and an infrared spectrum was taken. Preparation of an adequate mull proved difficult. Absorption bands were seen at 1259 (m), 1075 (m), 800 (m,b), 720 (m), 700 (m), 621 (w), 515 cm^{-1} (m), and the spectrum was generally poorly defined.

DISCUSSION

The spectrum shows the features of trithiazyl trichloride, and its poor definition might be expected from the presence of excess mercuric oxide. The black deposits suggest formation of mercury and/or mercuric sulphide, and so it appears that such reaction as does occur is too vigorous. There are no spectral indications of any sulphur-nitrogen compound other than trithiazyl trichloride.

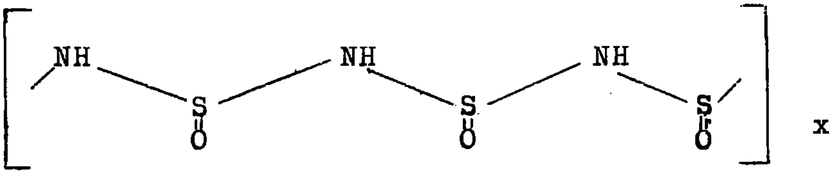
It seems, therefore, that whilst mercuric oxide can oxidise sulphur (II) and sulphur (IV), it is of no use in this case probably due to the instability of the sulphur-nitrogen ring in its presence. There seems to be little scope for modification, as the allotropic yellow mercuric oxide is, because of its smaller particle size, more chemically active than the red oxide.

REACTIONS OF TETRATHIONYLIMIDE

Thionylimide, $O{=}S{=}NH$, or "sulphinimide", is prepared by reacting stoichiometrically equivalent quantities of thionyl chloride and ammonia at low concentrations in the gaseous phase.[64,65]

$$SOCl_2 + 3NH_3 \longrightarrow OSNH + 2NH_4Cl$$

It is a gas with freezing point -85°C., and has several polymeric forms. It can be stored under low pressure for a few hours at room temperature,[66] but gradually deposits a yellow solid whose composition is as yet unknown. On warming, this solid yields the dark brown polymer (XX).[67,68]

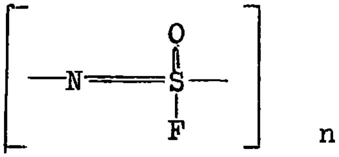


(XX)

A cyclic tetramer also exists, its ring consisting of alternate sulphur and nitrogen atoms. This tetramer was prepared and reacted with sulphuryl chloride (p.44) in an attempt to produce sulphanuric chloride, by analogy with the reaction between sulphuryl chloride and tetrathiotetraimide,[69] which produces trithiazyl trichloride.

The tetramer itself decomposes to the brown polymer above room temperature if kept for more than a few days, and had therefore to be used as soon as possible after its preparation.

It was also planned to react the tetramer with chlorine, in the hope that adjustment of ring size might produce sulphanuric chloride after hydrogen abstraction (tetrameric NSOCl is unknown, and the only known polymer other than the trimer is the acyclic.



$$\left[-N{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle F}{|}}{S}}- \right]_n$$ [70] .

EXPERIMENTAL

Preparation of Tetrathionylimide

Tetrathionylimide was prepared by Becke-Goehring's method[71]. The tetrathiotetraimide used was supplied by D. Younger, who prepared it by reduction of tetrasulphur tetranitride using methanolic stannous chloride.[72]

Tetrathiotetraimide (5 gm.) was mixed with powdered sulphur (20 gm.) in a 250 ml. flange flask. An air condenser was fitted and the temperature of the reaction flask raised to 120°, the contents being left exposed to air. Although Becke-Goehring reports exothermic reaction after fusion of the reactants, it was found necessary to continue the heat supply. A small amount of sulphur sublimed onto the upper parts of the flask, and a dark red melt formed. A sublimate began to form on the condenser, appearing red at first, then orange-red.

The reaction was stopped after three hours, and the product extracted by shaking with chilled methanol. The resulting red solution was concentrated *in vacuo*, whilst being cooled below -20°C. in an acetone/carbon dioxide bath to avoid formation of the yellow polymer.

In this way, a yellow compound was obtained in a yield so low as to be immeasurable. Its i.r. spectrum showed absorptions at 1656 (w), 1408 (m), 1160 (s), 1098 (s), 1048 (s), 1036 (m), 1016 (s), 941 (m,b), 830 (m), 819 (m), 806 (m), 725 (w), 701 (w), 668 (w), 659 (w), 594cm^{-1} (w,b). Comparison with Becke-Goehring's work[71] showed that the compound was tetrathionylimide.

Reaction of tetrathionylimide and sulphuryl chloride

The tetrathionylimide was stirred in carbon tetrachloride until most of it had dissolved to give a clear yellow solution. An excess of sulphuryl chloride was syringed into the solution, which after a few seconds adopted a dark, clear green colour. Some specks of dark solid were observed in the liquid.

Filtration separated the black solid, and the solution, when concentrated at the vacuum pump, yielded very small amounts of a dark green solid. This could not be converted into a mull, so the i.r. spectrum in carbon tetrachloride solution was obtained. Nothing other than features of carbon tetrachloride could be discerned in the spectrum excepting some activity between 1110 and 1000cm^{-1}.

Attempts to sublime out a product from the dark green solid onto a liquid nitrogen cold finger at 150°C. and 0.02 m.m. failed.

DISCUSSION

The initial green colour formed on mixing the reagents may indicate the formation of trithiazyl trichloride as an intermediate, or be due to the dark green solid eventually obtained. Although the nature of this solid is not known, there are valid arguments against proceeding further with this project. Firstly, there is no indication that the desired products have been obtained, and the difficulty in mulling the dark green solid suggests that it is far from being a pure compound.

Secondly, the yield of this solid is extremely small (0.01 gm. from 0.18 gm. tetrathiotetraimide), and that of any worthwhile constituent would be even smaller. Furthermore, the majority of the tetrathiotetraimide starting material is wasted in preparing the tetrathionylimide.

Hence even if small quantities of a desirable product were obtained, this would hardly form an improvement over preparative techniques extant for sulphur-nitrogen compounds. Since the objective of this research is to find such routes, further investigation, including the proposed reaction with chlorine, was not undertaken.

REACTIONS OF THIODITHIAZYL DICHLORIDE WITH PLUMBIC OXIDE AND ACETATE

INTRODUCTION

Numerous uses of plumbic oxide (lead dioxide, PbO_2) as an oxidant can be cited. It can oxidise vigorously, for instance with hydrogen sulphide,[73] in which combustion occurs without external heat supply, and with sulphur dioxide,[74,75] where the reaction is sufficiently exothermic to cause incandescence.

The exothermicity of plumbic oxide acting as an oxidant was investigated by Lambiev[76], who found that during the oxidation of hydrogen or carbon monoxide, the temperature of the plumbic oxide rose considerably, even though the temperature of the containing oven was controlled to within 1°C. However, this degree of exothermic behaviour is not so widespread as to limit the use of plumbic oxide. It has recently been used to prepare α,β - unsaturated ketones by oxidative decarboxylation of γ-oxo-acids,[77] and to oxidise thiols to disulphides (in aqueous or aqueous acetic acid medium).[78]

The reactions of plumbic oxide with sulphuryl chloride,[79] yielding lead sulphate, and with thionyl chloride[80] (at 150° in a sealed tube) to yield sulphuryl chloride, have been known for some time.

By reacting plumbic oxide with thiodithiazyl dichloride it was hoped to oxidise the two (NSCl) fragments contained in the molecule, and to eliminate the remaining sulphur atom by formation of lead sulphide. The two main disadvantages to this method are, firstly, that the oxidant will not be reacting in solution form, and secondly, that if reaction does occur, it may be so exothermic that desirable products cannot be obtained.

These disadvantages prompted consideration of plumbic acetate as an oxidant in the event of lack of success with plumbic oxide. Reactions can be conducted in solution, and its well-documented oxidising action is not so vigorous as that of plumbic oxide.

Plumbic acetate can be used as a specific oxidising agent, for instance in the preparation of disulphides from thiols.[81] However, the specificity depends greatly on the reaction medium,[82] disulphides being oxidised further to sulphones[83] if the correct solvent mixture is chosen.

The mechanism of oxidation by plumbic acetate was claimed by Kharasch et al[84] to involve free radicals (acetate and lead triacetate), but both Criegee[85] and Mosher[86] proposed ionic species as intermediates. Criegee postulated that oxidation of double bonds occurs via addition of acetate ion folowed by attack of the cation $[Pb(OAc)_3]^+$. Field,[87] working on the specific oxidation of disulphides to sulphinic esters, proposed that what appeared to be the reacting species $[Pb(OAc)_3]^+$ was in fact a combination of plumbous acetate and acetoxonium ion.

Barron[88] found both ionic and free radical oxidations by plumbic acetate; di-n-butyl sulphide is oxidised to the sulphoxide most efficiently in polar solvents (by acetoxonium ion), whereas phenols and benzyl ethers are oxidised by a free radical process. Thus plumbic acetate can provide either acetate radicals or acetoxonium ions.

Whereas solvents of high dielectric constant encourage the ionic mechanism and those of low dielectric constant facilitate free radical reactions, both radicals and ions may form in a solvent with medium dielectric constant. Thus if a substrate has more than one site of attack, both species may react, resulting in a non-specific oxidation.[88]

EXPERIMENTAL

(i) Thiodithiazyl dichloride and plumbic oxide

Thiodithiazyl dichloride (2 gm.), prepared as previously described, was stirred in dry carbon tetrachloride (125 ml.) until dissolved, and a small amount of plumbic oxide (BDH Laboratory Reagent) added. The resulting dark brown slurry contained a few light-coloured specks of solid, but these were probably due to sulphur impurities in the thiodithiazyl dichloride.

Neither heat nor gas evolution was observed, and so the amount of plumbic oxide was made up to the 1 : 1 reactant ratio (2.4 gm.). Filtration yielded a pale brown-green solution which on evaporation produced a dirty yellow solid. The solid's infrared spectrum showed peaks at 1266 (s), 1099 (s,b), 1020 (s,b), 935 (m), 812 (m,sh), 799 (s), 726 (m), 697 (s), 553 (m), 545cm^{-1} (ms). The absorptions at 1099, 1020, 812 and 799cm^{-1} are due to silicone grease contamination, and the other peaks were characteristic in position and shape of tetrasulphur tetranitride.

(ii) Thiodithiazyl dichloride and plumbic acetate

Plumbic acetate was prepared from red lead and glacial acetic acid as described by Brauer,[89] and recrystallised from glacial acetic acid. Though not air sensitive, it was handled under nitrogen to avoid hydrolysis.

REACTION OF THIODITHIAZYL DICHLORIDE AND PLUMBIC ACETATE

(a) Using acetic Anhydride solvent

Thiodithiazyl dichloride (0.73 gm.) and plumbic acetate (1.9 gm.:- 1 : 1 stoichiometry based on the hoped for equation:- $3Pb(OAc)_4 + 3S(NSCl)_2 \longrightarrow 2(NSOCl)_3 + 3PbS + 6Ac_2O$) were stirred in separate large volumes (100 ml.) of acetic anhydride ("AnalaR", analytical reagent) to achieve dissolution, though a certain amount of solid remained in the sulphur compound's solution. The plumbic acetate was added to this solution by syringe; after a small amount had been added, a dirty green colour developed. This quickly gave way to yellow, and the solid matter went into solution.

A white solid formed in the solution, having a silky appearance when stirred, and was separated by filtration. It dissolved in nitric acid to form a solution which yielded a white precipitate with silver nitrate solution, and a yellow colouration with sodium chromate solution, indicating the presence of lead chloride.

The clear filtrate was evaporated to dryness <u>in vacuo</u> at 50°C., leaving a yellow solid. Within an hour, much of this solid had become orange in colour, but small amounts of yellow solid were obtainable, showing infrared absorptions at :- 1264 (s.), 1156 (m), 1052 (ms), 736 (w,sh), 720 (w), 700 (m), 681 (m), 677 (m), 564 (m), 466cm^{-1} (ms). Contamination by silicone grease obscured the regions 1100-1000 and 830-770cm^{-1}. The spectrum of the orange solid showed it to be the result of partial hydrolysis of the yellow compound; it exhibited the same peaks less distinctly, with extra absorptions due to moisture.

Because of this contamination, analyses were not obtained.

Action of Acetic anhydride on $S_3N_2Cl_2$

A small amount of thiodithiazyl dichloride was stirred for two hours in acetic anhydride, and the solvent removed in vacuo. The infrared spectrum of the dark red solid showed absorptions at 977 (m), 946 (s), 718 (s, sh), 712 (s), 699 (s), 585 (m), 580cm^{-1} (w), 457 (w), 431cm^{-1} (m), which showed it to be thiodithiazyl monochloride, S_3N_2Cl.[90] Small traces of contaminants may be responsible for the red colour, as the colour of the pure monochloride is green.[91]

(b) Reaction using Ether as Solvent

Ether was chosen for its higher volatility cf. acetic anhydride, despite inferior solvent ability for thiodithiazyl dichloride. Thiodithiazyl dichloride (0.25 gm.) and plumbic acetate (0.6 gm.) were each stirred in dry diethyl ether (50 ml. in each case). Most, but not all of the $S_3N_2Cl_2$ dissolved. In ether, the solid plumbic acetate became yellow, but on removal of ether the colour faded, and the solid was found (by infrared spectrum) to consist of unchanged starting materials.

The plumbic acetate solution was syringed into the flask containing thiodithiazyl dichloride; at first, a slight reduction in the brown-orange colour was observed, and then deposition of a dark brown solid. Stirring was continued for one hour, during which the colour of the solution changed through golden yellow to red. After filtration, the dark solid was found to have a featureless infrared spectrum; it evolved hydrogen sulphide gas (identified by smell only) when added to dilute nitric acid, and formed a yellow solid when sodium chromate was added to the nitric acid solution.

On evaporation of the filtrate *in vacuo*, a solid deposit, with black and dark red components, was obtained. It would not form a mull, so that an infrared spectrum was not obtained.

The reaction was repeated; all traces of undissolved reactants having been previously removed by filtration. A light brown solid was deposited, again with featureless infrared spectrum, and the reaction solution filtered off whilst still yellow. Evaporating this solution to dryness gave an upper ring of red solid on the sides of the flask, with brown and black deposits below this. All these substances showed the same infrared absorptions:- at 1264 (s), 1202 (m), 1170 (m), 922 (s), 726 (s), 698 , 546cm^{-1} (s). These peaks are characteristic of tetrasulphur tetranitride.

Action of diethyl ether on $S_3N_2Cl_2$

Stirring $S_3N_2Cl_2$ in ether produced a black solid, which, after filtration, was identified by infrared spectrometry as thiodithiazyl monochloride, S_3N_2Cl.

DISCUSSION

(i) Thiodithiazyl dichloride and Plumbic Oxide

Reaction has occurred to produce tetrasulphur tetranitride probably without involvement of the plumbic oxide, since the formation of tetrasulphur tetranitride or thiotrithiazyl chloride (S_4N_3Cl) is common on addition of thiodithiazyl dichloride to any of a wide range of solvents.[92]

It appears, therefore, that plumbic oxide does not oxidise thiodithiazyl dichloride or tetrasulphur tetranitride under the conditions employed. This may be because of a considerable thermodynamic disadvantage or at least high activation energy, due to the high lattice energy of lead dioxide.

(ii) Thiodithiazyl dichloride and Plumbic acetate

a. In acetic anhydride

The formation of lead chloride immediately suggests the reaction

$$S_3N_2Cl_2 + Pb(OAc)_4 \longrightarrow S_3N_2O_2 + PbCl_2 + 2Ac_2O.$$

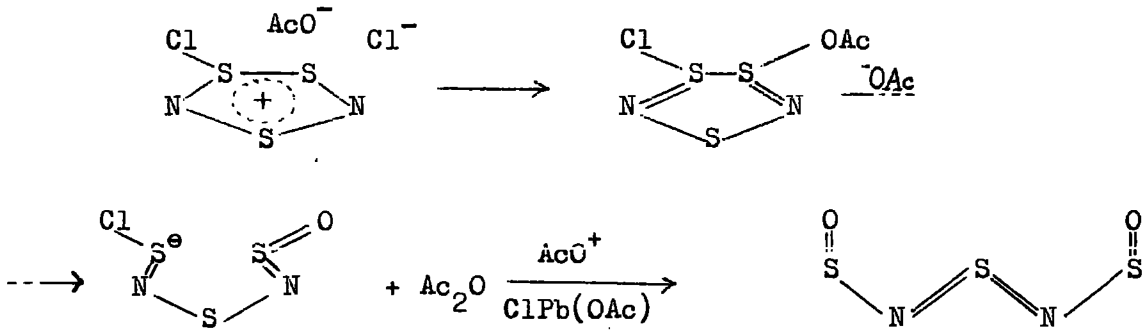
The infrared spectrum of the yellow solid shows considerable similarity to that of $S_3N_2O_2$,[90] particularly in the relative intensities of the absorptions, but differences in absorption frequency are noticeable:-

ν cm^{-1}

Yellow solid	Comparable peaks in $S_3N_2O_2$
1264 (s)	1183 (s)
1156 (m)	1162 (m)
1052 (ms)	1041 (ms)
736 (w,sh)	
720 (w)	720 (w)
700 (m)	682 (m)
681 (m)	655 (m)
677 (m)	555 (w)
564 (w)	503 (w)
466 (ms)	

In spite of the differences in frequency between the spectra, the overall qualitative similarity does suggest the formation of thiodithiazyl dioxide or some closely related compound. Perhaps spectral alterations were due in part to the partial hydrolysis.

Acetic anhydride has a dielectric constant of 20.7 at 19°C.[93], which compares with 2.24 (20°) for carbon tetrachloride, 35.74 for nitrobenzene (20°), and 80.37 (20°) for water. It may well, therefore, be capable of acting as a medium for both acetate radicals and acetoxonium ions. However, in view of the ionic nature of thiodithiazyl dichloride,[94] the reaction mechanism is more likely to involve ions than free radicals. A possible route is suggested below, based on the proposals of Field[87] and Criegee.[85]



The red colour observed late during the reaction may be due to the presence of a coloured decomposition product, possibly formed by reaction of some acetate radicals from plumbic acetate.

Because of the recovery of thiodithiazyl monochloride from acetic anhydride solution of the dichloride, it cannot be certain that thiodithiazyl dichloride is in fact the reacting species. However, since the monochloride is probably polymeric,[95] it is unlikely that it can exist in solution. It is, therefore, probably the dichloride which reacts.

b. Reaction of Thiodithiazyl Dichloride and Plumbic Acetate in Diethyl Ether

The tetrasulphur tetranitride obtained from the ether could have arisen in two ways:-

(i) Reaction of thiodithiazyl dioxide with damp nitrogen,[96] and/or

(ii) Plumbic acetate removes two chlorines and one sulphur from the $S_3N_2Cl_2$ molecule, and the remaining molecular fragments combine to form tetrasulphur tetranitride.

This different set of products may be due to a free radical rather than ionic reaction (dielectric constant of diethyl ether = 4.34 at 20°).

Conclusion

Indications are that a sulphur-nitrogen-oxygen compound has been produced. However, the yellow solid product's very high susceptibility to hydrolysis and its ambiguous infrared spectrum cast uncertainty over its nature. Also, choice of an adequate solvent is a problem, although the desired reaction path can be seen to occur better in polar solvents.

PREPARATION AND REACTIONS OF TRISULPHIMIDE SALTS

INTRODUCTION

The work undertaken on trisulphimide salts can be divided into three sections; the preparation of sulphamide, its use to prepare sulphimide salts, and attempts to chlorinate these salts to produce sulphanuric chloride.

a. Sulphamide, $SO_2(NH_2)_2$

The first of the numerous preparations of sulphamide was reported in 1838,[97] and utilised the action of gaseous ammonia on an excess of sulphuryl chloride in an inert solvent. This and other methods[98,99] based on the same principle did not provide any pure sulphamide. However, they and all subsequent preparations have involved ammonolysis of sulphuryl compounds or chlorosulphonyl imides.

The pure compound was eventually obtained[100] by having the ammonia, not the sulphuryl compound, in excess, and in spite of a reported high yield using gaseous ammonia,[101] better yields are generally obtained using the liquid. The other reagent commonly chosen is sulphuryl chloride, though sulphur trioxide[102] and sulphuryl fluoride[103a] have also been used. The fluoride gives sulphamide even with aqueous ammonia, but its high toxicity[103b] and corrosiveness make it hazardous to use.

In the sulphuryl chloride reaction, yields are low in the absence of precautions, due to the facility with which addition reactions (rather than the desired condensation reaction) can occur during the overall reaction. It is thought that sulphamide is formed by the reaction sequence:-[104]

$$SO_2Cl_2 \rightleftharpoons SO_2Cl^+ + Cl^-$$

$$SO_2Cl^+ + NH_3 \longrightarrow SO_2NH_2^+ + HCl$$

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$SO_2NH_2^+ + NH_2^- \longrightarrow H_2N.SO_2.NH_2$$

However, like sulphur trioxide, with which it is isoelectronic, the SO_2Cl cation is a strong Lewis acid, and tends to undergo addition reactions as well as the required condensation reaction. Hence a number of products other than sulphamide is to be expected.

b. <u>The Trisulphimides</u>

Sulphimide itself, SO_2NH, is not known, and the salts originally thought[98] to be derived from it were later shown[105] to be derived from the cyclic trisulphimide $(SO_2NH)_3$. The trisulphimide system is obtained from the pyrolysis of sulphamide, most closely studied by Ito;[106] above about 120°, two reactions occur:-

(i) $2SO_2(NH_2)_2 \longrightarrow NH_4N(SO_2NH_2)_2$ (imidodisulphamide)

I II

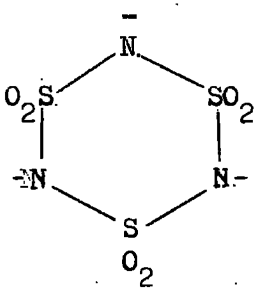
(ii) $3NH_4N\ (SO_2NH_2)_2 \longrightarrow NH_2(NH_4NSO_2)_2SO_2NH_2 + (NH_4NSO_2)_3$

II III IV

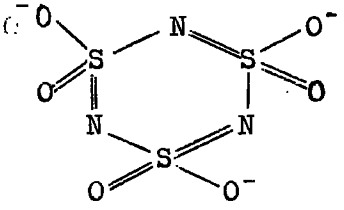
Reaction (ii) becomes effective above 170°, and at 200° complete conversion to the ammonium trisulphimide occurs at the expense of III, ammonium N,N' disulphonamidosulphamide, which is also produced in (ii). Metal salts are preparable from aqueous ammonium trisulphimide solution, e.g. those of thallium, lead, mercury, cobalt, and silver.[107] The silver salt has been shown by X-ray crystallography to have a planar, six-membered ring anion composed of alternating sulphur and nitrogen atoms.

Free trisulphimide, $(HNSO_2)_3$, has not been isolated, though it can be prepared and kept for some hours as a dilute aqueous solution.[105,109] It can be isolated in a polymeric form as a dipyridinium salt[109], and appears to be a tribasic acid[109] from which the third proton cannot readily be removed.

The importance of trisulphimides as a potential source of sulphanuric chloride is illustrated by consideration of the canonical forms (XV) and (XVI):-



(XV)



(XVI)

Although both canonicals will contribute to the electronic structure of the anion, (XVI) will be the more important due to the greater electronegativity of oxygen compared with nitrogen. If this acid anion could be converted, by typical routes, to the acid chloride, sulphanuric chloride would be obtained.

c. Sulphanuric chloride from trisulphimide anions

Moore attempted to react both silver and ammonium trisulphimides with thionyl chloride.[110] In the first case, no reaction was observed. In the second, reaction occurred only in the presence of small traces of dimethylformamide in the reaction mixture. The product, however, was an ammonium compound similar to the starting material. In each case, the salt had been refluxed for some hours under an excess of thionyl chloride.

Work undertaken for this thesis utilised two trisulphimide salts, one (barium) of high lattice energy and the other (sodium) of comparitively low lattice energy. Reactions were conducted using chlorinating agents under various conditions.

EXPERIMENTAL

a. Preparation of Sulphamide

The method used is based on that of Degering & Cross,[111] reacting sulphuryl chloride with excess liquid ammonia.

Purification of ammonia

To liquid ammonia (450 ml.) in a round-bottomed flask (Il.), prevented from evaporating by cooling in a carbon dioxide/acetone bath, sodium metal was added until a permanent deep blue colour was obtained (indicating that sodium was dissolving as such in ammonia, having reacted with all moisture).

Pure ammonia was then obtained by allowing the flask to warm to room temperature whilst connected to a closed, evacuated system to which a second, empty flask, cooled in carbon dioxide/acetone, was attached.

Reaction of ammonia with sulphuryl chloride[111]

$$SO_2Cl_2 + 2NH_3 \longrightarrow SO_2(NH_2)_2 + 2HCl$$

Liquid ammonia (400 ml.) was placed in a 2-litre round-bottomed flask, to which were connected (a) a vertical condenser with phosphorus pentoxide drying tube; (b) a dropping funnel with phosphorus pentoxide drying tube; and (c) a nitrogen supply, flowing out via the condenser, and admitted close to the dropping funnel.

The whole was immersed in a carbon dioxide/acetone bath at -50°C., and the ammonia stirred very vigorously. Two aliquots of sulphuryl chloride (each of 25 ml.), each in pentane (250 ml.) were added slowly (each over about four hours) so that the ammonium chloride mist that evolved during the addition only occasionally left via the top of the condenser. The nitrogen flow assisted in preventing the mouth of the dropping funnel becoming blocked by deposits from the ammonium chloride mist.

The resulting transparent lime green solution was exposed to the atmosphere, and left to warm overnight, so that the ammonia evaporated to leave an off-white solid beneath the pentane. After removal of the pentane in vacuo a mixture of crude, pale yellow sulphamide, side products, and ammonium chloride remained. This solid was vacuum-dried for four hours at 70°C., and the chain-type imido compounds (formed as side products) hydrolysed to sulphamide by (i) dissolution in 10% hydrochloric acid (250 ml.), and (ii) immersion in a water bath at 80°C. for ten minutes.

The liquid phase was then removed, and the residual solid thoroughly dried, by heating at 80-90° in vacuo. The off-white solid was then shaken with Analar acetone (5 x 30 ml.), the resulting solution being decanted and evaporated at the pump. This yielded a pale yellow-brown solid, which was recrystallised from absolute alcohol, and left beneath the supernatant liquid overnight. Filtration followed by drying yielded a white solid showing infrared absorptions at 3174 s; 1613 w,sh; 1543 m; 1332 s,sh; 1157 s; 1134 ms,sh; 933 m; 920 m,sh; 720 ms; 557 ms,b; 526cm^{-1} ms,b. This showed[44] the solid to be sulphamide. Found : S, 32.0; N, 29.03; H, 4.33. Required for $SO_2(NH_2)_2$: S,33.3; N, 29.13; H, 4.13. Weight of sulphamide = 13.85 gm. ie. yield = 23.7%.

b. Preparation of Ammonium Trisulphimide

Sulphamide (13 gm.) was slowly heated in a 100 ml. flask immersed in an oil bath, the oil coming to just above the level of the sulphamide. The sulphamide melted at about 90°C., after which the temperature was raised to 180° over one hour. An increase to 200° was effected over the second hour, and this temperature maintained for five hours more.

On cooling, a hard, dark brown mass was obtained. This was dissolved in 0.88 ammonia, and the dark solution boiled with decolourising charcoal. Filtration gave a clear, yellow-tinted solution.

Preparation of Barium Trisulphimide

An excess of barium chloride solution (aqueous) was added to a portion of the ammonium trisulphimide solution, and a white precipitate immediately formed. After filtration, the precipitate was washed first with water and then with acetone. The infrared spectrum is described in table III.

The compound was oven-dried at 90°C. for 48 hours; reduction of the moisture absorptions in the i.r. spectrum showed this to have removed much, but not all, of the water of crystallisation.

No melting was observed on heating, though a yellow colouration was observed above 250°C., perhaps due to total destruction of the ring, and formation of elemental sulphur. The yield (1.74 gm.) based on sulphuryl chloride was only 8,2%, possibly because pyrolysis of sulphamide was not complete.

Preparation of sodium trisulphimide

a. Choice of cation exchange resin

The resin is required to extract ammonium ions from solution, replacing them with sodium ions. Two factors operate; the strength of attachment of the cations to the anionic functional groups of the resin, made up of both an electrostatic and covalent contribution; and the difference in solvation energy between sodium and ammonium cations in solution (another electrostatic factor). Both (opposing) electrostatic influences apply equally to strongly and weakly acidic resins, and sodium will undergo the stronger interactions.

However, sodium, being more able to polarise anionic charge than is the larger ammonium ion, will have a greater covalent contribution to the forces linking it to a weakly acidic anion (strongly acidic anions will be less liable to extensive polarisation); hence the ammonium ions will displace sodium ions more readily on a strongly acid resin. Two resins (Zeo-Karb 226, SRC 46, mesh 52-100 - weakly acid, and Zeo-Karb 225, mesh 40-80 - strongly acid) were tried to see whether the difference in effectiveness of the two types of resin was noticeable.

b. Preparation and use of column

Each of the resins was supplied in the hydrogen form, and converted to sodium form by leaching with excess 10% sodium hydroxide solution.[112b] This was followed by backwashing with distilled water overnight to clean the resin and to allow it to pack uniformly.

The ammonium trisulphimide solution was used immediately after its acquisition in the pure form, being split into two parts, and runs conducted with each resin. The solution was allowed to pass slowly down each column, the resin then being washed with two bed volumes of distilled water.

The resulting solutions, each evaporated <u>in vacuo</u>, yielded a white solid, which was vacuum-dried at 60°C. for three hours. Its infrared spectrum (see table III) was characteristic of trisulphimides, and whilst showing some N-H absorptions, showed the compound not to be ammonium trisulphimide. The vivid yellow colouration imparted to the bunsen flame by the solid showed sodium to be present.

Analysis showed :- For Zeo-Karb 225,

%N = 21.4% (in $(NH_4.NSO_2)_3$ %N = 29.2%, in $(Na.NSO_2)_3$ %N = 13.9%).

The nitrogen percentage after using Zeo-Karb 226 (sodium form) was 23%, signifying the more strongly acid resin to be the more effective. The exchange appears to have been incomplete, but some sodium trisulphimide had been obtained. A more dilute solution of ammonium trisulphimide would appear to have been desirable.

Before describing the reactions of these salts, it is appropriate to comment on the comparison of their infrared spectra. Table III shows that whilst the infrared spectra of the silver, ammonium, and sodium salts are very similar, that of the barium salt is different (although a qualitative resemblance is shown - see fig. III). The

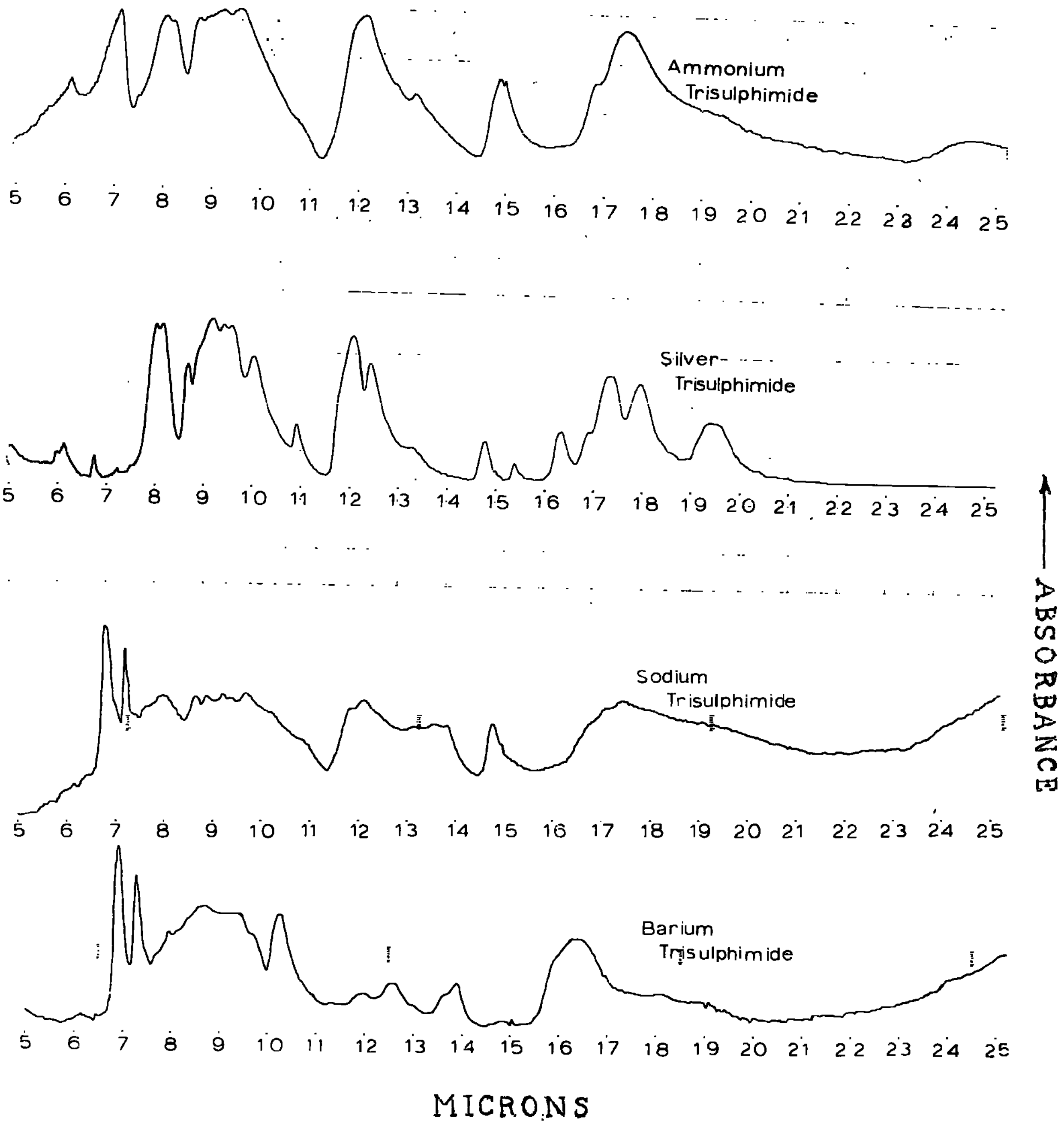
TABLE III - TRISULPHIMIDE SALTS

Infrared Absorptions cm^{-1}

Ammonium Trisulphimide[44]	Sodium/Ammonium Trisulphimide *	Silver Trisulphimide Trihydrate[44]	Barium Trisulphimide*
3425 sh		3650 s	
3175 vs	3175 vs		3106 mw
3030 vs			
2841 sh	2732 m		2762 mw,b
1634 m	1626 w	1637 w	1634 vw
1404 vs	1439 s		1351 ms
	1290 s,sh	1282 s,sh	
1242 vs	1250 vs	1244 vs	1256 s
1217 sh		1218 vs	
	1152 vs	1149 vs	1156 vs
1143 vs	1123 vs	1115 vs,sh	
1081 vs	1085 vs	1090 vs	1065 vs
1047 vs	1027 vs	1042 vs	
		1005 s	
966 m,sh	948 m,sh	990 m,sh	978 vs
	840 s,sh	837 s,sh	840 w
825 vs	824 vs	823 vs	792 m
760 ms	760-722 s,b	756 m,b	728 w,sh
672 s	676 s		720 w
667 s	669 s	664 m,b	
595 s,sh	594 s,sh	590 s,sh	619 s,sh
575 vs	571 vs,b	571 vs	613 vs
		554 s	553 m,b

* = this work.

Fig. III.


Ammonium
Trisulphimide
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
Silver-
Trisulphimide
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
Sodium
Trisulphimide
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
Barium
Trisulphimide
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
MICRONS
ABSORBANCE

higher polarising power of the Ba^{2+} ion (charge/radius for Ba^{2+} = 1.48; cf. Na^{+}, 1.05; NH_4^{+}, 0.70)[113] is probably responsible, causing greater distortion of the π - system of the anion. This in turn causes a change in bond strengths which may affect the symmetry of the anion, and thereby the infrared selection rules.

c. Trisulphimide salts with thionyl chloride and phosphorus pentachloride

Barium Trisulphimide and Thionyl Chloride

Barium trisulphimide (0.6 gm) was stirred vigorously in dry carbon tetrachloride (15 ml.) in one limb of a Schlenk at room temperature. Thionyl chloride (10 ml.) was added by syringe, and a pale green colour observed. Gas was evolved without vigour, but had virtually ceased after ninety minutes.

The liquid was taken through the Schlenk sinter, and when evaporated *in vacuo* left no residue whatsoever.

The white solid was found(by infrared spectrum) to be barium trisulphimide, unchanged except for a slight reduction in the moisture content.

The reaction was repeated in the absence of carbon tetrachloride, the mixture of trisulphimide (0.6 gm.) and thionyl chloride (20 ml.) being refluxed for 24 hours. Again, no reaction was observed, but a degree of satisfaction was derived from the substantial reduction in water of crystallisation shown by the infrared spectrum.

Barium Trisulphimide and Phosphorus Pentachloride

(i) in solution

Barium trisulphimide (0.73 gm.) and an excess of phosphorus pentachloride (2.8 gm.) were stirred in carbon tetrachloride (15 ml.) at room temperature. No visible indication of reaction resulted, so the reaction temperature was increased to 66°C. for 19 hours. Filtration produced a colourless filtrate which on evaporation gave a white solid. The infrared spectrum of the solid is compared with that of phosphorus pentachloride in table IV:-

TABLE IV

Absorptions cm^{-1}

White Solid	Phosphorus * Pentachloride
1302 w	1302 w
	1258 w
1149 w	1149 w
1095 w	
	1029 w
820 m	
803 m,sh	
	719 w
717 s,sh	
702 s	
	683 w
647 vs,b	643 vs
585 vs,sh	582 m,sh
579 vs	577 ms
	451 vs

* = this work.

(ii) in sealed tube

Under an atmosphere of nitrogen, barium trisulphimide (0.7 gm.) was placed in a glass tube fitted with side-arm and breakseal, and an excess of phosphorus pentachloride added. The tube was evacuated, and heat applied to seal the side-arm. It was then immersed in oil whose level exceeded that of the solid mixture, and the temperature raised to 140-145° for five days.

A yellow liquid was observed above the white trisulphimide, and some pale yellow crystals formed on the glass above the melt. After cooling, the tube was opened to release a gas identified by its infrared spectrum as sulphur dioxide. On grinding, the solid contents of the tube yielded a pale yellow powder. Analysis showed this powder to contain no sulphur. The infrared spectrum showed the solid to be phosphorus pentachloride, with indications of P = O (absorbing at $1307 cm^{-1}$)[114] and PN (at 1180 and $700 cm^{-1}$).[115]

Sodium/Ammonium Trisulphimide and Phosphorus Pentachloride

(i) in solution

The trisulphimide salt (0.26 gm.) was stirred vigorously in carbon tetrachloride (75 ml.) containing phosphorus pentachloride (1.24 gm., four times theoretical equivalent) at room temperature. No sign of reaction was observed, so the temperature was raised to 80°C. As the temperature increased, the salt became more finely divided, making the solution cloudy.

Soon after commencement of refluxing, however, the solution became clear, and a lump of solid formed at the base of the flask. After separation by filtration, this "solid" appeared to be a pale yellow, syruppy semi-solid (which did not solidify on heat <u>in vacuo</u>) covering a hard, white solid.

Evaporating the filtrate to dryness yeilded a white solid whose infrared spectrum showed it to be phosphorus pentachloride, with no traces either of trisulphimide or sulphanuric chloride.

(ii) <u>in sealed tube</u>

Sodium/ammonium trisulphimide (0.55 gm.) and phosphorus pentachloride (0.50 gm., slightly more than required for $(NaNSO_2)_3 + 3PCl_5 \longrightarrow (NSOCl)_3 + 3NaCl + 3POCl_3$) were mixed in a glass tube (fitted with side-arm and breakseal) which was sealed <u>in vacuo</u>.

The tube was heated gradually (in view of the excessive reaction with the barium salt) until the phosphorus pentachloride fused (130°C.). However, after fourteen hours, the trisulphimide salt could still be seen to be unreacted. On raising the temperature further, no reaction was observed below 150°C., when small amounts of a white sublimate formed on cooler parts of the tube.

On cooling, an orange-brown solid was observed beneath a dark brown liquid. Opening the tube to the vacuum line released sulphur dioxide (identified by infrared spectrum). On distilling <u>in vacuo</u>, a clear liquid was collected from the residue of the tube. This liquid showed infrared absorptions at 1470 (s), 1379 (m), 1307 (s), 1085 (m), 730 (vs), 719 (vs), 623 (vs,b), 482 cm^{-1} (m); This coincides exactly with the infrared spectrum of phosphorus oxychloride.

Removal of this liquid left a pale yellow-brown solid, which was very difficult to mull and gave an indistinct infrared absorption spectrum with high background. Distinguishable peaks appeared at 1335, 1174, 1163, 1022, 978, and 733cm^{-1} (the last peak strong and broad - the strengths of the other peaks were difficult to estimate due to the background).

The mass spectrum of this compound exhibited peaks up to mass number of 430, contrast $(NSOCl)_3$ which shows[116] parent peak at 291, with P + 2 and P + 4 also present. These peaks are not observed for the yellow-brown solid, nor does it exhibit the peaks at 260, 258, and 256 as required for sulphanuric chloride.[116] Indications of phosphorus (31) and chlorine (35 and 37) are present, but none of sulphur - a peak at 32 must be due to oxygen, as no isotopic peak at 34 is observed. (Although any peak at 34 due to sulphur would have only 4.4% intensity cf. the peak at 32, no peak whatsover is observed here).

Reaction of Sodium/Ammonium Trisulphimide and Thionyl Chloride

The mixture of trisulphimide salts (1.50 gm.) was stirred in refluxing thionyl chloride (40 ml.) at 70° for six days. This yielded a transparent red solution above a mass of small, yellow, needle-like crystals, themselves above lumps of unreacted trisulphimide. After filtration, the yellow solid and red solution were treated separately.

a. Treatment of yellow solid

Attempts to recrystallise from hot carbon tetrachloride failed, but it was possible to "decant" the yellow compound from the unreacted starting material. On drying in vacuo, a pale yellow solid was obtained.

Attempts to recrystallise from hexane, toluene, cyclohexane, methylcyclohexane, benzene, and thionyl chloride were fruitless. The infrared spectrum is compared to that of sulphanuric chloride[44] in table V and Fig. (IV).

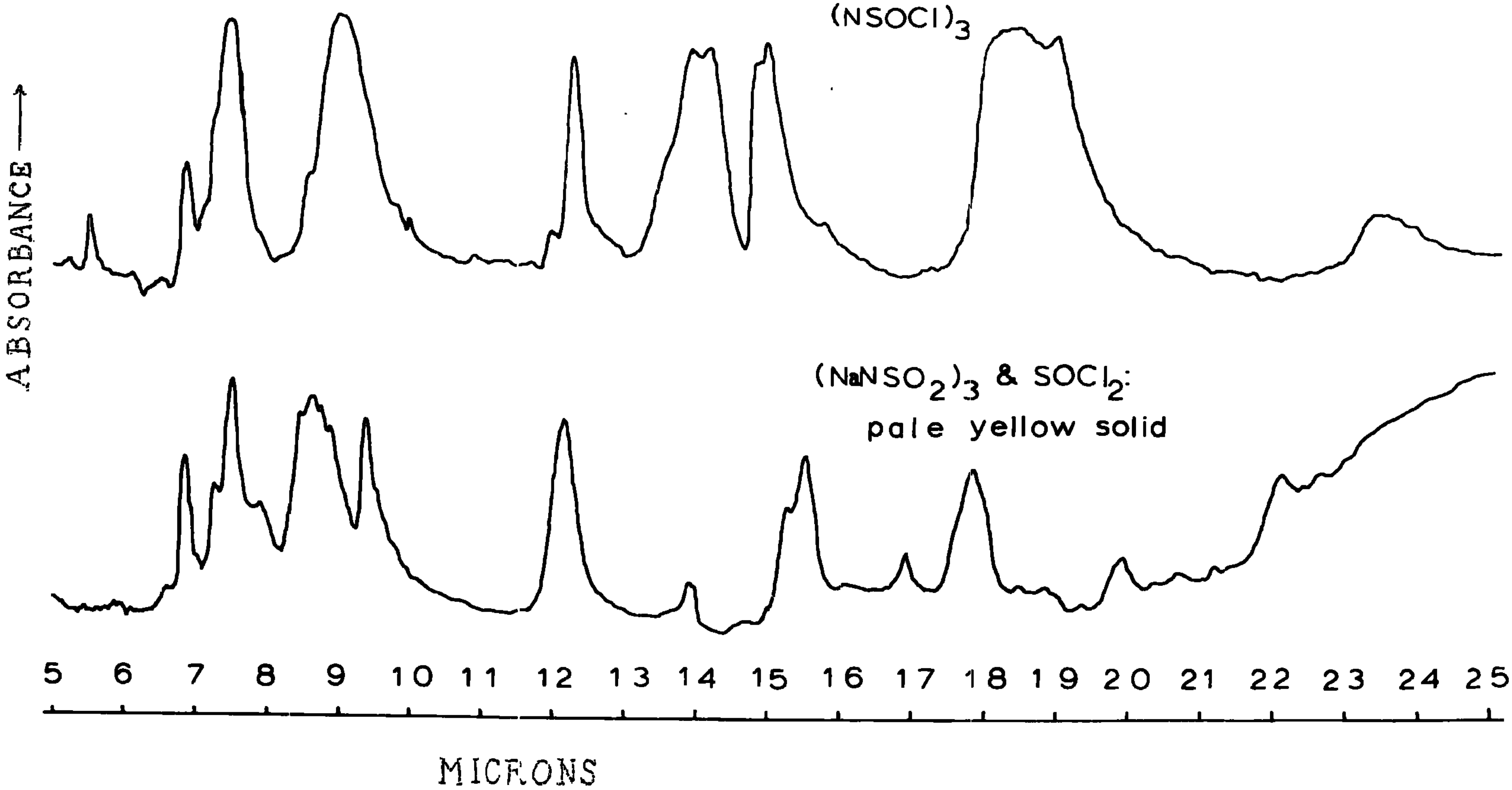
TABLE V

Absorptions cm^{-1}

Yellow Solid	Sulphanuric Chloride	Yellow Solid	Sulphanuric Chloride
	1815 w	822 s	814 s
1330 vs	1335 vs	719 w	717 s
1266 m	1267 w	717 w	705 s
1182 s		655 sh,m	672 s
1160 vs	1167 sh,m	644 ms	668 s
1143 s	1112 vs		635 sh,w
1127 s		591 w	
1065 s		561 ms	543 vs,b
1060 sh,m	1025 sh,w	502 w	525 vs
1005 sh,w	1012 sh,w	452 ms	
	912 w		

The solid was subjected to heat at 150° under a pressure of 0.005 mm.Hg, and small amounts of a red sublimate collected on a liquid nitrogen cold-finger, the yellow solid becoming off-white. The infrared spectrum of this off-white solid showed only slight merging

Fig. IV


$(NSOCl)_3$
$(NaNSO_2)_3$ & $SOCl_2$:
pale yellow solid
ABSORBANCE →
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
MICRONS

of closely-spaced peaks, indicating only slight decomposition. The spectrum of the red sublimate showed it to be thiodithiazyl monochloride (see p. 51).

Within thirty minutes of the pale yellow compound's exposure to air, decomposition to a darker yellow compound occurred. The infrared spectrum showed all original peaks above $1000 cm^{-1}$ to have merged and to be accompanied by moisture (1460 and $1550 cm^{-1}$), and continuous absorption over the range $1000-400 cm^{-1}$, with maxima around 870 and $550 cm^{-1}$.

The pale yellow solid had not melted in a sealed capillary at 320°C., though was coloured deeper yellow. Reversion to pale yellow occurred on cooling. Analyses gave

S, 37.2; Cl, 10.4 or 8.45; N, 14.82; H, 0.79.

- indicating atomic ratios $S_4N_{3.7}Cl$.*

In a flame, the yellow solid gave rise to a vivid orange/yellow colouration.

Mass spectrum of yellow solid

Peaks occurred at most mass numbers up to 200, and above at intervals. Consideration of the mass spectrum is therefore postponed until the discussion .

---

* Owing to the unknown ratio of sodium to ammonium cations, analyses can only be used to predict relative amounts of sulphur, nitrogen, and chlorine, and not to find entire empirical formulae.

b. Treatment of red solution

On removal of approximately 20% of the thionyl chloride in vacuo a small amount of yellow crystals was deposited, sufficient to obtain an infrared spectrum after isolation. Absorptions appeared at 1757 (m,b) 1408 (s); 1272 (s); 1167 (ms); 1048 (m); 1004 (s); 799 (m); 683 (m); 609 (w); 581 (m); 565 (s); 539 (w,sh); 536 (w); 469cm^{-1} (s). The bands at 1167, 1004, 683, 609, 565, and 469cm^{-1} are characteristic of the thiotrithiazyl cation, $S_4N_3^+$. Insufficient solid was obtained for analysis.

Further concentration yielded a more substantial deposit; the supernatant solution was removed by syringe, and the solid washed with thionyl chloride (2 x 3 ml.) and carbon tetrachloride (5 ml.). Drying in vacuo yielded an orange-yellow solid whose infrared spectrum proved equivalent to that of the solid obtained on completely evaporating the thionyl chloride solution. The total amount of this solid was only a small fraction (approx. 1%) of the quantity of pale yellow solid described earlier.

The infrared spectrum of the orange-yellow solid contained peaks at 1332 s; 1264 m; 1156 m,sh; 1127 s,sh; 1101 vs; 1064 s,sh; 1032 s,sh; 978 m; 800 m; 713 m,sh; 703 s; 651 w; 625 ms; 606 m; 554 m; 504 s; 441cm^{-1} vs,b. The compound analysed to S, 56.9%; N, 21.06%; H, 1.75%; Cl, 2.54% which for a single compound would suggest the atomic ratios $S_{24}H_{24}N_{21}ClO_{15}$, taking oxygen to constitute the 17.74% of substance unaccounted for by analyses. It was moisture-sensitive, becoming brown on exposure to the atmosphere.

DISCUSSION

i. Barium Trisulphimide and phosphorus pentachloride

The product from the reaction in carbon tetrachloride solution shows infrared absorptions which tables III and IV show to be due to neither of the starting materials, at 1095, 820, 803, 717 and 702cm^{-1}. These are to be compared with absorptions at 1112, 814, 803, 717, and 705cm^{-1} in sulphanuric chloride.[44] Other regions in which sulphanuric chloride absorbs are masked in the product spectrum by phosphorus pentachloride. That coincidence of peaks is not exact suggests that the desired chlorination of the trisulphimide anion may have taken place at some but not all of the ring sites.

However, the sealed tube reaction appears to have destroyed the sulphur-nitrogen ring, overcoming the high lattice energy of the salt of a doubly charged, small cation. Refluxing thionyl chloride cannot accomplish this, however, and no reaction occurs.

It seems, therefore, that the desired result should be achievable in a solution reaction. However, in view of the difficulty (due to time and yield) in obtaining barium trisulphimide, work on the salt was not continued beyond this point. The thionyl chloride and sealed tube reactions indicate that matching of reaction conditions with the stability of the salt (e.g. as indicated by lattice energy) is very important, the balance between destroying the sulphur-nitrogen ring and leaving it unharmed being delicate.

ii. Sodium/ammonium trisulphimide and phosphorus pentachloride

The absence of reaction in phosphorus pentachloride solution is surprising considering that the barium salt reacted, and that salts of a singly charged cation such as sodium should have smaller lattice energies than those of doubly charged cations like barium. The difference between the infrared spectra of the two salts suggests that the anions have different conformations; the spectrum of the sodium/ammonium salt resembles that of silver trisulphimide (whose anion is planar)[108] more closely than does the spectrum of the barium salt (see table III and fig. III). It appears that the more highly polarising barium cation distorts the π-system of the anion and destroys its planarity; this may somehow encourage the reaction. It was in view of the failure of this reaction that the reagents were fused in the sealed tube (even though the destruction of the sulphur-nitrogen ring seemed likely, having occurred with the barium salt).

Reaction with thionyl chloride

(a) Nature of yellow solid

The pale yellow solid formed as the major product of this reaction appears, from its melting point and insolubility in organic solvents, to be ionic and/or polymeric in nature. In spite of its additional insolubility in polar thionyl chloride, the well-defined, reproducible infrared spectrum suggests that it is monomeric, and moreover a single compound. This is supported by the only small changes in the infrared spectrum after the vigorous attempt at sublimation; a mixture with constituents decomposing at different rates, might be expected to show considerable changes. The sublimate obtained may be due either to slight impurity or to partial decomposition of the pale yellow solid. One must be circumspect over firmly concluding that only one major compound is present; the only absorptions not due to the anion in the infrared region are those due to the ammonium ion. The infrared spectrum will not show whether or not the proportion of ammonium ion is the same in each molecule present.

The compound's infrared spectrum shows a strong resemblance (see table V) to sulphanuric chloride, which indicates the possible retention of the sulphur-nitrogen ring. The main differences lie in the sulphur-oxygen double-bond region (1270-1100cm^{-1}, more complex in the yellow compound and indicating more than one type of doubly-bound oxygen) and the sulphur-chlorine region (from 720-500 cm^{-1}; S-Cl absorptions have not yet been systematically assigned), which is less active in the yellow compound.

Because of the uncertainty of relative amounts of different cations in the product, analyses can be of little help beyond indicating sulphur/nitrogen/chlorine ratios.

A structure is now suggested for the product by considering the possible reaction mechanisms and their products, in view of the above observations and of the mass spectrum of the pale yellow solid.

Mass spectrum of pale yellow solid

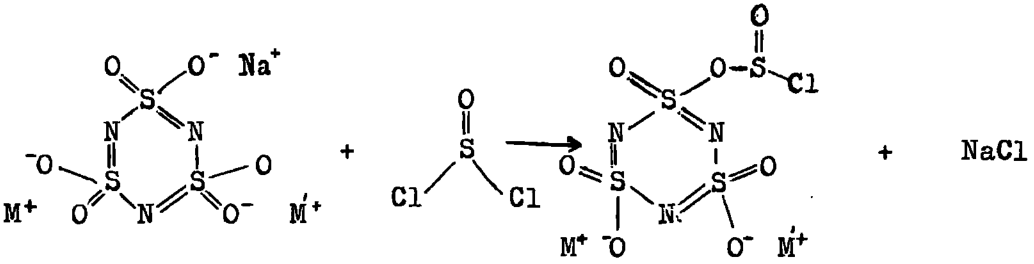
A complication frequently encountered in the mass spectrometer used for this work is the emergence of several peaks due to long forgotten samples, removed into the ion beam at last after a long sojourn adsorbed on the source. Three peaks, unfortunately at the higher end of the spectrum, may be due to this - at 402 (intensity relative to 100% peak at 46 : 25), 331 (rel. int. 12), and 252 (rel. int. 20).

The peak at 402 is the largest of a small group beyond which nothing appears, and does not show a chlorine isotope pattern (approx. 3:1 ratio between peak and peak + 2), although analyses show chlorine to be present. The peak at 252 is characteristic of many mass spectra run on the departmental machine,[117] and cannot be satisfactorily explained in terms of the reagents used here. The peak at 331 may be invalid (in spite of a P + 2 peak as required for chlorine at 333, rel. int. 4) for reasons given below. Only a few weak peaks, between 275 and 285, are observed between these three peaks, whereas there is much activity from 210 downwards.

The presence of ammonium is proved by intense peaks at 18 and 17 (rel. int. 84 and 250 respectively). The mass spectrum of a salt is not expected to show peaks due to cation and anion combined.

Possible Mechanisms

It seems likely that the first step for all mechanisms will be attack on thionyl chloride by anionic oxygen :



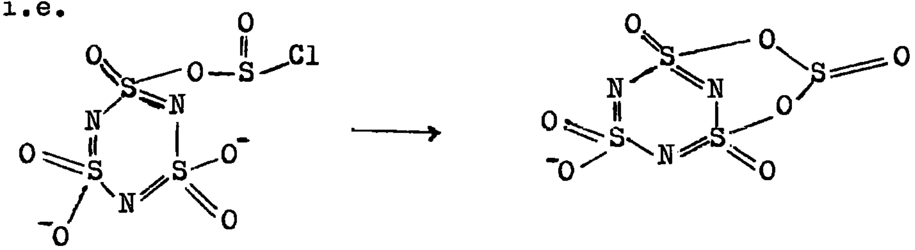
(XVII)

(M or M′ = Na or NH_4)

Possible subsequent steps are :-

1. Intramolecular cyclisation

i.e.

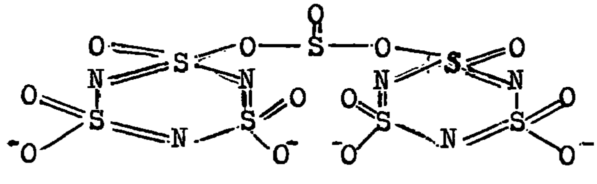


(XVIII)

Such a step forms a second six-membered ring which may well be stable. However, the infrared spectrum of a molecule such as (XVIII) would not be expected to resemble that of the monocyclic sulphanuric chloride, and also does not explain the chlorine content of the product evidenced by analyses.

2. Polymerisation of (XVII) and trisulphimide anions

Polymerisation, e.g. by attack on the exocyclic sulphur of (XVII) by an anionic oxygen of another trisulphimide anion would yield (XIX).



(XIX)

This may polymerise further. Three factors militate against formation of (XIX): (i) the well-defined infrared spectrum, which is not characteristic of a polymer, (ii), the absence of chlorine (although chlorine could be present, after such a reaction, as SO_2Cl end groups (as in XVII)), (iii) the mass spectrum: A cationic fragment derived solely from removal of electrons from (XIX), should have a mass number of 516. No peak is observed here. Even rupture at the link between the rings could produce at most only a fragment (one ring plus O_3S link) of mass No. 298. Neither here nor at other mass numbers which would result from other reasonable fragmentations are any peaks in fact observed. Thus any extensive polymerisation seems unlikely.

3. <u>Formation of (XVII) as product</u>

It appears that only one exocyclic SO_2Cl group has attached to the sulphur-nitrogen ring from the chlorine analysis of 10.4% (for (XVII), Cl content is about 11%, and with a second exocyclic SO_2Cl group, nearly 17%).

Furthermore, although a second exocyclic group would confer mass 401 on the parent ion, the peak observed at 402 exhibits no chlorine isotope patterns.

It therefore appears that only one site per ring is attacked by thionyl chloride.

Comparison of (XVII) with data:-

i. Mass spectrum

This could be explained in terms of (XVII) as follows:-

The exocyclic SO_2Cl group detaches from the parent fragment without formation of a parent peak, and appears at mass numbers 99 and 101 (rel. int. 20 and 7 respectively), exhibiting the required chlorine isotope pattern. The largest peak observable due to breakdown of the remaining cyclic fragment ($N_3S_3O_5$) is N_2SO_2 (peak at 92, rel. int. 22). The remaining fragment, NS_2O_3 (mass 126) does not appear as such, but in the form of NSO (at 62, rel. int.33) and SO_2 (at 64, rel. int. 30).

ii. <u>analyses</u>

For one or two ammonium cations, (XVII) gives percentage compositions as follows:-

$M = M^{i} = NH_4$: S 40.2; N, 22.0; Cl, 11.2; H, 2.5.

$M = Na$, $M^{i} = NH_4$: S 39.6; N, 17.3; Cl, 10.99; H, 1.2.

Found : S 37.2; N, 14.8; Cl, 10.4; H, 0.79.

Approximate agreement is obtained if one sodium and one ammonium cation per molecule are accepted. Several possible explanations for discrepancy exist; firstly, it is possible that not all molecules contain both sodium and ammonium cations; (see p.64); secondly, the fate of the sodium chloride produced after the first proposed reaction step has not been determined - some may not have remained with the unreacted trisulphimide; thirdly, some reaction between ammonium cations and thionyl chloride may have occurred (as in the reaction of ammonium chloride and disulphur dichloride, which produces thiodithiazyl dichloride[30]) - this may account for the secondary products obtained from the thionyl chloride solution (see later).

This last possibility might explain the high sulphur and nitrogen figures.

iii. Infrared spectrum

Structure (XVII) is consistent with an infrared spectrum similar to sulphanuric chloride. Differences would be expected in the form of a more complex series of S = O absorptions, which is observed between 1270 and 1110cm^{-1} (see table V), and a difference in S—Cl absorptions (which may account for the spectral differences between 720 and 450cm^{-1}).

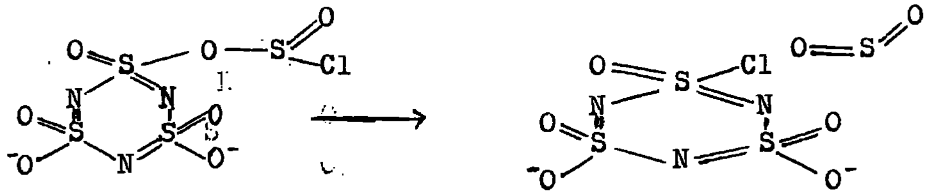
iv. Physical properties

The high melting point and general insolubility of the pale yellow solid could be ascribed to the ionic nature* of two of the three ring sulphur atoms in (XVII). The sulphur-chlorine bond in the attached group —OSOCl may be principally responsible for the moisture sensitivity.

The most powerful argument against (XVII) is that a second trisulphimide anion might be expected to attack the -OSOCl group under the conditions used here (cf. pyridine, which attacks thionyl chloride at -78°C. :- see pg.19). However, a large excess of thionyl chloride, such as was used here, may cause each trisulphimide anion to react with thionyl chloride alone, and not with a second ring.

4. Intramolecular rearrangement of (XVII) to form product

i.e.



(XVII) (XX)

Species (XX) would explain infrared spectra and physical properties as well as would (XVII). It can also be accommodated in the mass spectrum:- the intact anion (XX) would give rise to a cationic species of mass 253. This parent peak is not observed, but the breakdown of the ring can be traced through N_2SO_2 (at 92, rel. int. 22), NSO (62, rel. int. 33), and SO_2Cl (at 99, and 101). However, it is difficult to see how an SO_2Cl fragment can derive from (XX). Chlorine cannot be detected in quantity in any other form; a small peak exists at 35 (rel. int. 5), but at 37 the relative intensity is 35. Thus most chlorine appears as SO_2Cl, suggesting that any contribution from species (XX) must be small.

Analyses for (XX) agree only very poorly with those found experimentally:

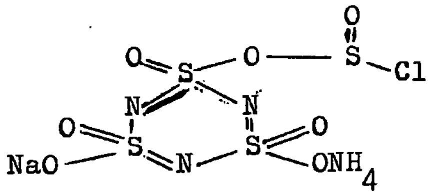
for two ammonium cations : S,32.2; N,24.2; Cl,12.3; H,2.6.

for one sodium, one ammonium cation: S,32.6; N,19.02; Cl,12.3; H,1.4.

experimentally : S,37.2; N,14.82; Cl,10.4; H,0.79.

In the absence of further likely mechanisms, a choice between (XVII) and (XX) remains. Analyses and mass spectra suggest (XVII) to be the product; the appearance of SO_2Cl cationic fragments in the mass spectrum, and the weak chlorine peak, argue against (XX).

Small amounts of (XX) would explain the high nitrogen and slightly high chlorine analyses, but on the basis of this work, the major product appears to be (XXI):



(XXI)

(b) Products from Thionyl Chloride Solution

Two compounds were obtained, one on slight concentration of the thionyl chloride solution, and the other on further concentration. The first compound is shown by its infrared spectrum to be a thiotrithiazyl compound, and other absorptions can be attributed to the halosulphate anion. Paul et al ,[118] in reporting thiotrithiazyl chlorosulphate, attributed absorptions at 580, 1040, 1180, and 1260cm^{-1} to the anion; these are to be compared with 581, 1048, 1167, and 1272cm^{-1} in the spectrum of the compound obtained here.

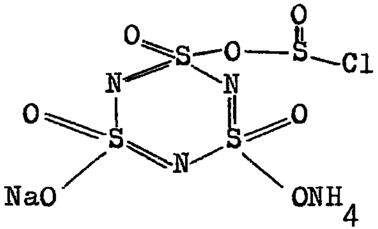
The second compound obtained from thionyl chloride solution is more difficult to identify. The very low percentage of chlorine suggests it to be a mixture, and traces of both tetrasulphur tetranitride and thiodithiazyl dichloride are observed in the infrared spectrum. The presence of thiodithiazyl dichloride can also be inferred from the monochloride obtained on sublimation; House[119] found that attempts to sublime thiodithiazyl dichloride lead to formation of the monochloride. Some sodium chloride will have dissolved in the thionyl chloride, and may account for the chlorine analysis.

Further time was not devoted to the identification of these products, as they are only minor constituents of the reaction product, and probably result from interaction between ammonium cations and thionyl chloride.

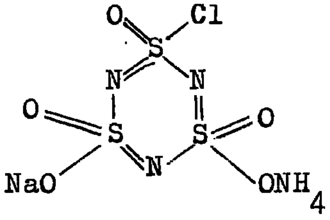
Summary

Indications are that sulphanuric chloride could eventually be obtained by solution reactions of trisulphimide salts. The more directly promising of the results achieved was using barium trisulphimide. However, there is reason to suppose that the yield of this salt might in general be low, and that its lattice energy could make the yield of sulphanuric chloride even lower. However, a repeat reaction using a 1:3 ratio of barium trisulphimide and phosphorus pentachloride in refluxing carbon tetrachloride would be interesting.

The product from the reaction of the ammonium/sodium trisulphimide salt appears to consist mainly of the compound (XXI), with smaller quantities of compound (XX), and other sulphur-nitrogen compounds in even smaller quantities, formed by reaction between thionyl chloride and ammonium cations. Neither of the above structures can explain the previously mentioned peaks at 331 and 333, and we cannot at this stage attribute them to anything other than some foreign species in the mass spectrometer.



(XXI)



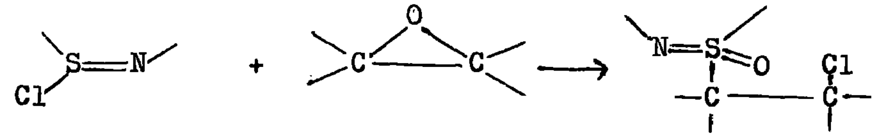
(XX)

Further work on this project should begin by attempting to find a more efficient preparation of sodium trisulphimide, perhaps simply by passing ammonium trisulphimide solution much more slowly down the ion-exchange column, or perhaps by fusing sulphamide (m.p. 91·5°) and sodium chloride,[120] and subliming out ammonium chloride.

REACTION OF TRITHIAZYL TRICHLORIDE AND THIOCYANATES

INTRODUCTION

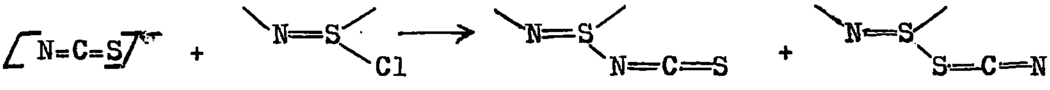
Trithiazyl trichloride has been found to react with various substances containing multiple bonds or strained systems. For example, previous work has shown that it behaves as a sulphenyl chloride, RSCl, with epoxides,[121] with which it reacts as below:-



It also behaves as a source of thiazyl chloride, N≡S—Cl. This has been utilised in reactions with various nitriles,[122] e.g. benzonitrile and trichloroacetonitrile, producing the compounds $S_2N_2CClC_6H_5$ and $S_2N_2C_2Cl_4$ respectively. These compounds probably contain five-membered sulphur-nitrogen-carbon rings (see p.2 &89) and have potential chemotherapeutic importance. A similar product results using tetrachloroethylene[123] (see p.88).

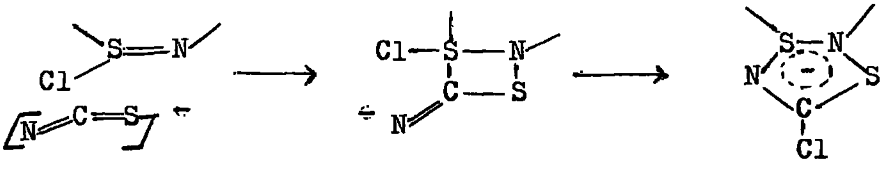
The title reaction was undertaken in the hope that similar reactions to the above might occur. For instance;

1: simple elimination of potassium chloride to produce compounds (XXII);&2: and copolymerisation might lead to another five-membered ring as ino. in (XXIII).



1.

(XXII)



2.

(XXIII)

Potassium thiocyanate reacts with chlorophosphazenes (phosphonitrilic compounds)[124] to produce isothiocyanate derivatives (cf.reaction no.1):

$$(PNCl_2)_{3,4} + 6(8)KSCN \longrightarrow [PN(NCS)_2]_{3,4} + 6(8)KCl.$$

Moore[125] attempted to react sulphur - chlorine links (in sulphanuric chloride) instead of phosphorus - chlorine links,with potassium thiocyanate.The product obtained was not fully characterised owing to extensive polymerisation.

Thus there are drawbacks which may extensively reduce the worth of the trithiazyl trichloride/potassium thiocyanate reaction. However,since the salt can be readily obtained,it was planned to carry out an initial experiment and proceed only if some readily isolable non - polymeric species were obtained.

EXPERIMENTAL

Potassium thiocyanate (0.974 gm.) (BDH Laboratory Reagent) was oven-dried at 70°C. for three days, finely ground, and added to a stirred solution of trithiazyl trichloride (0.81 gm.) in carbon tetrachloride (25 ml.) at room temperature. A dark green colouration was observed on the surface of the crystals, but this disappeared as stirring continued. Evaporation of the solvent *in vacuo* left a solid whose infrared spectrum showed absorptions compared below with those of the starting materials :-

TABLE VI

Absorptions cm^{-1}

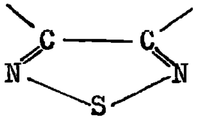
Trithiazyl Trichloride	Solid	Potassium Thiocyanate
	2045 (vs)	2045
1076	1076 (s)	
1016	1016 (vs)	
	971 (s)	971
	954 (s)	954
800	800 (s)	
	749 (s)	749
	738 (s,sh)	739
700	700 (m)	
621	621 (w)	
	549 (w)	
515	515 (m)	
	485 (s)	485
	471 (ms)	471

The table illustrates that only unreacted starting material had been retrieved. In the absence of early positive signs of reaction, the work was discontinued. It may be that deposited potassium chloride coated the solid potassium thiocyanate, preventing further reaction. It would be interesting to repeat the reaction in a more polar solvent which dissolves potassium thiocyanate and (unlike many polar solvents) is unaffected by trithiazyl trichloride (e.g. nitrobenzene, or possibly acetic anhydride).

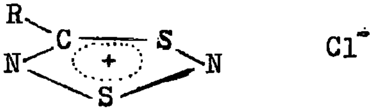
PREPARATION AND PROPERTIES OF "DITHIADIAZOLES"

Nature of "Dithiadiazoles"

The inverted commas about the word "dithiadiazole" are intended to point out that at this stage, work on them has largely, but not completely identified them as such. Their proposed structure is most similar to the 1, 2, 5 - thiadiazoles[5] (XXIV) with a second carbon atom of the five-membered ring replaced by sulphur (XXV); whether the chlorine can be associated with any one ring site or is fully ionised is not yet known, but it seems that full ionisation is not achieved, the chlorine remaining associated with one of the two sulphur atoms (see p.89)



(XXIV)



(XXV)

The first dithiadiazole preparation resulted from the work of Banister,[123] who heated a solution of trithiazyl trichloride in tetrachloroethylene, obtaining orange crystals, whose analyses suggested the empirical formula $S_2N_2C_2Cl_4$. Use of olefins containing hydrogen gave too vigorous a reaction.

A compound showing the same infrared spectrum resulted from the reaction between trithiazyl trichloride and trichloroacetonitrile[122] (which suggested that the CCl_3 group might be present), and the use of benzonitrile gave compound(s) S_2N_2CClPh[122] (Ph= phenyl); the infrared spectrum of this compound exhibits minor variations depending on the experimental conditions (discussed in more detail under "Experimental").

Evidence has been collected[126 a–e] to show that the structure of these compounds is as in (XXV), with a phenyl or trichloromethyl group attached to the carbon atom of the ring. The five-membered ring is indicated by the mass spectrum,[126a] and by the resemblance between the infrared spectra of these compounds and the 1, 2, 5-thiadiazoles.[126b]

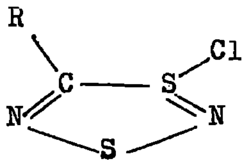
The weak absorption at $1600cm^{-1}$ suggests a CN bond order close to two, though it is very weak, possibly due to π- delocalisation over the ring. Its position varies depending on the preparative method (see later).

Both S_2N_2CClPh and $S_2N_2C_2Cl_4$ have high melting points (231-40° and 213° respectively),[126c] are each crystalline and involatile,[126c] and dissolve best in polar solvents.

The compound $S_2N_2CPh_2$ can be prepared[126d] by the reaction of phenyl lithium or diphenyl mercury and S_2N_2CClPh, and forms as black crystals. These crystals appear to be photosensitive[126e] (again of potential importance, e.g. in agriculture), and in their decomposition produce diphenyl disulphide. This important reaction suggests that, since a phenyl group is attached to sulphur in the product, so may have been the chlorine in S_2N_2CClPh. Hence either (a) this picture of an ionic molecule is partly tempered by some localisation of the chloride ion at one of the two ring sulphur atoms, or (b) the fully ionic halide gives rise to covalent derivatives, the exchanged group being attached to a sulphur atom.

Thus while it appears on the basis of experiments to date that the compounds S_2N_2CClPh and $S_2N_2C_2Cl_4$ are ionic or covalent dithiadiazoles, confirmation is awaited in the form of an x-ray structural analysis on $S_2N_2C_2Cl_4$, now in progress.[127]

Reactions of dithiadiazoles



Should the dithiadiazoles have the above structure, one might expect them to show a resemblance to the sulphenyl chlorides, RSCl. However, some reactions of dithiadiazoles are not typical of sulphenyl halides, possibly due to high polarity of the sulphur-chlorine bond, or even to ionic chloride. For example, the compounds S_2N_2CClR do not react with either diphenyl acetylene or tetrachloroethylene; both of these react with sulphenyl chlorides.[128,129]

Aims of work on dithiadiazoles

These are twofold, the first concerning the reaction between trithiazyl trichloride and tetrachloroethylene:- the identification of secondary products not hitherto undertaken. The second aim is to prepare air-stable, moisture-stable derivative (s) of $S_2N_2C_2Cl_4$ and S_2N_2CClPh, which may or may not exhibit biological activity.

In deciding upon possible ways of achieving this object, the dithiadiazoles were considered as being similar to sulphenyl chlorides; the reactions of sulphenyl chlorides were then surveyed, and the chance of successfully applying each to dithiadiazoles considered. Five main classes of reaction could be distinguished:

1. Reaction with salts (MX)

Such a reaction might attach the anion (X^-) of the salt to the dithiadiazole ring, the metal chloride precipitating out:

$$RSCl + MX \longrightarrow RSX + MCl\downarrow$$

For instance, phenols react with sulphenyl halides:[130]

$$RSCl + PhOH \longrightarrow RSC_6H_4OH + HCl$$

However, because of possible chlorination of the phenol by the dithiadiazole and protonation of the dithiadiazole ring, phenols could lead to complications which might be avoided with sodium trichlorophenolate. Ketimines have also been reacted with sulphenyl chlorides,[131] both lithium and magnesium ketimine salts giving sulphenyl ketimines.

2. Reactions involving active hydrogen

Numerous reactions of sulphenyl chlorides involve active hydrogen. Aromatic hydrocarbons are induced to form diaryl sulphides in the presence of aluminium trichloride[132] (Friedel-Craft reaction), though such a catalyst may induce side reactions with dithiadiazoles. Acetone forms stable derivatives of sulphenyl chlorides,[133] as do both ammonia[134] and amines.[135] However, the use of reactions involving such active hydrogen is to be avoided, due to uncertainty over the effects that would result on the dithiadiazole ring, and possible difficulties over separation from other products (e.g. amine hydrochloride).

3. Reduction of sulphenyl chlorides

Potassium iodide,[128] mercury,[136] and zinc[137] have been used to extract halogens from sulphenyl halides to form the disulphides, a reaction which should be convenient to perform. Potassium thiocyanate has also been used,[138] but the danger of polymerisation discourages its use here.

$$\mathrm{RSCl} + \mathrm{KSCN} \longrightarrow \mathrm{RSSCN} + \mathrm{KCl}$$

4. Use of diazomethane derivatives

i.e. $\mathrm{Ar_2CN_2} + \mathrm{RSCl} \longrightarrow \mathrm{RSCAr_2Cl} + \mathrm{N_2}$.[139, 140]

This reaction has no obvious large drawbacks; the preparation of diphenyldiazomethane[141] consists of two relatively straightforward stages: first, the refluxing of benzophenone, absolute ethanol, and hydrazine; second, reaction of the resulting benzophenone hydrazone with mercuric oxide. The method is of general use.

5. Other reactions

There still remain numerous other reactions[142] of sulphenyl chlorides which may provide stable derivatives of dithiadiazoles, but which are more specific in nature than those already mentioned; for instance, the reaction with organic disulphides: 2,4-dinitrobenzenesulphenyl chloride has been found[143] to react as follows:-

$$\mathrm{ArSCl} + \mathrm{RSSR} \longrightarrow \mathrm{ArSSR} + \mathrm{RSCl}$$

However, the possible lack of general applicability of such methods discourages their use.

From this catalogue of some reactions of sulphenyl chlorides, the reactions with ketimine salts, mercury, and diazomethane derivatives appeared to be most promising. Time only permitted attempts at the first two reactions, plus the reaction with acetone, attempted because of its convenience.

EXPERIMENTAL

1. Reaction of Trithiazyl trichloride and tetrachloroethylene

The procedure due to Banister and Caygill[123] was used, trithiazyl trichloride (4.05 gm.) being stirred at room temperature in tetrachloroethylene (25 ml., an excess, which had been purified by distillation onto, and storage over, anhydrous magnesium sulphate). A vertical water-cooled condenser was fitted to the reaction flask, and the temperature of the system, which was flushed with dry nitrogen, raised to 60°C. After three hours the liquid had become red in colour, and the solid appeared to be orange. After twenty four hours a few, mainly needle-shaped orange-brown crystals formed on the condenser.

Reaction was ceased after forty eight hours, the amount of solid in the condenser not having increased. The condenser was removed, and the crystals it contained dried *in vacuo*. The remainder of the reaction mixture was separated by filtration to give a red solution and an orange solid. The infrared spectrum of the solid showed absorptions at 1278 sh, 1264 w, 1052 s, 1020 sh, 909 w, 856 m, 814 s, 760 m, 723 w, 675 s, 669 sh, 542 m, 535 sh, and 515 cm^{-1}, w. This shows[44] the compound to be $S_2N_2C_2Cl_4$, as expected from previous work.[123]

Treatment of crystals from condenser

When collected after drying, this solid was seen to consist of both orange-brown crystals, and a pale yellow, flakey solid. These were separated manually, and their infrared spectra compared with the infrared spectra of other sulphur-nitrogen compounds.[44] This showed the compounds to be thiodithiazyl dichloride and trithiazyl trichloride respectively; the orange-brown crystals contained 49.1% sulphur ($S_3N_2Cl_2$ requires 49.2%).

Treatment of red solution

This solution, observed in one run to deposit nothing[123] and in another[144] to form red, needle-like crystals which turned white on exposure to air, was in this work concentrated *in vacuo*. During the evaporation, the colour became dark green, and some specks of a similarly coloured solid were observed. However, on stopping evacuation, and admitting nitrogen to the system, the red colour returned. Further concentration produced a blood-red tar, which did not yield solid on addition of hexane.

Hexane was removed by pumping, and the tar redissolved in carbon tetrachloride (10 ml.). After two days of standing in a refrigerator (at -10°C.), a small amount of solid was deposited, and on filtration found to be yellow. Its infrared spectrum showed absorptions at 1724 (vs), 1629 (w), 1196 (m), 958 (w), 872 (s), 823 (vs), 806 (vs), 742 (w,b), 722 (w), 674 (w), 649 (m), 636 (m), and 438cm^{-1} (w) (excluding absorptions due to silicone grease). Analyses showed C, 17.25; N,8.26; Cl,61.1; S absent, indicating atomic ratios $C_5N_2Cl_6$. However, these analyses total only 86.61%, and no oxygen is present in the reactants. This may be due to contamination during the isolation of the tar.

2. Reactions of $S_2N_2C_2Cl_4$

i. Reaction with mercury

$S_2N_2C_2Cl_4$ (2.35 gm.) and metallic mercury (0.9 gm., calculated for the equation; $S_2N_2C_2Cl_4 + Hg \longrightarrow (S_2N_2C_2Cl_3)_2 + Hg\ Cl_2$) were stirred vigorously in benzene (70. ml.). Not all of the $S_2N_2C_2Cl_4$ was dissolved. The originally orange solution became yellow-brown after two hours and then dark red. After filtration, quantities of unreacted $S_2N_2C_2Cl_4$ were obtained, together with a grey, flakey solid. No mercury was observed.

Concentration of the red solution <u>in vacuo</u> produced only small quantities of a very dark red solid. Attempts at recrystallisation using ether, carbon tetrachloride, and benzene failed as the solubility of the compound was too great. Heptane was eventually used, but the product appeared as amorphous as before. It could not be mulled adequately to obtain an infrared spectrum, and analyses showed chlorine to be completely absent.

The grey solid contained no carbon, but turned white in, and caused decomposition of, concentrated nitric acid. It was not visibly soluble in ethanol, ethyl acetate, or ether. These tests show[145] that the compound contains mercurous, not mercuric chloride.

ii. Reaction with acetone

$S_2N_2C_2Cl_4$ (0.76 gm.) was stirred in dry Analar acetone (12 ml.)

The colour of the solid diminished in intensity, and after twelve hours a white solid remained beneath a yellow solution. After filtration, attempts to concentrate the solution produced a dark semi-solid. The white solid showed infrared absorptions at 1689 (vs), 1508 (m,sh), 1404 (s), 1316 (m,sh), 1263 (m), 1160 (w), 1105 (m), 1060 (s), 1041 (m), 953 (m), 855 (m,sh) 849 (s), 831 (vs), 804 (s), 774 (s), 720 (m), 696 (s), 636 (w), 623 (m), 606 (m), and 591cm^{-1}(m). Analyses showed C, 10.65; H, 2.23; N, 13.94; Cl, 73.6; S, absent. i.e. atomic ratios of $C_8H_{20}N_9Cl_{19}$ and a total of 100.42%.

REACTION OF S_2N_2CClPh AND DIPHENYLKETIMINOLITHIUM

i. Preparation of S_2N_2CClPh

This was supplied by Miss B. Bell, who prepared it by heating trithiazyl trichloride (3 gm.) and benzonitrile (25 ml. acting as both reactant and solvent), to 60°C. for twenty four hours.[146] The supernatant benzonitrile solution was filtered off the solid product, which was washed with carbon tetrachloride (2 x 20 ml.). The product is obtained as long, fine, orange-red needles. Its formulation as a five-membered ring with ionic or loosely bound chlorine, as in (XXV), is supported[147] by analyses, mass spectra, infrared spectra, and chemical evidence.

Howêver, research into improved preparative procedures has recently shown[148] that use of a solvent (e.g. chlorobenzene, nitrobenzene) in place of excess benzonitrile gives products with similar, but not identical infrared spectra; some peaks can be seen to consist of two components whose relative intensities vary according to the preparation used. At present, in the absence of analyses on the samples obtained by the new procedures the implications of these results are uncertain. The differences may be due to impurities or to a mixture of isomers with chlorine loosely bound to either ring sulphur atom. It is therefore possible, though not at this stage ascertainable, that the S_2N_2CClPh used in this work was a mixture of very closely related compounds.

The infrared spectrum of a sample prepared by the same method as was the sample used in this work is compared with that of the products obtained from it on page 102 and fig V.

ii. Preparation of diphenylketiminolithium

The diphenyl ketimine used was supplied by R. Snaith, and the preparation was as described by K. Wade et al.[149]

Diphenyl ketimine (1.81 gm., 10 m.mole) was placed in a 50 ml. round-bottomed flask, and the viscous, yellowish liquid stirred with dry ether (30 ml.). The flask was cooled in liquid nitrogen, and a solution of n-butyl lithium in hexane (2.4N solution, 4.2 ml., i.e. 10 m.mole) was syringed in. A transparent, cherry red solution of diphenylketiminolithium immediately formed. To avoid irreversible formation of the yellow polymeric form of the solute, the solution was used as soon as possible.

iii. Reaction in benzonitrile solvent

Benzonitrile (Koch-Light laboratories) was purified by distillation from calcium chloride onto phosphorus pentoxide, thence twice more onto phosphorus pentoxide, and finally onto calcium chloride.

S_2N_2CClPh (2.05 gm., 10 m.mole) was stirred for some hours in benzonitrile (300 ml.), in which about half the solid dissolved to give a dark orange solution. At room temperature, a small amount of the diphenylketiminolithium solution was added by syringe, and a dark purple colour was immediately observed where it entered the solution. The remainder of the ketimine (10 m.mole in all) was then added.

The liquid became dark brown, and the solid particles contained lost the orange colour due to S_2N_2CClPh. After stirring for two hours the solid appeared light brown, and filtration, after overnight stirring, slowly separated a very dark red solution from a fine, light brown solid. This solid was washed with benzonitrile (2 x 20 ml.) and carbon tetrachloride (2 x 20 ml.), after which it was white. It had a featureless infrared spectrum and imparted a vivid red colour to a flame, i.e. it was lithium chloride.

The red solution was concentrated with difficulty at 60°C. on a rotary evaporator, and yielded a viscous, dark red tar, from which methyl cyclohexane (immiscible), hexane, and carbon tetrachloride failed to precipitate solid. However, a 1:3 mixture of toluene and hexane (5 ml.) precipitated a very dark red, lumpy solid which could not be made into a mull.

The solid was stirred in diethyl ether (5 ml.), forming a fine, very pale brown powder and a red solution. Further quantities were obtained by treatment of the tar with the toluene/hexane mixture followed by stirring in ether. The solid was washed in hexane (2 x 10 ml.) and recrystallised from hot toluene, which (by comparison of infrared spectra) was seen to purify, not decompose the compound. The yield could not be measured, since the solid was obtained by several additions of hexane/toluene, but was low (overall weight of solid less than 0.3 gm.).

The recrystallisation yielded a white solid which could be analysed only with difficulty because of its very low density. Analyses showed

S, 14.5; N, 14.2; C, 55.4; H, 4.2; i.e. atomic ratios $S_2N_{4.5}C_{20.4}H_{18.7}$. $S_2N_2CPh.NCPh_2$ requires S,17.7; N,11.16; C, 66.4; H, 4.1.

The light weight of the samples analysed probably reduced the accuracy of the analyses. The infrared spectrum of the solid is compared with S_2N_2CClPh and $Ph_2C = NH$ in table VI and fig. V. These show that many of the solid's absorptions correspond, with slight shifts, to those of the starting materials.

The solid was exposed to air for 48 hours, over which time neither its appearance nor its infrared spectrum altered. There was also no change after overnight immersion in a 1:1 methanol/water mixture.

When gradually heated in a sealed capillary, the solid remained unchanged until 209-210.5°C., when melting and decomposition took place. The mass spectrum of the compound is discussed later; it showed no absorptions above mass number 211 except at about 361 (intensity 9 relative to 100% peak at 181); the molecular weight of $S_2N_2CPh.NCPh_2$ is 361.

Treatment of Tar

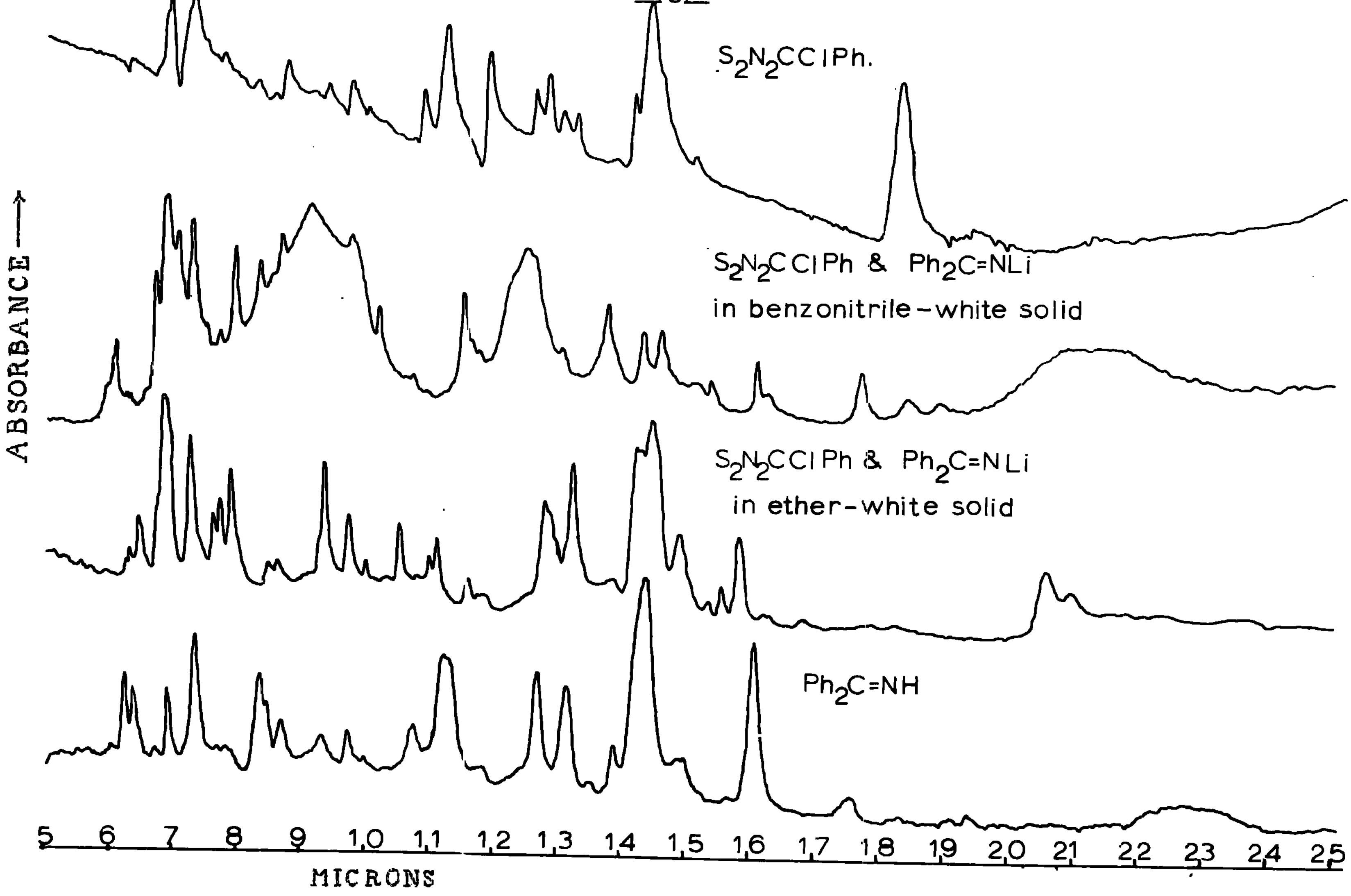
Before complete removal of the white solid, a spot of the red tar was placed on a glass plate coated with silica gel (Art.7730 Kieselgel GF 254), and a thin-layer chromatogram obtained from

TABLE VI

Absorptions (cm^{-1})

$Ph_2C=NH$	White Solid	S_2N_2CClPh	$Ph_2C=NH$	White Solid	S_2N_2CClPh
1603 ms	1647 m	1600 w		870 ms	893 s
1572 ms				842 s	
	1499 s			803 s	
1449 ms			787 s	785 m,sh	784 s
	1425 vs			770 w	
		1392 s,sh	760 s		
1364 s	1372 s			728 ms	
	1340 w	1346 m	719 m		
1299 w	1302 w	1299 w	696 vs	700 m	702 vs
1263 m	1264 s	1263 w		686 m	690 m,sh
1196 ms	1204 s			652 w	
1179 m,sh		1171 w	623 s	623 m	
1149 m	1157 s	1150 m	569 w	566 m	549 m
1072 m	1062 vs	1073 m		543 w	
1029 m	1026 s	1028 m		529 w	
1001 w					
	983 m				
927 m	934 w	921 m			
891 s		899 s,sh			

Fig. V.



S_2N_2CClPh.
S_2N_2CClPh & $Ph_2C=NLi$
in benzonitrile-white solid
S_2N_2CClPh & $Ph_2C=NLi$
in ether-white solid
$Ph_2C=NH$
ABSORBANCE
5
6
7
8
9
1,0
1,1
1,2
1,3
1,4
1,5
1,6
1,7
1,8
19
2,0
21
2,2
23
2,4
25
MICRONS

both benzene and chloroform solutions. After twenty five minutes, only two major spots were observable, and the absence of signs of a coloured trail behind the more advanced, red spot indicated neither to be greatly air-sensitive.

The infrared spectrum obtained from the tar shows great similarity to diphenylketiminodisulphide[150] and benzonitrile[44] (see table VII). Exposure to air for one hour occasioned no noticeable change in the infrared spectrum, which shows no indication of any ring structures other than phenyl groups.

TABLE VII

Absorptions (cm^{-1})

$(Ph_2C{=}NS)_2$	Tar	PhCN	$(Ph_2C{=}NS)_2$	Tar	PhCN
	2232 m	2232 m	951 m	952 m	
	1608 w			924 m	920 m
1553 m	1553 m		914 w	194 w,sh	
	1495 m	1495 m		895 w	
	1451 ms	1451 m	845 w	846 w	
	1366 w		784 m	779 s,sh	
1314 m	1319 m		778 ms	778 s	
1297 m	1295 m			758 s	758 s
	1272 m		741 m	746 w,sh	
	1188 m,sh	1188 w	704 s	706 m,sh	
	1185 m	1185 w	693 s	694 vs	
	1161 w	1161 w		690 vs,sh	689 vs
	1099 w	1100 w	672 m	672 m	
	1073 m	1053 m		636 w	
1028 w	1028 ms	1028 m		629 w	
	1003 m	1003 w		548 ms	548 vs

REACTION OF S_2N_2CClPh AND DIPHENYLKETIMINOLITHIUM IN DIETHYL ETHER

S_2N_2CClPh (4.7 gm., 20 m.mole) was slurried in dry ether (300 ml.); a small amount dissolved to form an orange-brown solution. Diphenylketiminolithium (20 m.mole, prepared as before) was then added by syringe. The solution immediately became dark red, and the orange colour of the S_2N_2CClPh quickly disappeared. Filtration yielded a buff-coloured solid and a red filtrate.

The solid was washed with ether (3 x 40 ml.) and then heated in toluene (80 ml., addition of which caused the solid to go brown) to 60-65°C for two hours. This caused some dissolution, but much solid (lithium chloride) remained. Partial concentration of the resulting red filtrate *in vacuo* yielded a white solid, which was washed with ether (3 x 5 ml.). In all, about 0.4 gm. was retrieved, which is more than, in the previous reaction. Two sets of analyses on different samples from the same preparation gave

C, 73.1; N, 8.39; H, 4.76. i.e. atomic ratios $C_{10.2}H_8N$

and C, 69.4; N, 8.51; H, 4.72 i.e. atomic ratios $C_{28.9}N_3H_{23.6}$

$S_2N_2CPh.NCPh_2$ requires C, 66.4; N, 11.16; H, 4.1.

The infrared spectrum shows the compound to differ from that obtained using benzonitrile solvent, but compares even more closely with the spectra of the starting materials - see table VIII and fig. (V). On heating the compound in a capillary, a very pale yellow colour was observed at about 130°, and melting to a dark, red-brown liquid took place at 150-152°C.

TABLE VIII

Absorptions (cm^{-1})

$Ph_2C=NH$	White Solid	S_2N_2CClPh	$Ph_2C=NH$	White Solid	S_2N_2CClPh
1603 ms		1600 w	891 ms		893 s
1572 ms	1587 w			863 w	
	1553 m			846 w	
1449 ms	1451 vs		787 s	782 s	
		1392 s,sh		778 s,sh	784 s
1364 s	1379 s		760 s	756 s	
	1314 m	1346 m	719 m		
1299 w	1295 ms	1299 w		704 vs	
1263 m	1269 s	1263 w		700 vs,sh	702 vs
1179 m,sh	1181 w		696 vs	692 vs	690 m,sh
		1171 w		672 m	
1149 m	1160 w	1150 m		670 m,sh	
1072 m	1074 m,sh			652 w	
	1071 s	1073 m		644 w	
1029 m	1028 ms	1028 m	623 s	633 ms	
1001 w	1001 w		569 w		549 m
	951 m			486 m	
927 m		921 m		477 w	
	910 w				
	900 m	899 s,sh			

Immersion of the white compound in water for twenty four hours at room temperature did not change its infrared spectrum.

Treatment of red solution

The ether was removed from the filtrate *in vacuo*, and the tar obtained redissolved in petroleum ether (30 ml., boiling fraction 60/80°C.) by warming. Filtration left no solid residue, but small amounts of a white solid rapidly precipitated in the receiver flask, which was at room temperature. This solid was washed in ether (3 x 5 ml.) after filtering off the red solution. Its infrared spectrum showed bands at 3333 vs; 3155 vs; 1689 vs; 1616 m; 1529 m; 1266 s,sh; 1220 vs,b; 1183 s,b; 1100 s,b; 1040 s,sh; 1016 vs; 935 w; 800 ms,b; 789 s,sh; 694 vs,b; 606 s,vb; 571 ms,b; 529cm^{-1} m,b.

The appearance of O-H bands (3333 & 3155cm^{-1}), the high background, and the broadness of the peaks suggest that this product is the result of partial hydrolysis of some compound. On exposure to air it rapidly discoloured, becoming yellow.

The unfortunate accidental loss of the red solution prevented any further work before time forced closure of experiments. It also prevents any real estimate of yield being made.

DISCUSSION

1. Reaction of trithiazyl trichloride and tetrachloroethylene.

The aims of this project did not include testing of the major product, $S_2N_2C_2Cl_4$, which has been characterised and discussed elsewhere.[123,147,151] It was merely planned to determine whether the minor products of the reaction merited further study. The crystals obtained from the condenser leave no more to conclude than that thiodithiazyl dichloride is produced in small quantities by this reaction.

The solid obtained from the red solution contains no sulphur, and must therefore contain carbon, nitrogen, and chlorine only. It is possible that the compound is cyanuric chloride, $(CClN)_3$, but analyses (particularly chlorine) do not support this. The solid is evidently not a sulphur-nitrogen species, and its poor analyses suggest it to be a combination of side products of no interest.

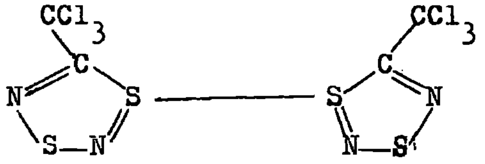
The cause of the red colouration may be only small amounts of impurities (in even lesser quantities than the solid obtained from solution) which remained in solution. The reversible change to green on evacuation may be due to some unreacted trithiazyl trichloride, which is shown by the solid retrieved from the condenser to be present.

In conclusion, it appears that none of the secondary products of the title reaction is worth further study.

2. Reactions of $S_2N_2C_2Cl_4$

i. With mercury

The object of this reaction was to produce the disulphide (XXVI).



(XXVI)

However, even at room temperature in the presence of an apparently insufficient amount of mercury, the product obtained, by its intractable nature and the absence of chlorine, appears to have resulted from extensive attack upon the ring. Thus it seems that no product related to (XXVI) can be obtained from the reaction, which is too vigorous.

The reaction with potassium iodide was not attempted owing to the lack of success obtained above. Such a reaction would raise the problem of solvent choice; the reported use of potassium iodide[128] utilises an aqueous acetone solvent, but $S_2N_2C_2Cl_4$ is sensitive both to moisture[152] and to acetone (see below).

ii. With acetone

The absence of sulphur in the white solid, together with the recovery of only a dark, oily product from solution, suggests that here also, the sulphur-nitrogen-carbon ring has been destroyed. The nature of the white solid is neither clear nor, for this work, important. The analyses, although totalling close to 100%, do not include oxygen. However, the intensity of the i.r. absorption at 1689cm^{-1} indicates the presence of the carbonyl group.

These experiments have therefore failed to prepare derivatives of $S_2N_2C_2Cl_4$. The reason may lie in the high electronegativity of the Cl_3C– group, which will draw electronic charge from the ring. However, the ring may, if the single chlorine is wholly or partially ionised, already be electron deficient i.e. there may be an inherent instability in $S_2N_2C_2Cl_4$ due to the polarity of the carbon-carbon bond, which is not found to any comparable extent in S_2N_2CClPh.

3. Reaction of S_2N_2CClPh and diphenylketiminolithium

Nature of white solid obtained from benzonitrile solution

The resemblance between the infrared spectra of this compound and of the starting materials (see fig. V and table VII), together with the formation of lithium chloride and the small group of peaks around mass no. 361 in the mass spectrum, suggest that a compound of the type $S_2N_2CPh.N = CPh_2$ has been produced.

The analyses must, because of the light weight of the samples used to obtain them, be considered to have low accuracy, but the atomic ratios suggested by them ($S_2N_{4.5}C_{20.4}H_{18.7}$) do correspond closely to $S_2N_2CPhN{=}\ CPh_2$, ($S_2N_3\ \ C_{20}H_{18.}$). Inaccuracy may also be due to the presence of side products.

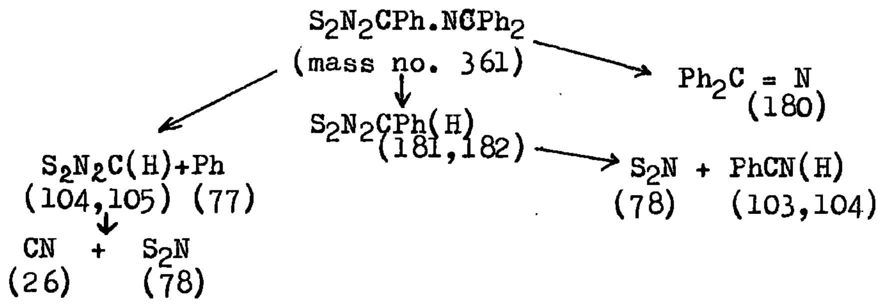
Mass spectrum

As anticipated, there is no indication of chlorine.

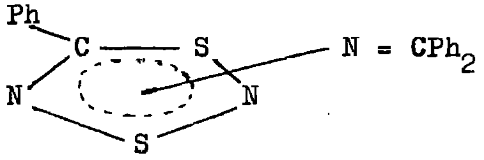
Intense peaks are observed at 180, 181, and 182 (relative intensities 28, 100, and 550 respectively) and are taken to be due to cations derived from fragments $Ph_2C = N$ (180) and S_2N_2CPh (181). The addition of a proton (giving peak 182) is not unexpected in the presence of three phenyl groups per molecule; these both furnish protons and stabilise the positive charge, due to their attachment to cationic fragments. The low relative intensity (9) of the parent peak at 361 indicates that breakdown of the molecule is almost immediate.

The peak at 103 (corresponding to PhCN, which might be expected to be cleaved from the ring) is small (rel.int.35) compared with the peaks at 104 (rel.int.1200, due either to PhCN(H) or to the S_2N_2C ring) and 105 (rel.int.104, due to $PhCN(H)_2$ or $S_2N_2C(H)$). Hence it appears that the product can either undergo ring cleavage via loss of PhCN, or can lose exocyclic substituents to form a bare or protonated ring (even though this does not occur in the mass spectrum of S_2N_2CClPh).[153] The bare ring is then cleaved to the fragments S_2N and CN (mass no. 26, rel.int.20).

Other modes of ring opening are not in evidence; no peak is seen at 135 (which would result from PhCNS formation) and at 149 (where the fragment (PhCN)SN would be observed) the relative intensity is only 10. Hence the breakdown pattern is:-



It can therefore be concluded from the mass spectrum that a compound of the type (XXVII) has been obtained:



(XXVII)

However, the position at which the ketimino group is attached is uncertain, and, as discussed later, is probably different in the two white compounds obtained from the reactions in benzonitrile and ether solvents.

Nature of white solid obtained using ether solvent.

Analyses are suspect here for much the same reasons as before. However, the infrared spectrum (see fig. V and table VIII) exhibits an even closer relationship to the spectra of the reactants than is shown by the white solid from benzonitrile solution. The mass spectrum is impossible to count accurately above 320 due to the almost total absence of activity, but a small peak (intensity 5 relative to intensity 100 peak for mass 181) is seen in the region 358–362. Otherwise, the mass spectrum is identical to that of the first white solid.

Position of ketimine group in both solids.

Differences are apparent between compound A, obtained from the reaction in benzonitrile solution, and compound B, obtained from the reaction in ether solution. Compound A exists longer than does B (which gives the weaker parent peak) under the conditions within the mass spectrometer, but below the region of the parent peak their mass spectra are the same, indicating that identical fragments have been produced. Also, the infrared spectra of compounds A and B differ.

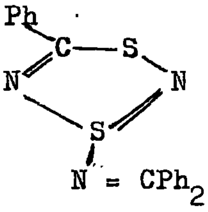
It therefore seems that two compounds of type (XXVII) (p.112) have been obtained, and the most likely distinction is in the position of the link between ring and ketimine.

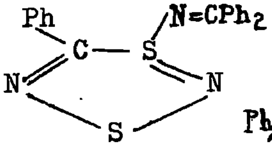
Reasons for difference between A and B.

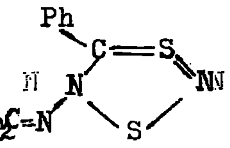
Compound A is formed in benzonitrile solution, whereas compound B, being insoluble in ether, precipitates out from the reaction solution. Such widely differing conditions could explain the isomeric difference, either because (a) solvent affects site of attack, or (b) both reactions give the same initial product(s) but rearrangement occurs in solution (due to the heat applied whilst removing benzonitrile, or to displacement of equilibrium during precipitation) to form a different ketimine - ring link site. The possibility of ring expansion by incorporation of the ketimine C = N group can be discounted because of the similarity between the infrared spectra of products and reactants.

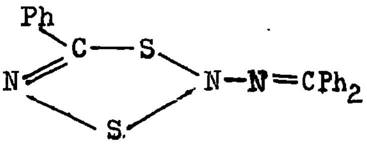
Nature of difference between A and B.

The most likely structures of the products obtained are:-


(XXVIII)


(XXIX)


(XXX)


(XXXI)

The cases for the attachment of the ketimine to sulphur or nitrogen are now discussed:-

The reaction of phenyl lithium and S_2N_2CClPh[126d] formed black crystals which decomposed in light to yield diphenyl disulphide, thus proving that the new substituent was attached to a sulphur atom. One might expect a similar reaction with diphenylketimino lithium.

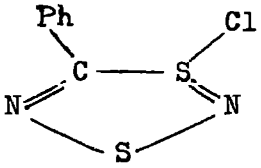
Also, it is possible that the peak observed at $728cm^{-1}$ in the infrared spectrum of A, and at 704 or $700cm^{-1}$ in the i.r. spectrum of B is due to a new sulphur-nitrogen link (one of the peaks in this doublet can be related to $Ph_2C = NH$, but which one is uncertain).

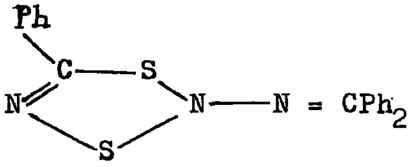
Further arguments in favour of the ketimino-sulphur link are: the low likelihood of a nucleophilic attack on nitrogen, and the comparative strengths of sulphur-nitrogen and nitrogen-nitrogen bonds, which by Sanderson's method[154] can be estimated at 53 k cal $mole^{-1}$ and 38 k cal $mole^{-1}$ respectively (the calculation is shown in appendix 1). It can be argued in favour of the nitrogen-nitrogen link that a delocalised lone pair on the ring nitrogen would, by reducing lone-pair/lone-pair repulsion, increase the bond strength (in $S_4N_4H_4$, the lone pair of the ring nitrogen is partly delocalised, giving SNS bond angle of about 126^0)[155]. However, an increase over single bond strength might also be expected for a sulphur-nitrogen link due to π-delocalisation between ring and ketimine systems.

The white colour of the compound (compared with orange S_2N_2CClPh and black $S_2N_2CPh_2$) can be explained in terms of each type of link:

i. if sulphur-nitrogen link exists:- the high energy visible absorption region for the ring, which is responsible for the orange colour of S_2N_2CClPh, is moved further into the ultraviolet, or sharpens. Thus no significant visible absorption remains. This could be due to an essentially single exocyclic sulphur-nitrogen bond order, i.e. little conjugation between ketimine and ring. For the frequencies (attributed to S - N in each compound) 728 and 700cm^{-1} the corresponding bond lengths can be calculated (from $r_{sn}=0.0483/\mu_{sn} + 1.099$)[45] as 1.76 and 1.79 Å respectively; the length of a single SN bond has been computed[156] at 1.73Å, so the bond order does appear to be close to (perhaps a little less than) one.

ii. if nitrogen-nitrogen link exists:- the electronic situation is now quite dissimilar to S_2N_2CClPh (see below) even if the lone pair on the ring nitrogen atom is partially delocalised:



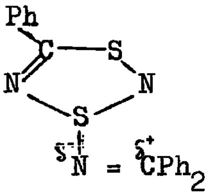


Hence a very different ultraviolet/visible absorption spectrum is to be expected.

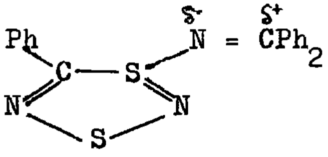
In summary, therefore, the possibility of a sulphur-ketimine link seems greater than that of a nitrogen-ketimine link. However, the latter cannot firmly be eliminated yet.

Comparison of the infrared spectra of A and B shows (fig. V) that neither sample is present in the other, and the melting ranges are sufficiently narrow to suggest that each sample consists of one compound only (with perhaps a minor impurity which could be the cause of the yellow colouration of B at 130°C.).

It thus appears that each sample will have one of the structures below:



(x)



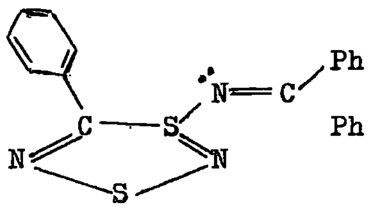
(y)

It is impossible to assign A and B to these structures on the basis of work so far.

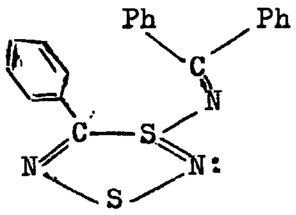
The closer proximity of the ketimine and phenyl groups in (y) suggests that the ketimine C = N absorption frequency may be lower in (y) due to the electron-withdrawing effects of the phenyl group; hence compound B (see fig. V) may have structure (y). However, no firmer support for this argument is yet available.

Optical and Geometrical isomerism

The structures (x) and (y) indicate the possibility of both geometrical and optical isomerism. For geometrical isomerism, (x) would require some double bond character for the exocyclic sulphur-nitrogen link (no large steric interactions seem likely). However, indications are (see p.115) that this bond order is approximately one, However, the molecules (i) and (ii) below represent



(i)



(ii)

geometrical isomers of (y) if rotation is restricted by steric interaction - between phenyl group hydrogens and ketimino nitrogen lone pair in (i), and between phenyl groups in (ii).

Optical isomerism is possible in both (x) and (y), the sulphur atom being the asymmetric centre; in the two isomers of (i) or of (ii) the ketimino group is on opposite sides of the ring.

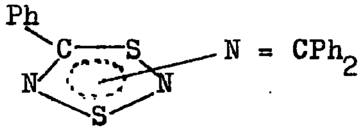
Nature of other components of product mixture

The formation of compound (A) is accompanied by formation of a red tar whose spectrum indicated the presence of both diphenylketiminodisulphide and benzonitrile. The former indicates that some ring destruction has occurred. One would expect such ring opening to produce other minor products which would explain the red colouration and tarry consistency. There was no indication that the tar contained any compounds worth further investigation.

It is possible that the partially hydrolysed white solid (obtained from ether solution after removal of compound B from the reaction mixture) derives from a second useful product. However, until further work is done on this reaction it is therefore concluded that at least one product of the desired structural type, and probably more than one, has been obtained.

Summary

Attempts to prepare derivatives of $S_2N_2C_2Cl_4$ have failed, possibly because of the presence of the $-CCl_3$ group. However, by reacting S_2N_2CClPh and diphenylketiminolithium, air and moisture-stable derivatives of dithiadiazoles appear to have been obtained. The general formula (XXVII) is proposed :-



(XXVII)

It seems likely that the two products obtained contain ketimine-sulphur rather than ketimine-nitrogen links, and that the nature of the product obtained depends upon the solvent used. The (tentative) structural evidence and the stability to water confer considerable chemotherapeutic potential on these products.

Each of the two products is obtained in low yield, and some ring destruction appears to occur during their production. An improvement in the yields would be a desirable aim for future work, which should also be directed towards assigning more definite structures to the white solids.

Distinguishing between links at each of the two sulphur atoms may be difficult. However, when other stable derivatives have been prepared, it may be possible to judge the position of substitution by comparing the phenyl group in the p.m.r. spectra of the various compounds; one might expect greater variation between compounds if substitution occurred on the nearer sulphur atom.

APPENDIX

Calculation of energy of sulphur-nitrogen single bond.

The method used is due to R. T. Sanderson[154], and may be summarized as follows:-

Total Energy = ionic contribution (E_i) + covalent contribution (E_c)

$$E_i = \frac{ti.\ 330e^2}{Ro} \quad \text{(Coulomb's law)}$$

$$\text{and} \quad E_c = tc\sqrt{E_{AA}E_{BB}}\cdot\frac{Rc}{Ro}$$

where :- A and B are the bound nuclei and E_{AA} and E_{BB} represent their homonuclear single bond energies;

e is unit electronic charge

Rc is the sum of the covalent radii of A and B;

Ro is the observed length of the A.B bond;

ti and tc are the weighting coefficients, which show the extent of ionic and covalent contributions. The calculation can then be considered as two stages:-

1. Evaluation of ti and tc.

ti. is the average of the partial charge on each atom after bond formation (if charges are opposite).

$$\text{Now partial charge on A} = \frac{\text{Change in electronegativity (S) on forming bond}}{\text{Electronegativity change on acquisition of unit charge}}$$

also, electronegativity of AB entity $=\sqrt{S_AS_B}$

and electronegativity change per atom on acquisition of unit charge = $2.08\sqrt{S}$. Hence ti can be calculated, as well as tc (=1-ti).

2. Calculation of Ei, Ec

Example for S-N bond:-

Electronegativity of sulphur = 4.11^{154}

Electronegativity of nitrogen = 4.49^{154}

$\therefore$ for acquisition of unit charge by sulphur, electronegativity change $= 2.08\sqrt{4.11}$;

on acquisition of unit charge by nitrogen, electronegativity change $= 2.08\sqrt{4.49}$.

Combined electronegativity of S-N $= \sqrt{4.11 \cdot 4.49}$

$= \underline{4.295}$

$\therefore$ partial charge $= \dfrac{4.11 - 4.295}{2.08\sqrt{4.11}}$ for sulphur.

$= \underline{0.0439.}$

similarly for nitrogen, partial charge $= \underline{0.0442.}$

$\therefore$ ti. = 0.04405, tc = 0.95595.

Now Rc = 1.77^{154} (1.76 in our SN paper)

and for a sulphur-nitrogen bond order of one, Ro = 1.70Å [157].

$$\therefore \text{Ei} = \frac{330 \times 0.04405}{1.70}, \quad \text{Ec} = 0.956\sqrt{50.9 \times 38.4} \cdot \frac{1.77}{1.70}$$

(homonuclear single bond energies obtained from ref. 154).

Thus bond energy = 8.57 + 44.01 k cal mole^{-1}

i.e. $\underline{52.58 \text{ k cal mole}^{-1}}$

Accuracy is limited by the accuracy with which the sulphur-nitrogen bond length is known. In this case it has been found by assuming a bond order of 1.0. Other limiting factors are the accuracy of the covalent radii, the evaluation of partial charge, and the appropriate electronegativity values (since these will vary with oxidation state) and the homonuclear single bond energies.

Sanderson[154] therefore refrains from setting a value to the error of this method.

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