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Three-coordinate sulphur(VI)–nitrogen species: an attempt to breathe some new life into an old topic

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Contents

Abstract

The review describes the syntheses, structures and reaction chemistry of three-coordinate nitrogen-containing sulphur(VI) compounds including the sulphur triimides $[(RN)_3S]$,

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sulphonyl diimides [$(RN)_2SO$], sulphonyl imides [$RNSO_2$] and sulphene imides [$R_2CS(O)NR$]. Comparisons are made with phosphorus(V) analogues.

Keywords: Nitrogen-containing sulphur(VI) compounds; Three-coordinate sulphur compounds; Three-coordinate phosphorus(V) compounds

1. Introduction

Sulphur trioxide, SO_3, one of the most industrially important chemicals, remained the only characterised three-coordinate sulphur(VI) species until 1970, when Glemser and Wegener reported the synthesis of tris(trimethylsilylimino)sulphur $(Me_3SiN)_3S$ [1]. In contrast to SO_3, this compound is completely stable at room temperature; no oligomers or polymers are known. The preparation of $(Me_3SiN)_3S$ marks a milestone in main group chemistry, since it was shown for the first time that a sterically demanding group kinetically stabilises low coordination numbers. Although this was not recognised and postulated as a guideline for the preparation of other systems, exciting developments followed, especially in the chemistry of Group 14 and 15 elements with the discovery of hitherto unknown p_π–p_π multiple-bond systems. It is not surprising that the first stable amino-imino phosphane, $Me_3SiNPN(SiMe_3)_2$, [2] was also prepared at Göttingen (by Niecke and Flick). Later, they oxidised this species with Me_3SiN_3 to give $(Me_3SiN)_2PN(SiMe_3)_2$ [3] the first stable three-coordinate P(V) system. Interest in this chemistry continues up to the present day; very recent results from this group are triply coordinated phosphorus(V) anions, e.g. $[P(NAr)_3]^-$ (Ar = 2,4,6-tris(*tert*-butylphenyl)) [4] isoelectronic with the previously mentioned sulphur(VI) species.

This review will be restricted to three-coordinate nitrogen-containing sulphur(VI) compounds. The chemistry of SO_3 has been reviewed [5], alkylidene derivatives of sulphur trioxide, the sulphenes R_2CSO_2, known only as intermediates, have been described in detail [6]. Recent investigations on fluoroalkyl sulphenes [7,8] resulted not in the isolation of a free sulphene with a three-coordinated sulphur centre, rather, they act as strong Lewis acids similar to SO_3 and add donors under formation of stable adducts. $(CF_3)_2CSO_2 \cdot NMe_3$ was isolated and characterised by X-ray crystallography [9].

2. Three-coordinate sulphur(VI)–nitrogen species

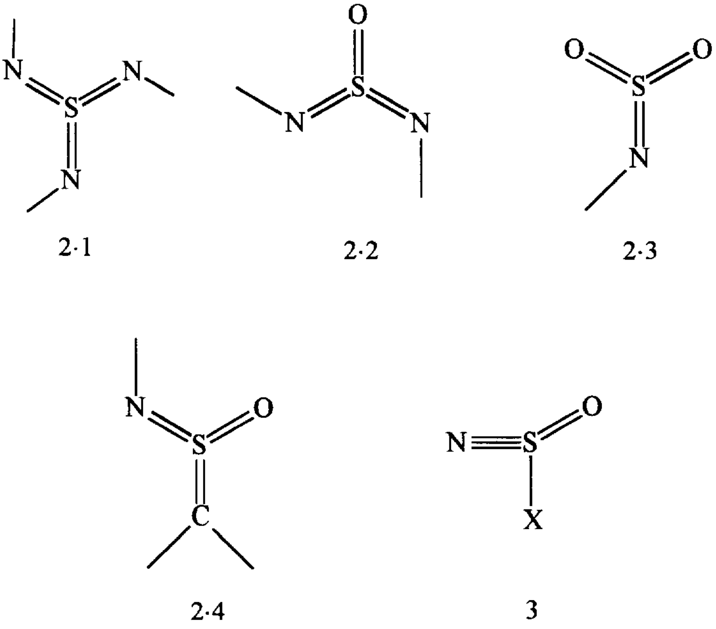
Although the first stable three-coordinate S(VI)N species was isolated more than 20 years ago, relatively little is known about this area of chemistry. A general discussion of this class of compounds has not been reported in the literature, although a collection of many synthetic aspects is given in a Houben-Weyl volume [10]. The purpose of this review is on one hand the comprehensive collection of the knowledge in this field and on the other hand the stimulation of research in this rather underdeveloped area.

Formal exchange of all oxygen substituents in SO_3 will lead to the sulphur triimides, discussed in Section 2.1. Sulphonyl diimides $(RN)_2SO$ (Section 2.2) and sulphonyl imides $RNSO_2$ (Section 2.3) are mainly observed only as reaction intermediates (Fig. 1).

The oligomers of the most simple member of the last class of compounds $(HNSO_2)_n$ will be briefly discussed in connection with published information on the NSO_2^- anion (Section 5). Some evidence is found in the literature for azasulphenes (RC)(R'N)SO (Section 2.6.2), but no unequivocal proof for the existence of oxothiazyl derivatives, $N{\equiv}S(O)X$ (Section 3), predicted by theoretical calculations [11], has been given. In Section 6, the chemistry of the three-coordinate sulphur(VI) species is compared with the properties of the isocoordinated neutral phosphorus(V) systems.

2.1. Preparation of sulphur triimides, $(RN)_3S$

Four methods for the preparation of sulphur triimides are reported in the literature: (Section 2.1.1) the reaction of thiazyl trifluoride; NSF_3, with lithiated silylamines; (Section 2.1.2) the reaction of sulphur oxide tetrafluoride with lithium or sodium trimethylsilyl amides; (Section 2.1.3) trans-iminations of sulphur tris(trimethylsilyl imide) and tris(*tert*-butyl imide); (Section 2.1.4) S–N bond-cleavage in $S(NSiMe_3)_3$ with acid anhydrides.



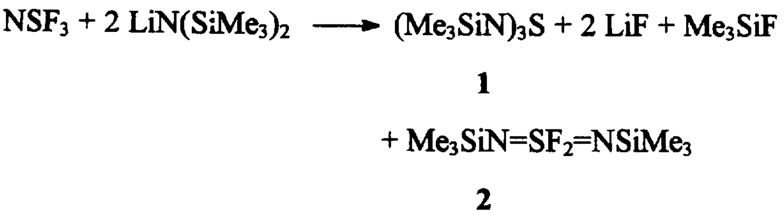
2·1 2·2 2·3

2·4 3

Fig. 1. Bonding modes in three-coordinate sulphur(VI) systems.

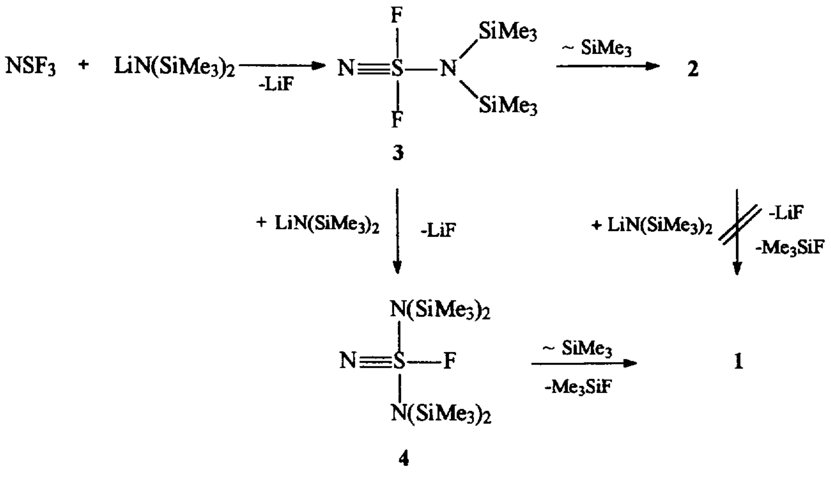
2.1.1. *From NSF_3 and lithiated silylamines*

As previously discussed, the first stable sulphur triimide, $(Me_3SiN)_3S$ (**1**) was reported by Glemser and Wegener [1] from the reaction of NSF_3 and $LiN(SiMe_3)_2$ at temperatures between −70 and 0 °C with yields up to 23% (Scheme 1). The by-product in this reaction is bis(trimethylsilylimino)sulphur difluoride **2**, a very interesting starting material for further N–S–F compounds [12]. The relative yields of **1** and **2** vary with temperature, solvent and with the procedure used. Similarly to the reaction of NSF_3 with alkyl amines [13], the primary step will be the exchange of one of the sulphur-bonded fluorine atoms to give the thiazyl difluoride amide **3** (Scheme 2). **3** can isomerise by silyl-migration to give **2**, or it is attacked by further $LiN(SiMe_3)_2$ to form bis-substituted **4**; under loss of Me_3SiF and silyl-migration, triimide **1** is formed. Because **2** does not react with excess $LiN(SiMe_3)_2$ under these conditions [14], it cannot be an intermediate in the formation of **1**. If $LiN(SiMe_3)_2$ in THF is slowly added to a solution of NSF_3 in the same solvent at −70 °C, only **2** is observed. Owing to the high migration tendency of the silyl groups, **2** is formed before the second nucleophilic attack, leading to formation



$$NSF_3 + 2\,LiN(SiMe_3)_2 \longrightarrow \underset{\mathbf{1}}{(Me_3SiN)_3S} + 2\,LiF + Me_3SiF + \underset{\mathbf{2}}{Me_3SiN{=}SF_2{=}NSiMe_3}$$

Scheme 1.

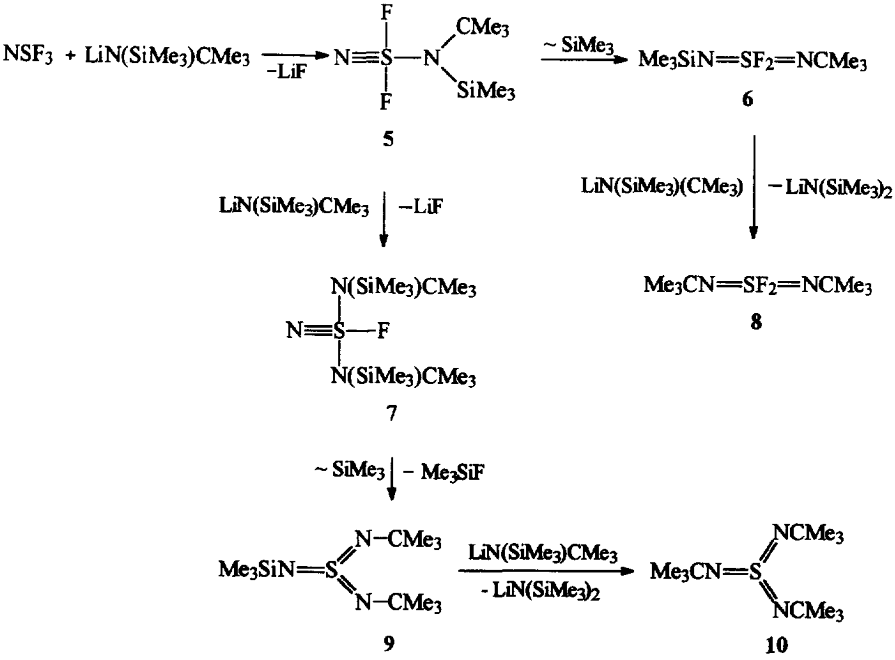


Scheme 2.

of **4**, can occur. If, however, NSF_3 is bubbled into a suspension of $LiN(SiMe_3)_2$ in hexane at 0 °C, formation of **4** and subsequently of **1** competes with the isomerisation of **3** to **2**.

When lithiated alkyl silyl amides, $LiN(SiMe_3)R$, are reacted with NSF_3, sulphur triimides were only isolated for $R = Me_3C$ (other bulky groups like mesityl, $CH(SiMe_3)_2$, adamantyl, etc., were not used at that time). With less sterically demanding substituents ($R = CH_3$, CH_3CH_2, $(CH_3)_2CH$, C_6H_5) unidentified polymeric products are formed [14,15].

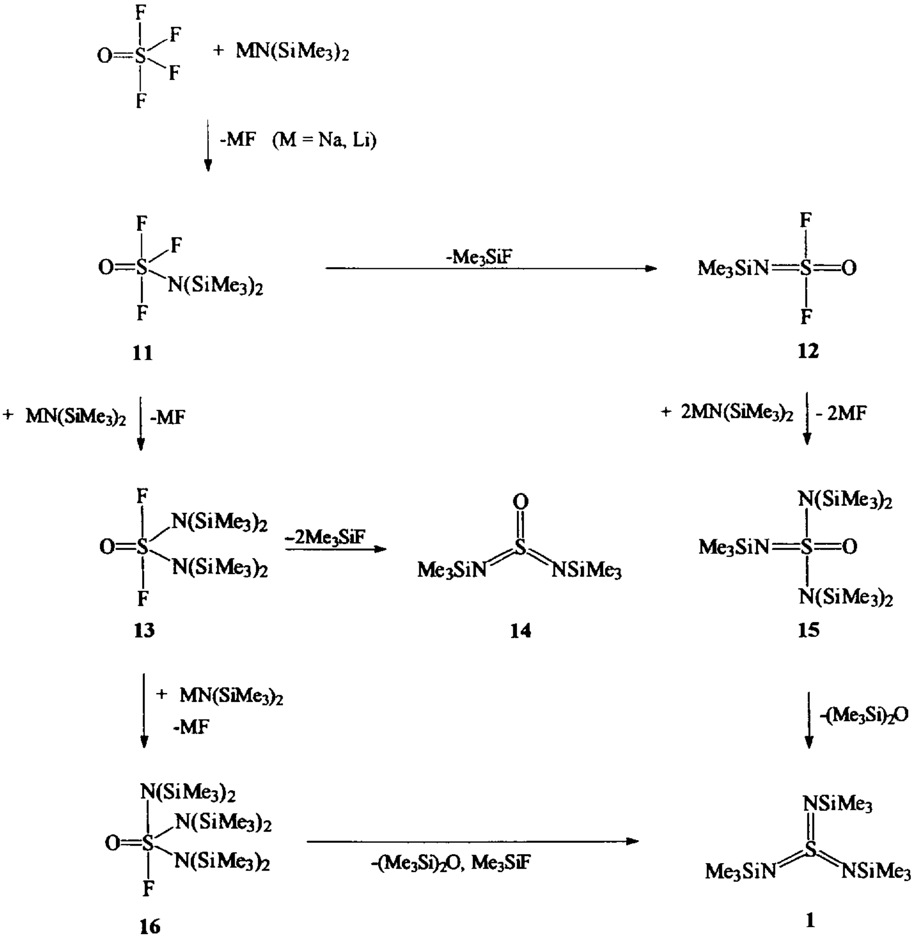
As for Scheme 2, a silatropic rearrangement to **6** is observed for the primary product **5** (Scheme 3); trans-imination affords **8**, also detected by NMR spectroscopy. Substitution of a second sulphur-bonded fluorine will give the unisolated intermediate **7**, from which **9** is formed. This reacts at higher temperatures with excess $LiN(SiMe_3)CMe_3$ to give **10**. Yields of **6** and **8** are always low. When the reaction is performed at −70 °C, in contrast to Scheme 2, only **9** is isolated. The activation barrier for the isomerisation of **5** to **6** is much higher than that for **3** to **2** (thiazyl difluoride dialkyl amides NSF_2NR_2 ($R =$ alkyl group) do not isomerise to sulphur difluoride diimides); disubstitution to give **7** seems to be more favourable. trans-Imination under formation of **10** occurs at room temperature.



Scheme 3.

2.1.2. *From sulphur tetrafluoride oxide, OSF_4, and bissilylated alkali metal amides, $MN(SiMe_3)_2$*

The reaction of $O{=}SF_4$ with $NaN(SiMe_3)_2$ is reported to give **1** in 56% yield [16]. Owing to the higher yield and the easier availability of OSF_4, compared with NSF_3, this method seems to be preferable. OSF_4 is dropped into a solution of $NaN(SiMe_3)_2$ in petroleum ether (40–60 °C) at −40 °C and, subsequently, the reaction mixture is warmed to room temperature. The primary step in this reaction is possibly formation of the unisolated amino sulphur oxide trifluoride **11** (Scheme 4). Its stable decomposition product **12** is obtained from 1 : 1 OSF_4–$LiN(SiMe_3)_2$ reaction mixtures in high yield [17]. From 1 : 2 mixtures the isolation of **14** is reported [17] (Section 2.2), while 1 : 3 mixtures give the triimide **1**. No proof for the existence of intermediates **13** and **16** is given in the literature. From the reaction of **12** with



Scheme 4.

$MN(SiMe_3)_2$ at room temperature, only **1**, but no **14**, is isolated [18]; it was, therefore, concluded that **12** is not an intermediate in the formation of **14**.

In a similar reaction, the triimide **10** is formed from $Me_3CN{=}S(O)F_2$ and $LiN(CMe_3)SiMe_3$ [19], while from OSF_4 and $LiN(CMe_3)SiMe_3$ the reduction product $(Me_3CN{=})_2S$ is unexpectedly isolated in 45% yield [19].

Although the literature reports are a little confusing, it seems to be possible to generate sulphur triimides from OSF_4 and $MN(SiMe_3)R$ ($M = Li$, Na) if R is a bulky group and the reaction temperature is higher than −40 °C. At low temperatures loss of Me_3SiF with formation of sulphur oxide difluoride imides is favoured over the disubstitution, which would lead to a different pathway.

Because there remain many uncertainties and open questions, a thorough reinvestigation of the reactions of OSF_4 and $RN{=}S(O)F_2$ with $MN(SiMe_3)R$ is necessary, but this might possibly be the most fruitful way to a variety of new sulphur triimides.

2.1.3. From trans-iminations of sulphur tris(tert-butylimide) and sulphur tris(trimethylsilyl-imide)

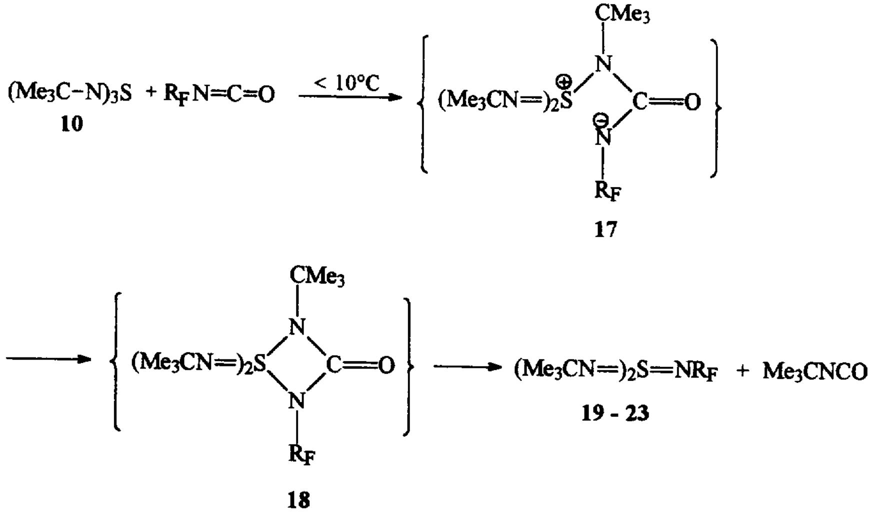
The primary step in the reactions of the sulphur triimides **1** and **10** is an electrophilic attack at one of the peripheral nitrogen atoms (Section 2.6.1. Isocyanates R_FNCO with strong electron-withdrawing groups, R_F, act as C-electrophiles [20,21]. **10** reacts with perfluoroalkyl isocyanates, sulphonyl isocyanates, pentafluorosulphanyl isocyanate, [20] and difluorophosphoryl isocyanate [21] even below +10 °C; CF_3SNCO and isocyanates with less electron-withdrawing groups do not react. Plausible intermediates are the betaines **17** and thiadiazetedinones **18** which decompose with formation of bis(*tert*-butylimino)sulphur triimides with one strong electron-withdrawing group (Scheme 5). **19**–**23** are isolated in 50–80% yield. The stability of these triimides depends on the steric requirements of the substituents R_F. While **19a** ($R_F = CF_3$) decomposes within 1 day at room temperature, **19d** and also **21** ($R_F = i\text{-}C_3F_7$ and SF_5) are almost as stable as **1** or **10**. It is worthwhile noting that in **21** sulphur(VI) in its highest (6) and lowest coordination number (3) are found in the same molecule. Much less stable are triimides with silyl substituents [20].

Only the perfluoroisopropyl derivative **24** was isolated (Scheme 6), but even this decomposes readily at room temperature with formation of **1** and unidentified polymeric products.

2.1.4. By cleavage of the Si–N bonds of sulphur tris(trimethylsilylimide)

Attempts to prepare new sulphur triimides $(RN)_nS(NSiMe_3)_{3-n}$ from the readily available tris(silyl)-substituted derivative date back more than 20 years. The cleavage of the SiN bond by acid anhydrides or by reactive covalent fluorides or chlorides is a well established synthetic method; **1** was expected to be a useful starting material for this type of reaction.

From **1** and $P_2O_3F_4$ only the decomposition product $OPF_2N(SiMe_3)_2$ was characterised [22], from **1** and $(CF_3C(O))_2O$ formation of the mono- and di-substituted trifluoroacetyl derivatives are reported [23]. The degree of substitution depends on the stoichiometry. Both compounds are described as reddish, high-boiling liquids (b.p. 120 and 140 °C at 30 Pa respectively) which decompose on heating. Despite



	R_F
19a	CF_3
b	C_2F_5
c	n-C_3F_7
d	i-C_3F_7

	R_F
20a	SO_2Cl
b	SO_2F
21	SF_5
22	$C(CF_3)=NSO_2F$
23	POF_2

Scheme 5.

$$\underset{\mathbf{1}}{(Me_3SiN=)_3S} + R_FNCO \longrightarrow \underset{\mathbf{24}}{(Me_3SiN=)_2S=NR_F} + Me_3SiNCO$$

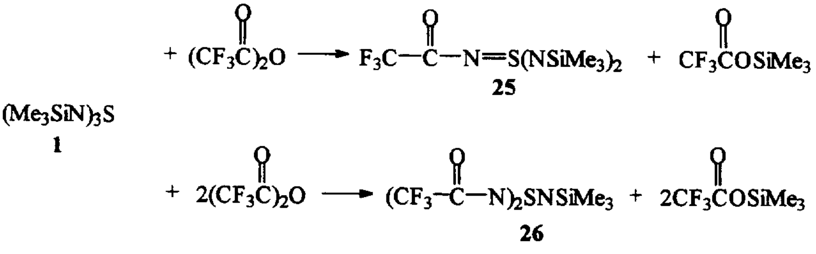
$$(R_F = (CF_3)_2CF)$$

Scheme 6.

this, according to the literature, **26** was isolated in a pure state (Scheme 7). Although the experimental data suggest that **25** and **26** are not unequivocally characterised, the reaction of Scheme 7 clearly shows that **1** might be a useful starting material for a variety of new sulphur triimides. Because the products are expected to be rather unstable, then highly specialised, low-temperature techniques will be necessary to tackle this problem.

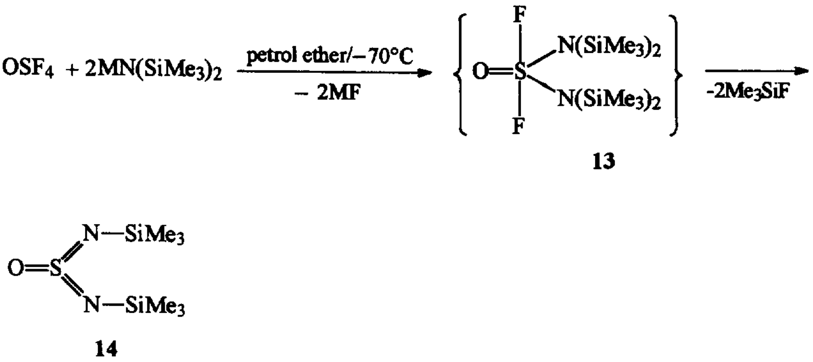
2.2. Preparation of bis(imido)sulphuroxides, $(RN)_2SO$

A useful precursor for the preparation of bis(imido)sulphur oxides seems to be $O{=}SF_4$. From its reaction with silylated alkali metal amides $MN(SiMe_3)R$ a widely



Scheme 7.

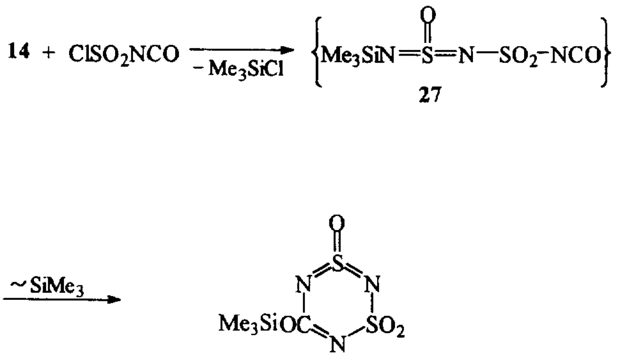
applicable synthetic pathway might be developed, if sterically demanding groups R are introduced. Up to now, only one reaction, already mentioned in Scheme 4, has been reported in the literature [17]. As indicated in Scheme 8, the silyl derivative **14** is reported as a colourless liquid with astonishingly high thermal stability (b.p. 169 °C). The preparation has been reproduced and **14** was used as starting material in the reaction with $ClSO_2NCO$ [24] (Scheme 9). According to spectroscopic investigations, the cyclic bis(imido)sulphur oxide **28** was suggested as the structure for the final product. Further bis(imino)sulphur oxides are only assumed to be intermediates in substituent exchange reactions of sulphur triimides (Section 2.6.1).



Scheme 8.

2.3. *Preparation of sulphur dioxide imides (sulphonyl imides), $RNSO_2$*

Owing to the low steric shielding of the two oxygen atoms, sulphur dioxide imides (sulphonyl imides) readily oligomerise or polymerise, and no kinetically stable derivatives have been isolated or structurally characterised. Trimeric and tetrameric cyclic sulphonyl amines $(RNSO_2)_n$ have been known for some time [25], and the more recently prepared dimers $(R_FNSO_2)_2$ with strong electron-withdrawing nitrogen-bonded groups R_F [26–30] are readily cleaved into monomeric units by nucleophiles. They can be regarded as 'stabilised' sulphonyl imides. In spite of their instability,



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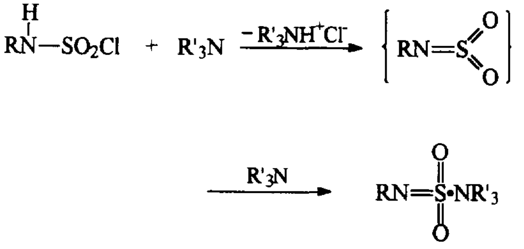
28

Scheme 9.

sulphonyl imides are useful reaction intermediates and, therefore, several routes to their preparation have been developed.

From dehydrohalogenation of halosulphonyl amides (Scheme 10) they are formed at −78 °C in solution. They can be stabilised by *tert*-amines or trapped by formation of heterocycles [31–41]. From the photolytic decomposition of $C_6H_5SO_2N_3$, phenyl sulphonyl imine is formed by a Curtius-type rearrangement as an intermediate [42] (Scheme 11). Special precursors for sulphonyl imines are 2,2-dioxo-1,2,3,5-oxathiadiazines, which are photolytically transformed into sulphonyl imines [43] (Scheme 12), and 1,4,3,5-oxathiadiazine-*S*,*S*-dioxides, which undergo thermal cycloreversions [44] (Scheme 13).



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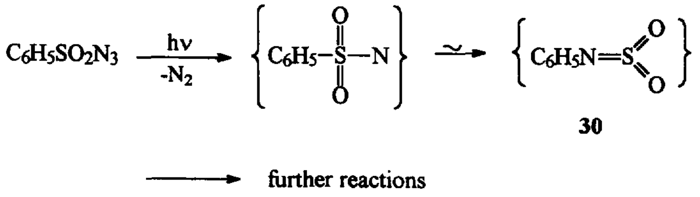
Scheme 10.



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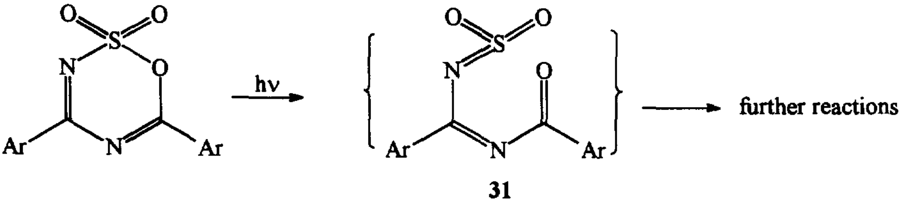
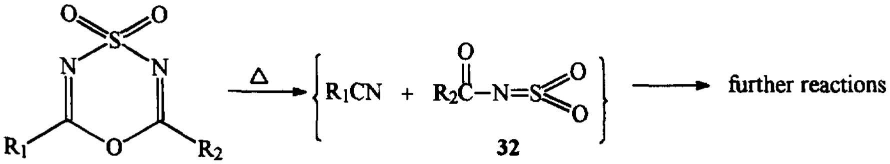
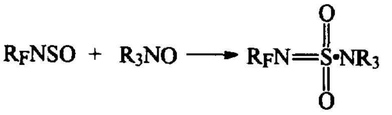
Scheme 11.



Scheme 12.



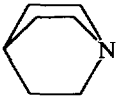
Scheme 13.



$$R_FNSO + R_3NO \longrightarrow R_FN{=}\overset{O}{\underset{O}{S}}{\cdot}NR_3$$

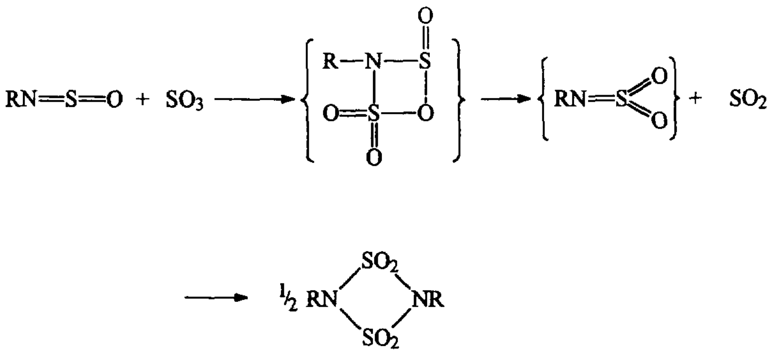
33

33a,b $R_F = C_6F_5, (CF_3)_2CF;\ R_3N = Me_3N$

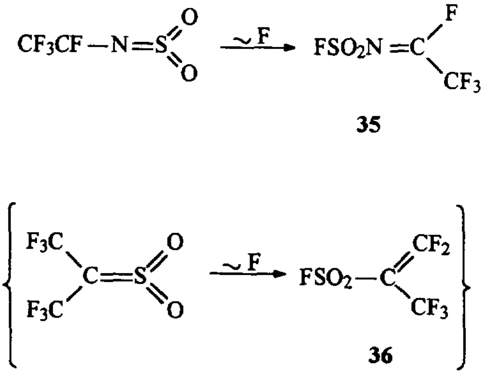
33c $R_F = C_6F_5;\ R_3N =$ 

Scheme 14.

An interesting new route to amine-stabilised *N*-perfluoroalkyl- or *N*-perfluoroaryl-sulphonyl imines is the oxidation of thionyl imides R_FNSO by amine oxides (Scheme 14) [30], similar to the long-since known oxidation of SO_2 to $R_3N \cdot SO_3$ [45]. In the reaction of RNSO with SO_3 (Scheme 15), an imination of sulphur trioxide appears to occur leading to the formation of dimeric sulphonyl imines, rather than oxidation of thionyl imides [26,27]. The degree of oligomerisation depends on the size of the substituent: with $R = CF_3$ dimers and trimers are formed in the ratio 3 : 1 [29]. The formation of monomeric sulphonyl imine intermediates is suggested by the partial isomerisation of the perfluoroethyl derivative according to Scheme 16. A comparable intramolecular stabilisation by F^--migration is found in perfluorinated sulphenes [7].



Scheme 15. **34a**, **b** R = FSO_2 [26], CF_3SO_2; **34c**, **d** R = CF_3 [29,30], C_2F_5 [29].



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36

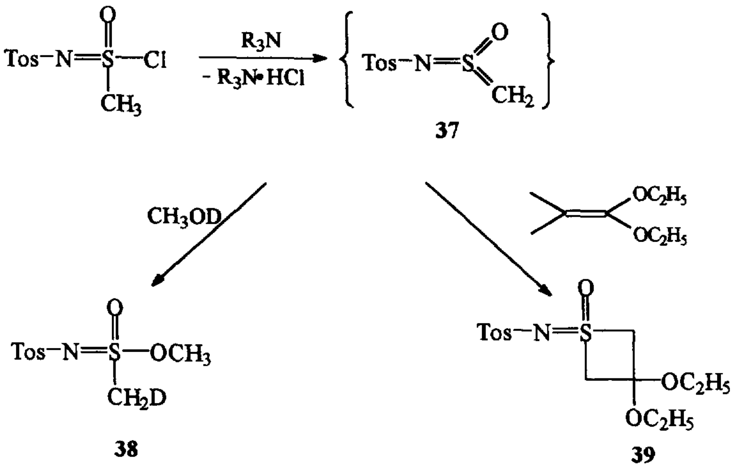
Scheme 16.

2.4. *Preparation of sulphene imides, $R_2C{=}S({=}O){=}NR'$*

Formal substitution of one oxygen in sulphonyl imides by an alkylidene group leads to sulphene imides (imino sulphenes) $R_2C{=}S({=}O){=}NR'$ [46]. Although very little as known about this class of compounds, their chemistry is more like that of sulphenes (addition to the C=S bond) than of sulphonyl imines. As with the preparation of sulphonyl imines or sulphenes, they might be generated by dehydrohalogenation of suitable precursors according to Scheme 17. Proof for the formation of **37** was found by trapping reactions [46].

2.5. *Structures and reactivity of $(RN)_nSO_{3-n}$*

SO_3 might be considered to be the parent compound of three-coordinate sulphur(VI) species. In the gas and liquid phases the monomer is in equilibrium with the trimer, in the solid state only the trimer is present [47]. Owing to the small and strongly electron-withdrawing oxygen substituents, the coordinatively unsatu-



Scheme 17.

rated and positively polarised sulphur centre acts as a strong Lewis acid. Anions and neutral Lewis bases will add to the sulphur with increase in the coordination number.

The gas-phase structure has revealed the expected D_{3h} geometry; an SO distance of 142 pm was determined [48]. This geometry is only slightly disturbed by the addition of nitrogen donors. In $SO_3 \cdot D$ ($D = NH_3$ [49], $NH(CH_3)_2$ [50], $N(CH_3)_3$ [51] and quinuclidine [45]) the expected pyramidalisation of the SO_3 framework is small (OSO 115–116°), the SO distance was found in the range 144(2)–140.5(2) pm. The SN bond distance is appreciably longer, especially in the trimethyl (184.4(2) pm) and quinuclidine (183.1(6) pm) adducts, than a normal SN single bond. These data show that useful information on the parent three-coordinate species can be deduced from the structures of the tertiary amine adducts.

No structure determination of the free three-coordinate species is found in the literature owing to the instability of sulphonyl imines $RN{=}SO_2$. The properties should be similar to those of SO_3, particularly when R is an electron-withdrawing group, e.g. perfluoroalkyl or aryl group, a sulphonyl group, etc. The only structure determination of a donor-stabilised sulphonyl imine was reported by Sundermeyer and co-workers [30]. In $C_6F_5NSO_2 \cdot$ quinuclidine, again only a slight pyramidalisation of the NSO_2 framework is observed (sum of the angles 348.3°). The SO (142.6(1), 142(1) pm) and SN distances (152.4(1) pm) should not differ too much from the free sulphonyl imine values since the interaction with the quinuclidine donor (d(SN) = 186.9(1) pm) is weak. The Lewis acid properties and the SN and the SO bond lengths in $RNSO_2$ will be dependent upon the substituent R. Alkyl groups R are expected to decrease the SN and increase the SO bond distances. Although the Lewis acidity will decrease, the primary step in the reactions of all sulphonyl imines will be a nucleophilic attack at the sulphur.

Probably the most interesting class of compounds of this series might be the bis(imino)-sulphoxides $(RN)_2S{=}O$. Unfortunately, nothing is found in the literature on the structures of the free three-coordinate species or an amine adduct. The amine adduct should be readily available, e.g. by oxidation of sulphur diimides by amine oxides. The properties of bis(imino)-sulphoxides are expected to be 'tuneable' by the properties of the substituent R. With electron-withdrawing substituents Lewis acidic behaviour will result, while with alkyl derivatives an electrophilic attack at the imino nitrogen is probably the first step in their reactions (Section 2.6.2).

Sulphur triimides, $(RN)_3S$ with sterically demanding groups $R = SiMe_3$ [1,52] and CMe_3 [15,52] have been isolated as stable monomers and characterised by X-ray crystallography (Figs. 2 and 3).

It is not known, with certainty, if the SN_3 framework of these 'Y-trienes' [15] is totally planar or not. In the structure determinations at −130 °C, the central sulphur shows unusually large thermal ellipsoids perpendicular to the SN_3-planar, suggesting that the planar structure is an average of statistically disordered, slightly pyramidal molecules. The experimentally determined planarity of the isocoordinated amino bis(imino)phosphoranes $(Me_3SiN)_2PN(SiMe_3)_2$ [53] and the isoelectronic tris(imino)metaphosphates, $(RN)_3P^-$ [4] has been confirmed by theoretical studies [54,55].

From Fig. 3 it can be concluded that oligomerisation or polymerisation of the triimide would be difficult for steric reasons, regardless of whether this sulphur has planar coordination or if it is at the apex of a flattened trigonal pyramid. Pyramidalisation would suggest localisation of electron density at the sulphur, and this would also prevent attack of nucleophiles (which is experimentally confirmed).

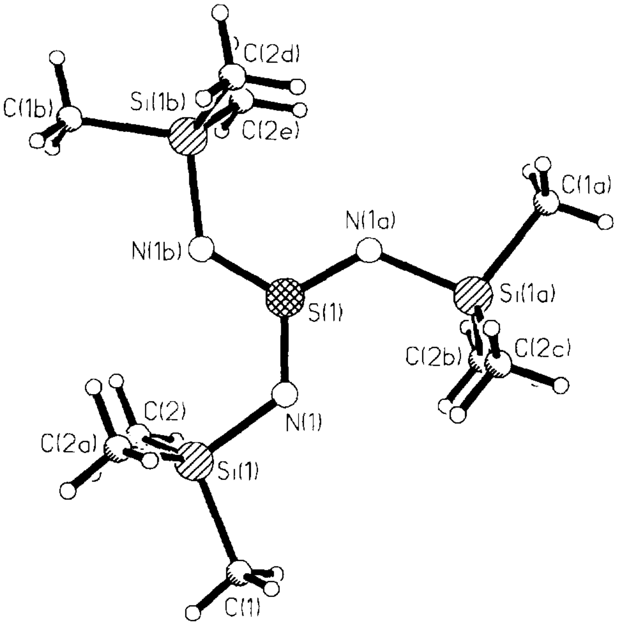


Fig. 2. Molecular structure of sulphur tris(trimethylsilyl imide) 1.

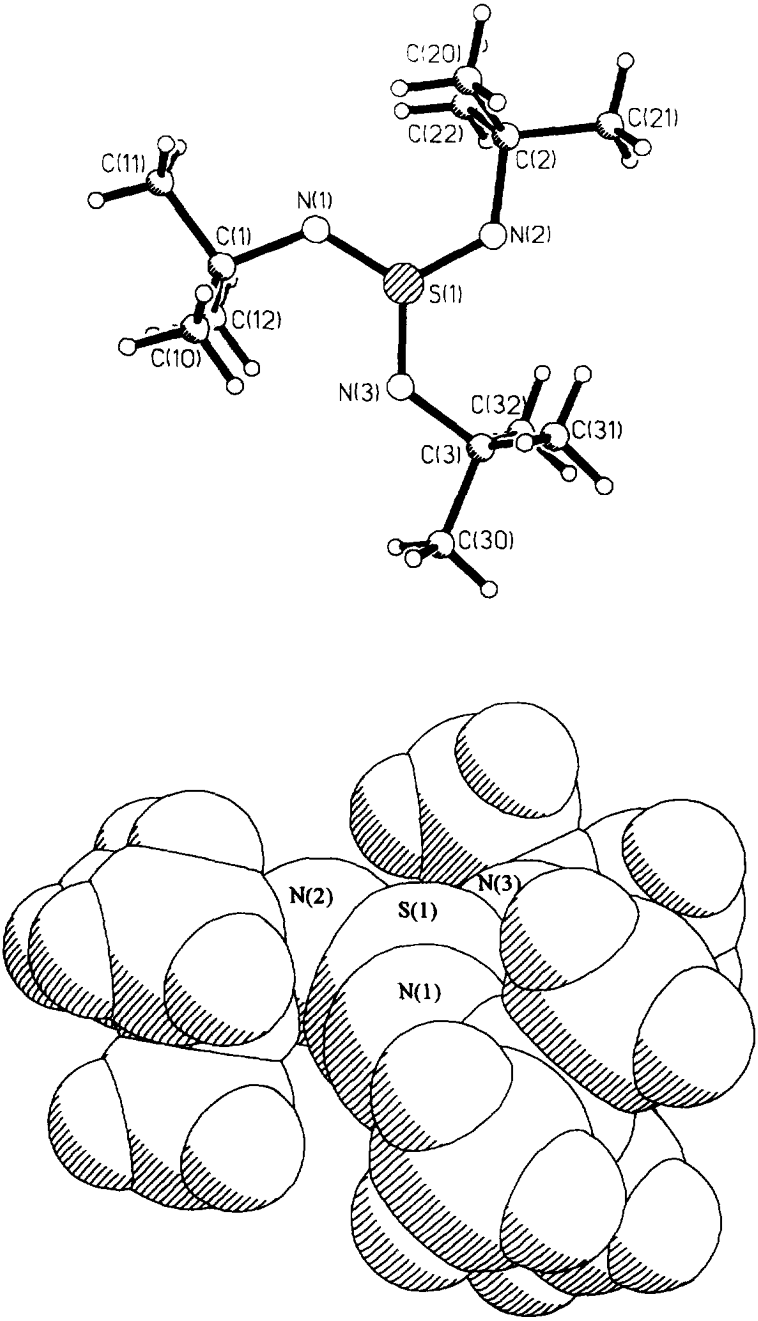


Fig. 3. Molecular structure of sulphur tris(*tert*-butyl imide) **10**.

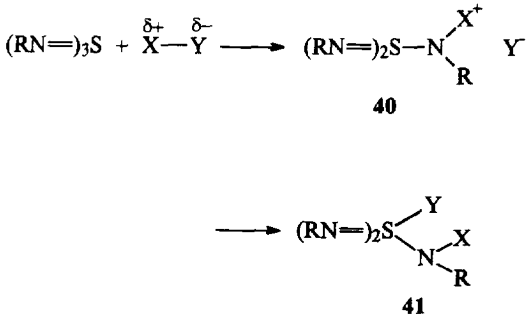
The primary step in the reactions of **1** and **10** is always an electrophilic attack at one of the peripheral nitrogen atoms. If the *tert*-butyl group in **10** is systematically exchanged by smaller and strongly electron-withdrawing groups, the character of **10** gradually changes from a Lewis base to a Lewis acid. This can be concluded from the reactions of this triimide, described in Section 2.6.

2.6. The chemistry of $(RN)_nSO_{3-n}$

2.6.1. Sulphur triimides, $(RN)_3S$

Only the chemistry of $(^tBuN{=})_3S$ **10** has been investigated in any detail. Some reactions of the tris(silylimino) derivative **1** are also reported in the literature. Reactions of these triimides follow a simple scheme: the primary step is the addition of an electrophile to one of the peripheral nitrogens, followed by addition of a nucleophile to the activated sulphur centre. The result is the saturation of one of the SN double bonds with coordination expansion at the sulphur. Because the crucial step is the primary attack, it is clear why tris(*tert*-butyl)sulphur triimide is appreciably more reactive than the silylated derivative.

As indicated in Scheme 18, for H_3COSO_2F (for $R = (CCH_3)_3$) the isolated product might be a salt of type **40** [56], but this has not been confirmed by a structural determination. If X–Y are protonic acids (RCOOH, ROH, H_2O) this primary step cannot be stabilised, Y will attack the sulphur to form **41**-type products. Successful reactions have been carried out with alcohols and water. EtOH reacts with both triimides to give simple addition products [3] (Scheme 19).

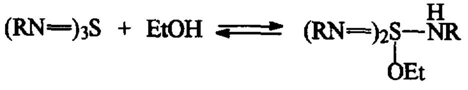


(R = Me3C, Me3Si)

Scheme 18.

The reaction is reversible; decomposition into the starting materials is observed above 100 °C. Alcohols with bulkier groups (*iso*-prop, *tert*-but) do not react, probably because the second step, the addition of the nucleophile to the sulphur centre, is not possible for steric reasons. With methanol the primary product reacts further (Scheme 20). Similarly, with moist ether the corresponding sulphamides are formed (Scheme 21).

Reactions of sulphur triimides with systems containing polar double bonds, e.g.

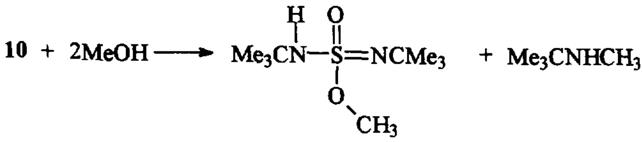


$$(RN{=})_3S + EtOH \rightleftharpoons (RN{=})_2\underset{OEt}{S}{-}\overset{H}{N}R$$

42

42a, b R = Me_3C, Me_3Si

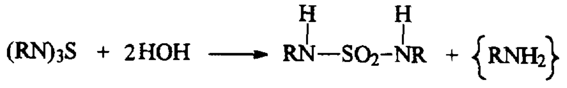
Scheme 19.



$$10 + 2MeOH \longrightarrow Me_3C\overset{H}{N}{-}\underset{O{-}CH_3}{\overset{O}{\overset{\|}{S}}}{=}NCMe_3 + Me_3CNHCH_3$$

43

Scheme 20.



$$(RN)_3S + 2HOH \longrightarrow R\overset{H}{N}{-}SO_2{-}\overset{H}{N}R + \{RNH_2\}$$

44

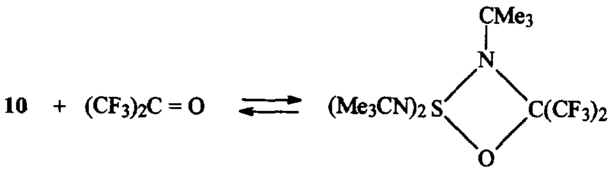
44a, b R = Me_3C, Me_3Si

Scheme 21.

$>C{=}N{-}$, $>C{=}O$, $-N{=}C{=}O$, $-N{=}S{=}O$, $O{=}S{=}O$, offer new routes to an interesting heterocyclic chemistry. These isolated or cumulated double bonds will only react if they are connected to electron-withdrawing groups in order to facilitate an electrophilic attack at a nitrogen.

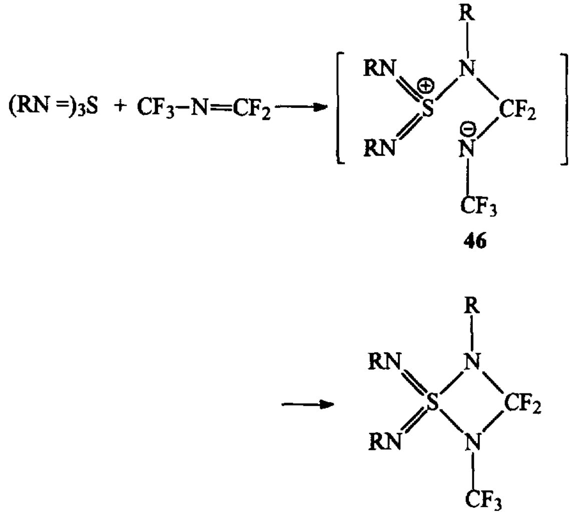
With hexafluoroacetone $(CF_3)_2C{=}O$ only the *tert*-butyl derivative forms an adduct [57], for which the most reasonable structure is **45** (Scheme 22). At room temperature this 1,2λ^6,3-oxathiazetidine will decompose into the starting materials. With both triimides, pentafluoroazapropene forms 1 : 1 adducts, for which the cyclic structure **47** is most likely [57] (Scheme 23). The betaine **46** is probably formed in the first step. **47a** and **47b** are not very thermally stable; while **47b** dissociates slowly into the starting materials at room temperature, **47a** decomposes above its melting point (43 °C).

A considerable number of reactions have been carried out with isocyanates [20,58,59] (Scheme 24). The primary step will be the formation of betaines followed by ring closure to give the unstable, not isolated λ^6-thiadiazetedinones. These decompose to give bis(*tert*-butylimino)sulphur triimides with one electron-withdrawing group, as reported earlier (Scheme 5) [20]. In the reaction of these triimides, electrophilic attack at one of the peripheral nitrogen atoms will also be the first step in



45

Scheme 22.



46

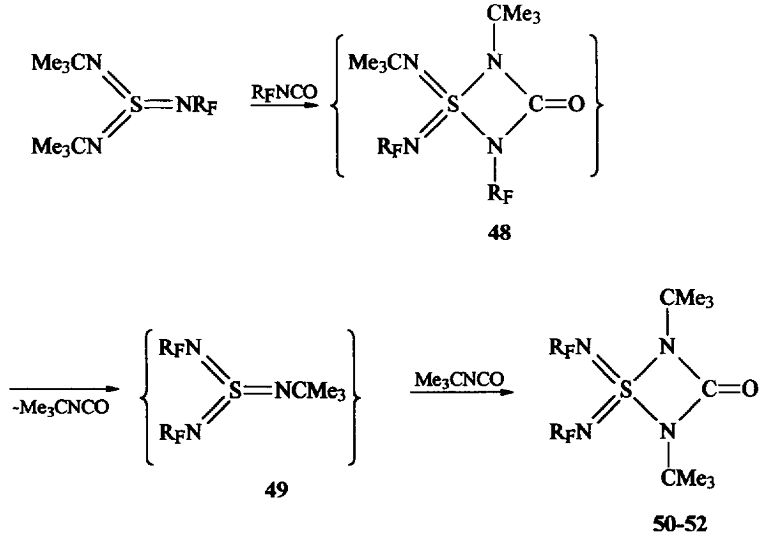
47a, b R = Me3C, Me3Si **47**

Scheme 23.

further reactions. Similarly, with excess R_FNCO, unstable, unsymmetrically bridged λ^6-thiazetedinones **48** are formed; decomposition of these leads to sulphurtriimides **49** with two electron-withdrawing groups. The consequence of these two electron-withdrawing groups is reversal of the reactivity. As with the sulphonyl imines, $RN{=}SO_2$, **49** show Lewis acidic behaviour, as they are attacked by nucleophiles at the central sulphur. The strongest nucleophile present in the reaction mixture is Me_3CNCO, which adds to **49** giving the stable final products **50**–**52** [58,59].

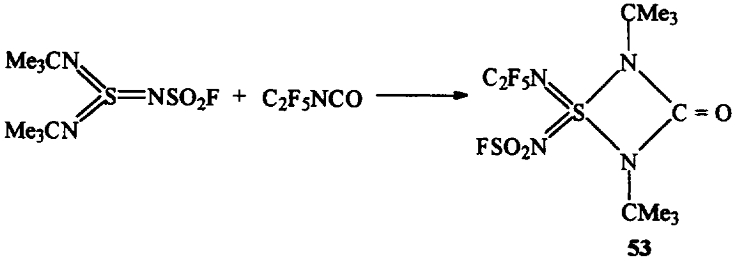
Thiadiazetedinones with two different R_FN– groups are obtained in good yield if a bis(*tert*-butyl)triimide is reacted with a different R_FNCO, as shown in Scheme 25.

Structure determination of **50b** ($R_F = FSO_2$) shows that the four-membered ring is planar [58]; although bulky groups (e.g. Me_3C) are known to stabilise small ring sizes, this seems to be unnecessary for λ^6-thiadiazetedinones. If the reaction of Scheme 24 is carried out in C_2H_5NCO as solvent, this will act as a nucleophile in the last step of the reaction sequence to give the *tert*-butyl-ethyl derivative **54** in reasonable yield [58,59] (Scheme 26). This was also regarded as proof for the



50a-c $R_F = XSO_2$ (X = Cl, F, CF_3), **51** = SF_5, **52** = $CF_3C(O)$

Scheme 24.

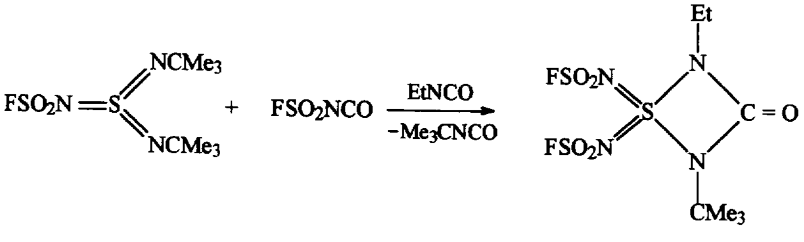


Scheme 25.

intermediate formation of mono(*tert*-butyl) derivatives **51** with Lewis acid properties.

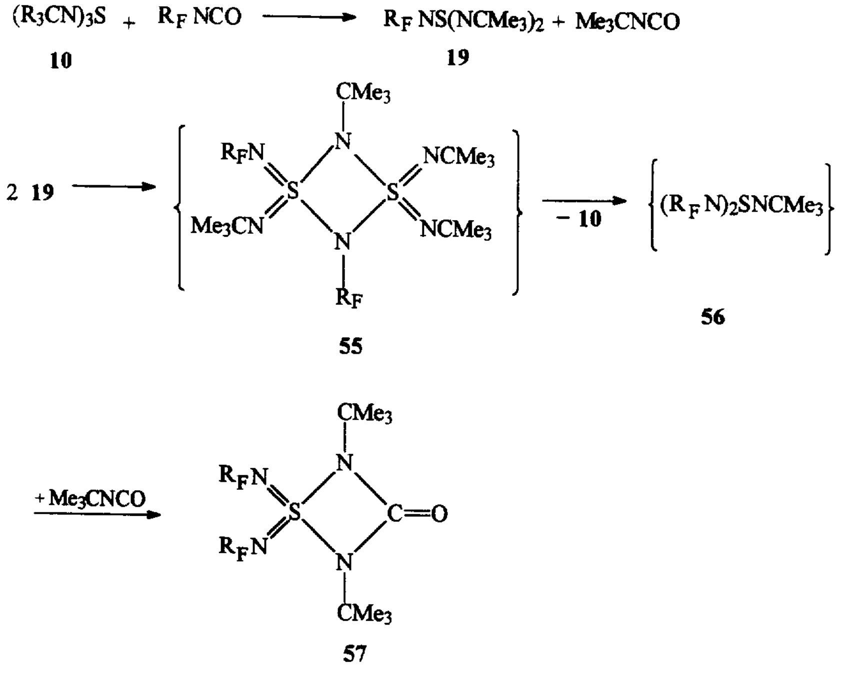
A different pathway is followed with the less reactive perfluoroalkyl isocyanates. After formation of the monosubstituted triimides $(R_FN)S(NCMe_3)_2$, the next step is not the attack of the isocyanate but the dismutation of **19** (Scheme 27). In a slow reaction, **56** is formed as an intermediate which reacts with the nucleophile Me_3CNCO to give the stable final product **57**. If the nucleophile Me_3CNCO is removed before dismutation, intermediate formation of **56** takes place, if pure **19** are kept at room temperature then *cyclo*-diazadithianes are formed [60].

56 reacts as a Lewis acid with **19** (as Lewis base) to form stable **59** according to Scheme 28. **10** is a stronger base than **19** and is expected to attack **56** more readily, but betaine **58** might not undergo ring closure to give a stable heterocycle because



54

Scheme 26.



10 **19** **55** **56** **57**

$R_F = CF_3, C_2F_5, n\text{-}C_3F_7$

Scheme 27.

the acceptor properties of the three-coordinate sulphur centre are too weak. The X-ray crystal structure of **59** ($R_F = C_2F_5$) is shown in Fig. 4.

10 reacts with $(CF_3)_2CFNCO$ to form the stable mono-substituted product $(CF_3)_2CFNS(NCMe_3)_2$ (**19d**), which undergoes no further reactions at room temperature. If **10** and $(CF_3)_2CFNCO$ are reacted at higher temperatures (40 °C), the primarily formed betaine **60** will undergo a kinetically controlled *O*-cyclisation, as shown in Scheme 29. Sulphuroxide diimide **62** is assumed to be an intermediate which can undergo a normal *N*-cyclisation to give **64** which decomposes to **65**.

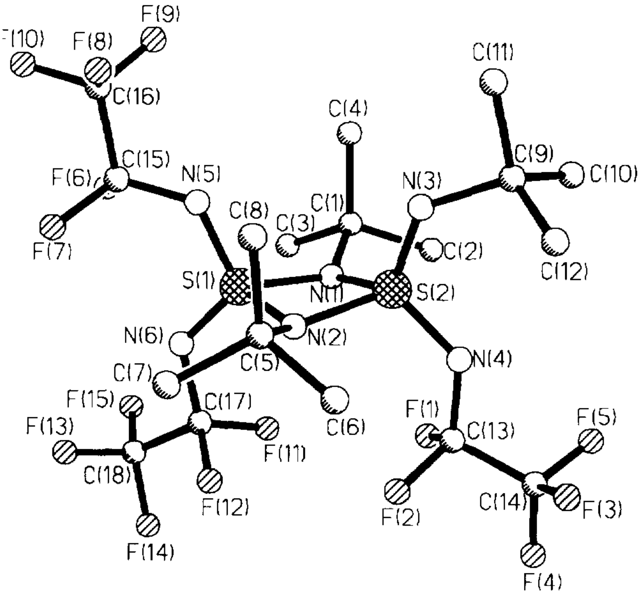
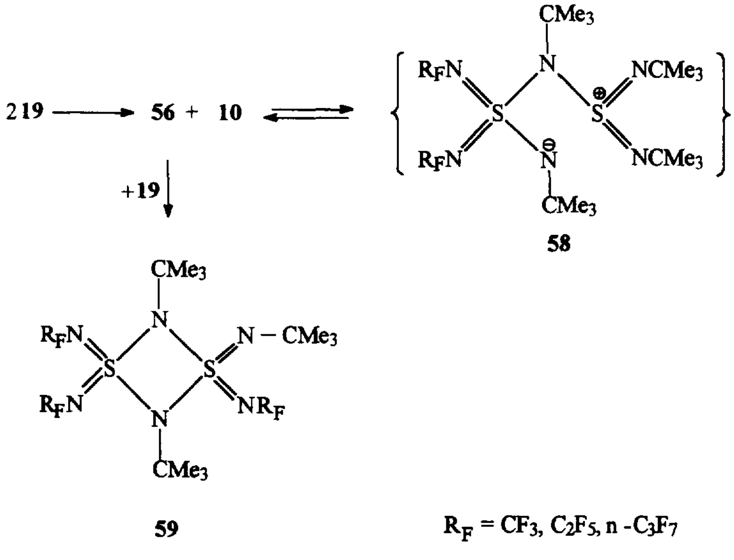
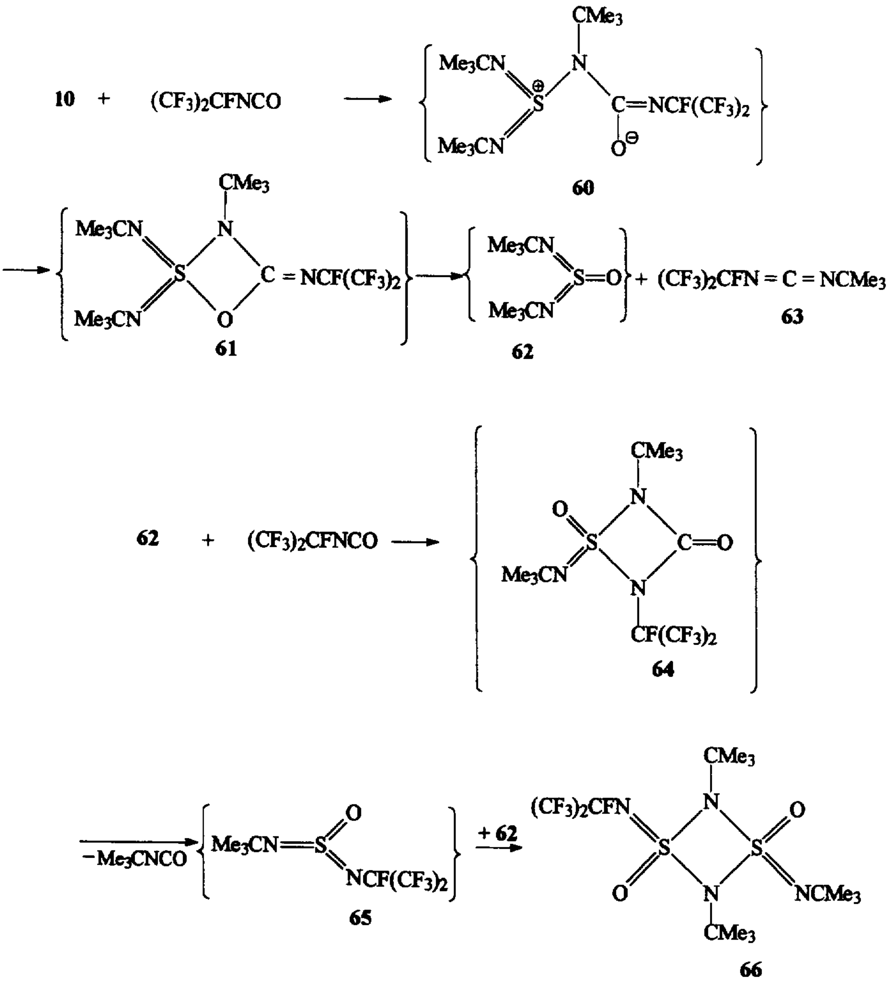


Fig. 4. Molecular structure of 1,3,3-tris(pentafluoroethyl imino)-(*tert*-butyl imino)-2,4-bis(*tert*-butyl)-*cyclo*-diaza-λ^6-dithiane **59**.



Scheme 28.

Again, formation of the stable final product **66** can be described as a Lewis acid–base reaction of **65** with **62**. Stable four-membered S(VI)N-heterocycles are isolated if at least three Me_3CN groups at the sulphur centres are replaced by electron-

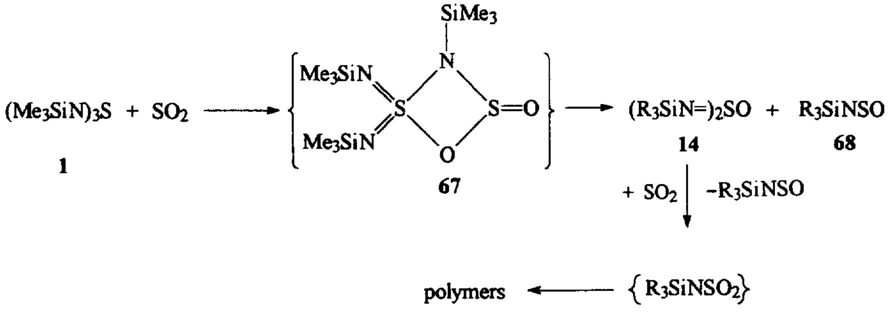


Scheme 29.

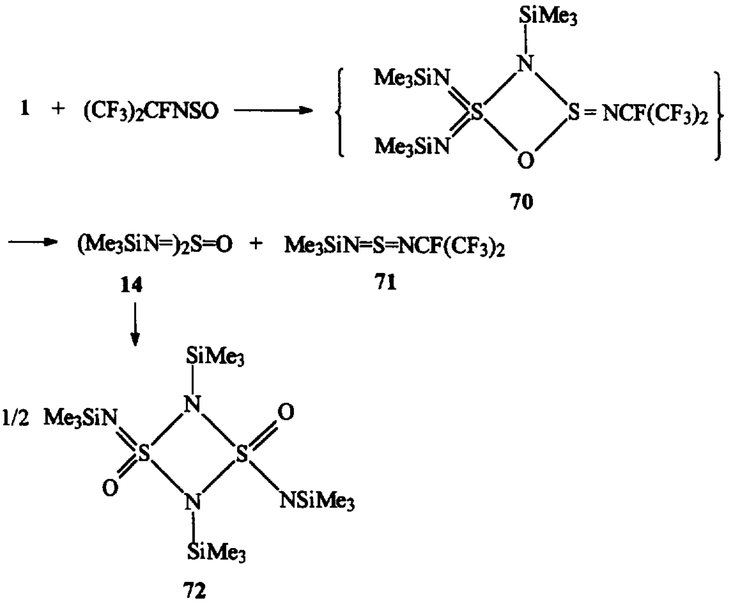
withdrawing groups (R_FN, O). Exchange of a $Me_3CN=$ group by oxygen using isocyanates R_FNCO is only possible if the R_F group is very bulky, as shown previously. Suitable reagents for the introduction of oxygen are SO_2 and thionyl imide R_FNSO.

1 reacts with SO_2 in an uncontrollable reaction [61] according to Scheme 30. **68** is isolated from the reaction mixture and **14** is detected by mass spectroscopy, but mainly polymeric material is formed.

In the reaction of **1** with $(CF_3)_2CFNSO$, *O*-cyclisation dominates [61] (Scheme 31). Decomposition of the intermediate **70** will give **14** and the sulphur diimide **71**, which was obtained in 86% yield. Bis(trimethylsilylimino)sulphur oxide



Scheme 30.



Scheme 31.

14 is not stable under these reaction conditions; the dimer **72** (Fig. 5) was isolated and structurally characterised [60,61].

Tris(*tert*-butyl)sulphur triimide **10** reacts in a similar way to **1** with formation of sulphoxide **73** as an intermediate (Scheme 32). As expected, the dimer **74**, containing only two electron-withdrawing substituents at the sulphur atoms, is not isolated. **73** probably reacts further to give sulphonyl imide **75**, which adds **74** to form stable **76** [61].

2.6.2. Bis(imido)sulphur oxides, $(RN)_2SO$, sulphur dioxide imides, $(RN)SO_2$, and sulphene imides, $(RN)(R'C)SO$

The chemistry of bis(imino)sulphur oxides and sulphene imides is poorly developed; only the reactions discussed in Schemes 9 and 17 have been reported.

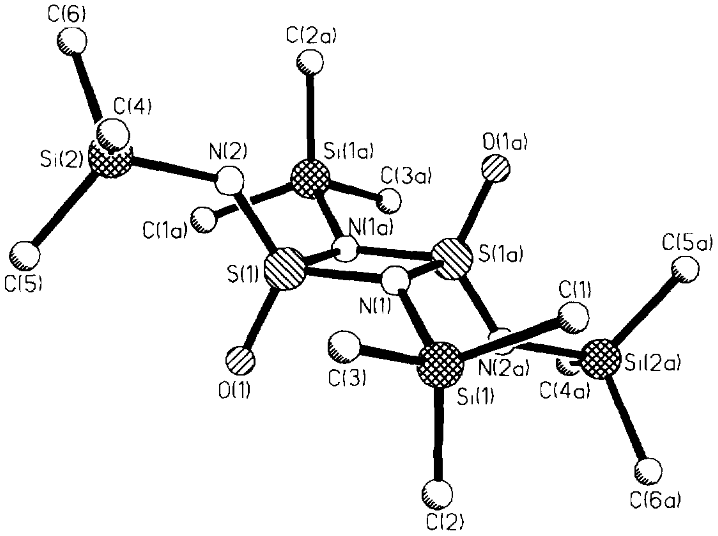
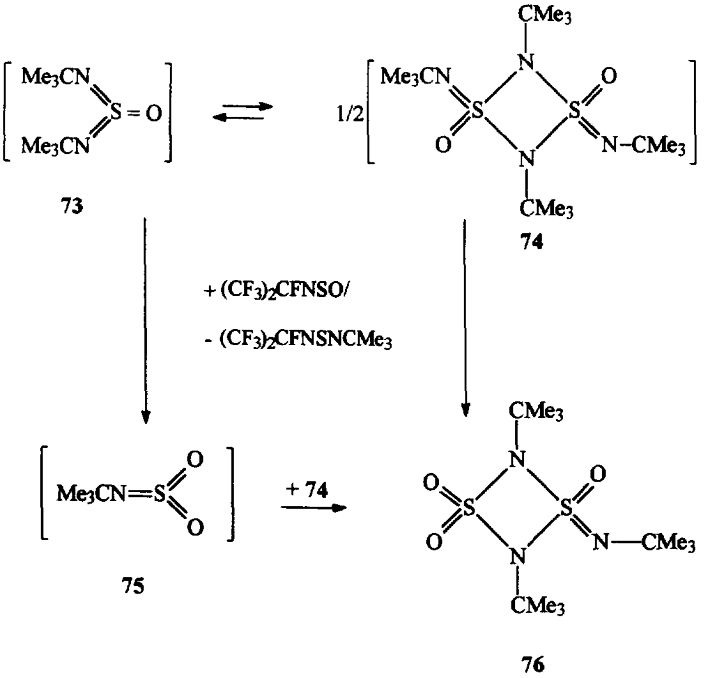


Fig. 5. Molecular structure of 1,3-dioxo-2,4-bis(trimethylsilyl)-1,3-bis(trimethylsilylimino)-*cyclo*-diaza-λ^6-dithiane **72**.

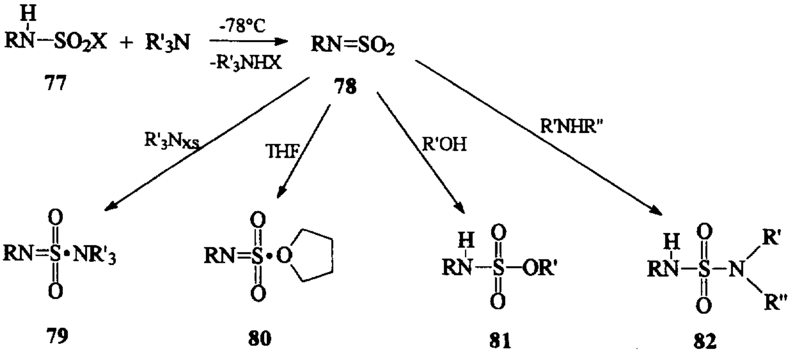


Scheme 32.

Furthermore, $(RN)_2SO$ are possible intermediates in the reactions of triimides, as discussed in Section 2.6.1.

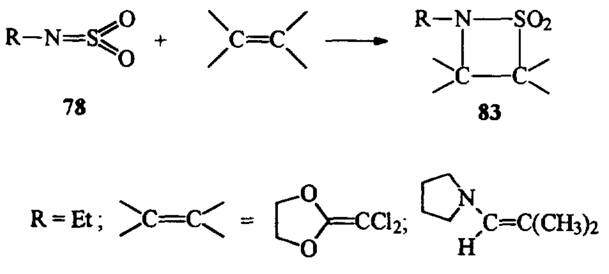
The chemistry of sulphonyl imines, $RNSO_2$, is strongly related to that of SO_3. Compared with the trioxide, the acidity is more or less decreased, depending on the nature of the substituent R. Some steric influence and kinetic effect is also expected from these substituents. Characteristic for SO_3 is its electrophilicity, nucleophiles (e.g. *tert*-amines, ethers and halide anions) will form stable adducts. Alcohols and *prim*- and *sec*-amines will add across the SO double-bond forming sulphuric acid esters and sulphamides; addition to double and triple bonds will lead to heterocycles. Sulphonation of aromatic systems and insertions into carbon-element bonds are reported [5,62]. The ether (Suter–Bordwell method) [63] and pyridine adducts (Terentjew method) [64] have been used as stabilised and 'tamed' monomeric SO_3 for further reactions.

Owing to their thermal instability, the chemistry of monomeric sulphonyl imines is a low-temperature chemistry. Their generation and their reactions normally being performed at −78 °C [10]. Therefore, only highly reactive nucleophiles are suitable as reagents. *tert*-Amines and ethers (e.g. THF) will form adducts, whereas alcohols and *prim*- and *sec*-amines will add across the SN double-bond [31,32,35–40,65–67], as shown in Scheme 33.

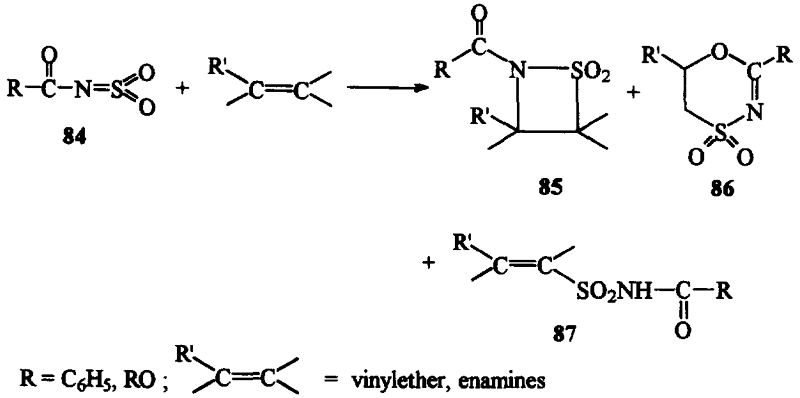


Scheme 33.

At low temperatures, monomeric, unstabilised *N*-alkyl sulphonyl amines will react only with strongly nucleophilic alkenes to form the aza-analogues of *β*-sultones. They might also be generated at room-temperature and reacted in situ. The more reactive *N*-benzoyl and carbamoyl derivatives undergo these (2+2) and also (4+2) cycloadditions (with participation of >C=O) with less electron-rich double-bond systems. Owing to the high polarity of the $R\text{–}^{\delta-}N{=}^{\delta+}SO_2$ bond, these reactions are very regioselective. Stabilisation of sulphonyl imines can be achieved by ethers and *tert*-amines, as previously mentioned. As with the Terentjew and the Suter–Bordwell methods, these adducts can be used as starting materials at higher temperatures in the reactions with nucleophiles, alkenes or alkynes or in aromatic sulphiminations. The usefulness of unstablilised and stabilised sulphonyl imines in organic syntheses is shown by the following reactions in Scheme 34 and Scheme 35. The product distribution **85**–**87** in Scheme 35 is dependent upon the alkene nucleophilicity and the solvent dielectric constant [36].



Scheme 34.

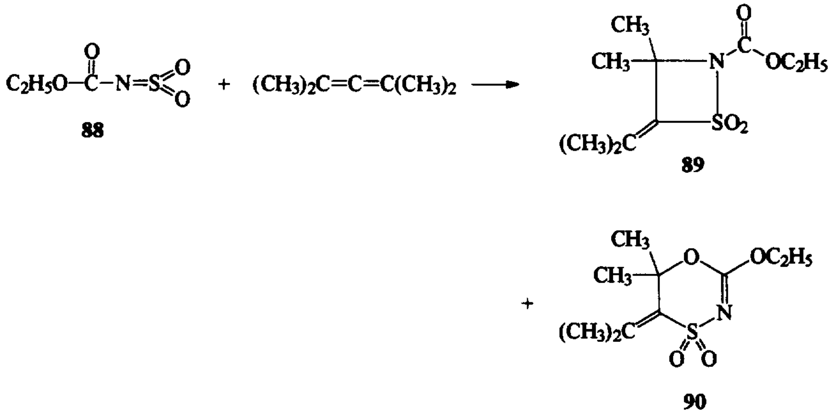


Scheme 35.

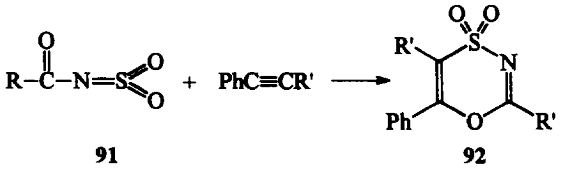
Tetramethyl allene reacts with the Et_3N adduct of **88** at 60 °C in CH_3CN to give two isomeric cycloadducts (Scheme 36). The isopropylidene-1,4,5-oxa-thiazine-4,4-dioxide structure **90** was assigned to the major product. With alkynes, only (4+2) cycloadditions are reported [36,40] according to Scheme 37. Activated dienes also form (2+4) cycloaddition products [39] according to Scheme 38.

Another possibility for stabilisation is reported for *N*-carbonyl sulphonyl imides in RCN solvents, which readily form (2+4) adducts [44,40] (Scheme 39). These heterocycles undergo thermal cycloreversions. Even at room temperature small amounts of the sulphonyl imine are present in the equilibrium [35–38,40,44].

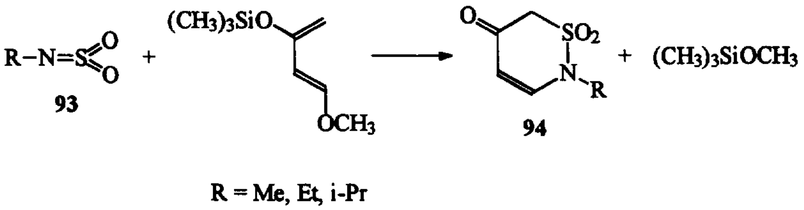
A fourth mode of stabilisation is the dimerisation observed for sulphonyl–sulphonyl imines RSO_2NSO_2. In their reactions with amines, alcohols and water [68], and with N-donors they act like monomers [27] (Scheme 40). Primary alkyl amines react too vigorously, even at −80 °C (Scheme 41). With nitriles, 1 : 2 cycloadducts (1,1-dioxo-1,2,4,6-thiatriazines) are formed [27] (Scheme 42). In the reaction with aryl isocyanates, sulphimination with subsequent ring-closure is observed [27] (Scheme 43). Sulphiminations of activated benzene derivatives were also reported in the literature [32].



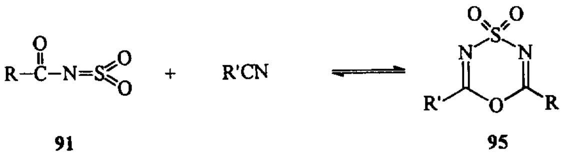
Scheme 36.



Scheme 37. R$=CH_3O$; R'=H [36], R_2N [40].



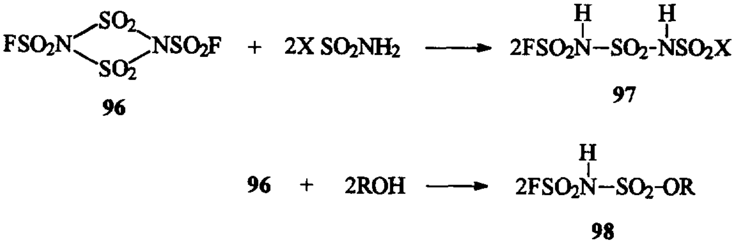
Scheme 38.



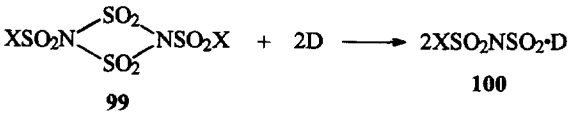
Scheme 39. R$=CH_3O$; R'=Me, p-$CH_3OC_6H_4$, $(CH_3)_2N$ [44]; R=R'$=C_6H_5(CH_3)N$ [44].

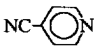
Further interesting examples for the use of sulphonyl imines as synthons in organic chemistry are the reactions with diazoalkanes, where a thiaziridine-1,1-dioxide was observed for the first time [33] (Scheme 44).

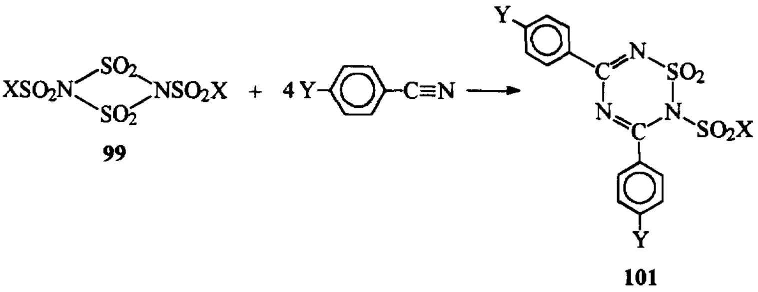
In the reactions with ketones and dimethyl sulphoxide, the corresponding



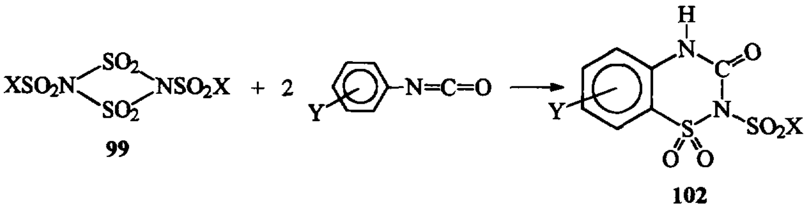
Scheme 40. X = F, Cl [68]; R = CH_3, C_2H_5, i-C_3H_7.



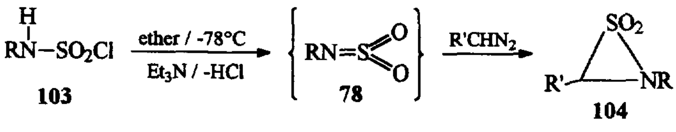
Scheme 41. X = F, CF_3; D = S_4N_4, , NC- [27].



Scheme 42. X = F, CF_3; Y = H, Cl, OCH_3; X = F, Y = NO_2 [27].

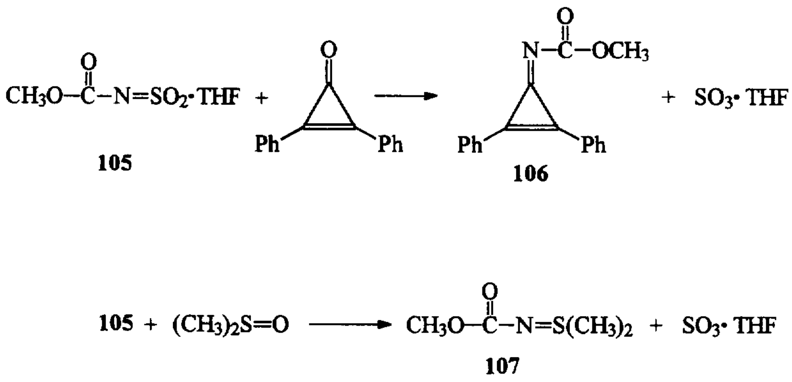


Scheme 43. X = F, Y = *p*-Cl; X = CF_3, Y = *m*-Br [27].



Scheme 44. R = Me_3C, R′ = Me_3C, adamantyl; R = ad, R′ = Me_3C, ad [33].

imino-derivatives are formed in a Wittig-type reaction [35] (Scheme 45). The driving force for the loss of SO_3 is adduct formation with THF, used as a solvent.



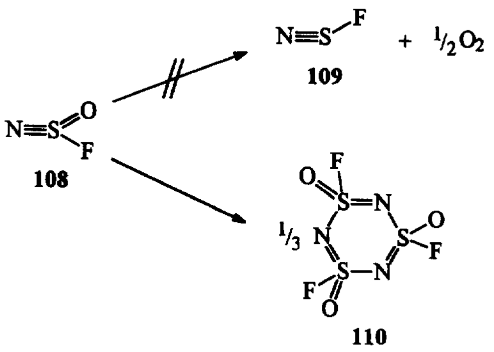
Scheme 45.

3. Thiazyloxide-derivatives, N≡S(=O)X

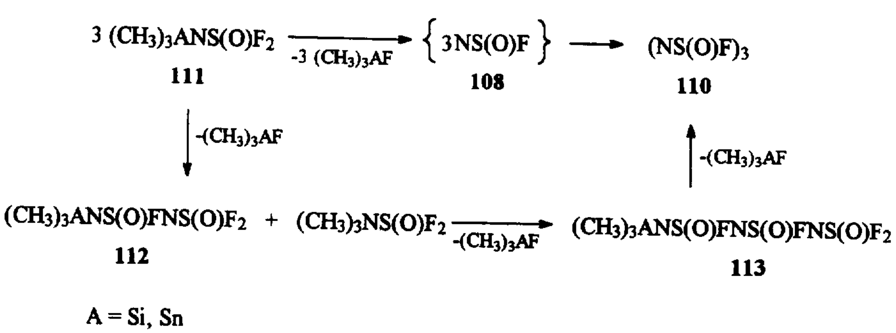
In Section 2, three-coordination for the central sulphur was reached by three doubly bonded substituents. A second possibility for the realisation of coordination number three is the exchange of two double-bonds by a triple and a single bond: thiazyl oxide and thiazyl imino derivatives N≡S(=O)X and N≡S(=NR)X are realistic examples. In the literature, however, only the first class of compounds is discussed.

According to ab initio calculations by Ehrhardt and Ahlrichs [11], thiazyl oxide fluoride, NS(O)F (**108**) should be an isolable molecule. The equilibrium geometry calculated at the SCF(B) level shows that this molecule must be regarded, according to the bond lengths (NS 141.2 pm, SO 142.0 pm, SF 155.5 pm), as thiazyl oxide fluoride, N≡S(=O)F, with a triple-, double- and single-bond connected to one centre. These investigations show that NS(O)F is stable, with respect to dissociation into NSF and O_2, but trimerisation to $(NS(O)F)_3$ [69] (Scheme 46) should occur more readily than for the related sulphur(IV) species, NSF [70]. Because monomeric NSF can be generated easily and stored at −80 °C as a liquid over a longer period of time without appreciable trimerisation, the detection of NS(O)F, at least in a matrix, is not unlikely.

Reactions where NS(O)F might have been generated are the decompositions of $Me_3SiNS(O)F_2$ and $Me_3SnNS(O)F_2$ [71] (Scheme 47). Monomeric NS(O)F need not necessarily be an intermediate in these reactions, oligomers of types **112** and **113** could be steps on the way to the trimer **110**. Hints for the formation of such oligomers were found in the CO_2-laser-induced irradiation of $Me_3SiNSOF_2$ at low pressures [72].

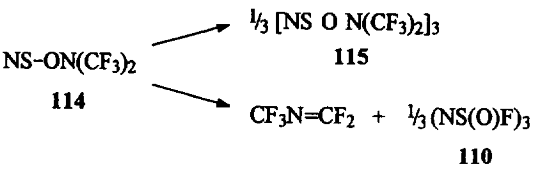


Scheme 46.



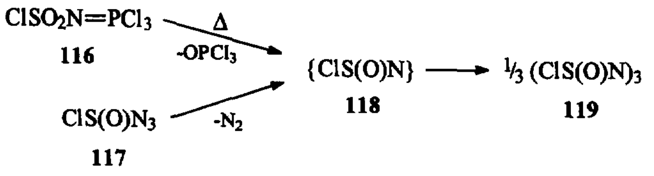
Scheme 47.

Another candidate for the generation of NS(O)F is $(CF_3)_2NOSN$ [73]; besides trimerisation, decomposition to $CF_3N{=}CF_2$ and sulphanuric fluoride is observed [74] (Scheme 48). Intermediate formation of oligomers is very unlikely in the last reaction. The chloro analogues of **108** and **110** are generated by the decomposition of $ClSO_2NPCl_3$ [75] or $ClS(O)N_3$ [76] (Scheme 49).



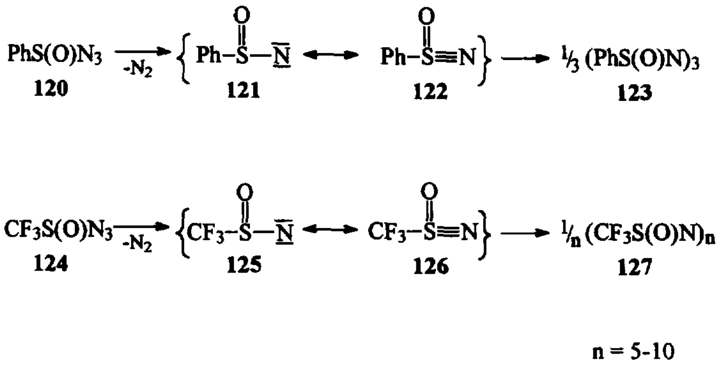
Scheme 48.

More recent investigations show that the results of the thermal decomposition of **117** are temperature dependent. At lower temperatures (0 °C) mainly $(NS(O)Cl)_2(NSCl)$ is isolated [77]. Although **108** seems to be stable against the loss of oxygen, **118** might not be.



Scheme 49.

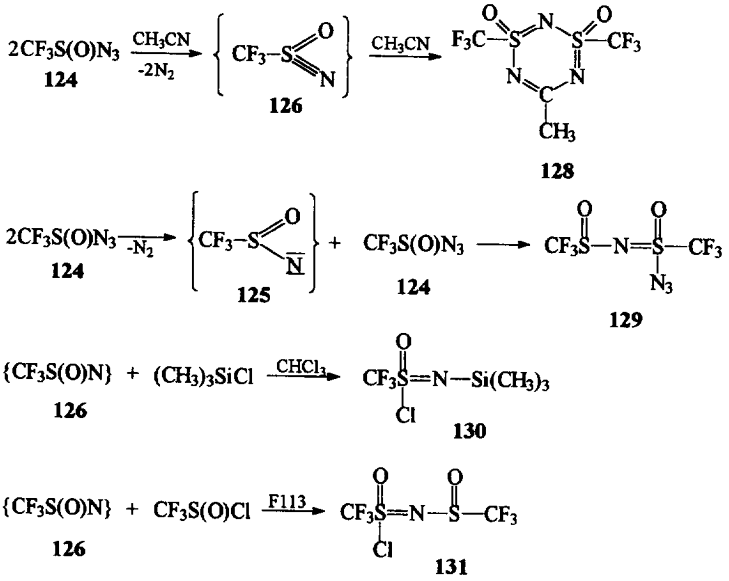
The first report on the decomposition of a sulphinyl azide is by Maricich [78]; he also isolated the trimer of the primary product according to Scheme 50. More recently, the generation and decomposition of trifluoromethyl sulphinyl azide, **124** was reported by Bechtold and Engelbrecht [79]. They assigned structure **126** to the primary decomposition product, which forms a complex product mixture of linear oligomers **127** with $n = 5–10$. **126** shows an interesting chemistry. Different products were isolated depending upon the solvents and reaction conditions used for the formation and decomposition of the azide **124**.



Scheme 50.

As shown in Scheme 51, cyclisation with participation of the solvent acetonitrile will lead to the dithiatriazine **128**, if high concentrations of **126** are present. During the formation of **129**, $CF_3S(O)N$ reacts like a sulphinyl nitrene, **125**, with oxidation of **124**. Addition of Me_3SiCl and $CF_3S(O)Cl$ to the SN triple-bond of **126** is reported to give **130** and **131**.

These few examples show that thiazyl oxide derivatives might be interesting intermediates in a variety of reactions. Their spectroscopic detection, and their stabilisation as ligands in transition metal complexes seems not to be impossible.



Scheme 51.

4. Three-coordinate sulphur(VI) cations

Because the neutral, three-coordinate sulphur(VI) derivatives are, in most cases, readily attacked by nucleophiles, the detection of three-coordination in the chemistry of sulphur(VI) cations should be even more difficult. Despite this, from the few reports in the literature, an interesting chemistry is expected from a systematic investigation of this field.

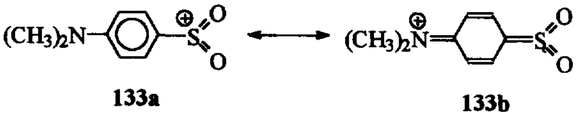
The first examples of three-coordinate sulphur(VI) cations were described by Lindner and Weber [80], who obtained sulphonylium cations by chloride-abstraction from p-$(CH_3)_2NC_6H_4SO_2Cl$ (Scheme 52).

$$\underset{\mathbf{132}}{p\text{-}(CH_3)_2N{-}C_6H_4{-}SO_2Cl} + AgMF_6 \xrightarrow[-AgCl]{SO_2/-25°C} \underset{\mathbf{133}}{[p\text{-}(CH_3)_2N{-}C_6H_4{-}SO_2]^+MF_6^-}$$

M = P, As, Sb

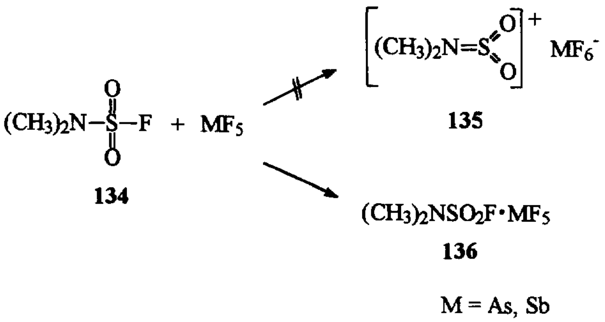
Scheme 52.

The relatively high stability of salts **133** is explained by mesomeric interaction with the aromatic system; the positive charge is transferred to the nitrogen (Scheme 53). The quinoid system **133b** can be regarded as a sulphene. The stability of **133** is dependent upon the counter-ion; the hexafluoroantimony salt is even stable at room temperature. Owing to the high electrophilicity of the sulphur centre, this acts as a Lewis acid abstracting F^- from the hexafluorometallates, MF_6^-, derived from the weaker Lewis acids PF_5 and AsF_5.



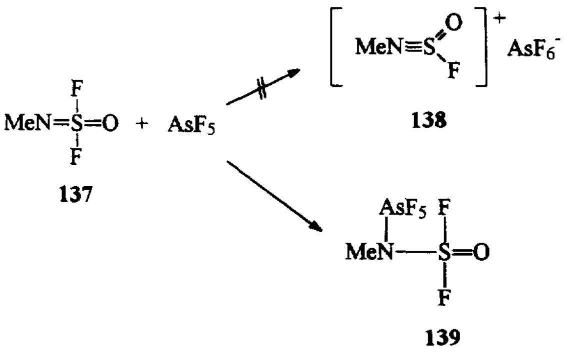
Scheme 53.

Many examples in the literature show that cations can be stabilised by the introduction of dialkyl amino substituents at the cationic centre. Attempts to generate sulphonyl iminium cations, **135** by F^- abstraction from Me_2NSO_2F **134** failed; only unstable adducts **136** were formed with AsF_5 and SbF_5 [80] (Scheme 54).



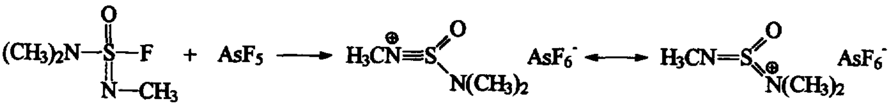
Scheme 54.

Salt **138**, which might be regarded as methylated thiazyl fluoride oxide **108**, is not observed in the reaction of sulphur oxide difluoride imide **137** with AsF_5; rather, the adduct **139** is prepared [81], which was characterised by X-ray crystallography [82] (Scheme 55).



Scheme 55.

If one of the fluoro-substituents in **137** is exchanged by a dialkyl amino group, the fluoride ion donor-properties will be enhanced. According to NMR spectroscopic investigations, cation **141**/**142** is formed (Scheme 56), which is stable in the solid state at room temperature [83]. Structural investigations should show whether these cations should be regarded as alkylated thiazyl oxide or bis(imino)sulphoxide derivatives.

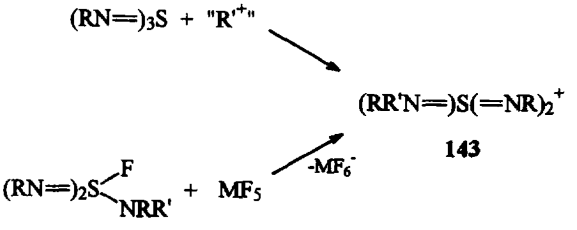


140 **141** **142**

Scheme 56.

Enhancing the halide donor ability of neutral sulphur(VI) species by the introduction of amino-substituents is one possible way for the generation of stable sulphur(VI) cations. Another route can be derived from the point of view that **135**, **138**, **141** or **142** can be regarded as alkylation products of sulphonyl imines, bis(imino)sulphoxides or thiazyl oxide derivatives.

Alkylation of stable sulphur triimides should lead to stable three-coordinate cations according to Scheme 57. As depicted in Scheme 57, bis(imino)amino sulphur fluorides, **144** (e.g. Ref. [84]) might act as fluoride ion donors, toward strong fluoro-Lewis acids to give cations of type **143**.

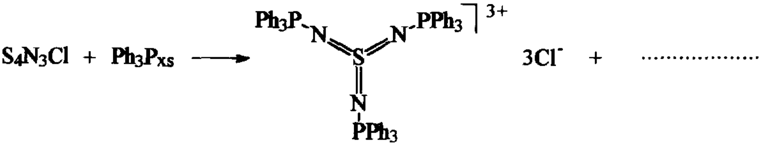


143

144

Scheme 57.

From the reaction of S_4N_3Cl with Ph_3P, Prakash and Sisler [85] reported, among many other products, the isolation of a compound to which they tentatively assigned the structure **145** (Scheme 58). Subsequently, the reaction of S_4N_4 with PPh_3 was



145

Scheme 58.

shown to produce $(Ph_3PN)_3S^+$ $S_4N_5^-$ **146** [86], $Ph_3PNS_3N_3$ and Ph_3PS (Scheme 59). This monocation is also likely to be the product in the reaction of Scheme 58 [86].

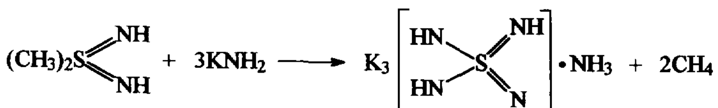
$$3S_4N_4 + 8Ph_3P \longrightarrow \underset{\mathbf{146}}{(Ph_3P{=}N\text{-})_3S^+\,S_4N_5^-} + Ph_3P{=}N\text{-}S_3N_3 + 4Ph_3PS$$

Scheme 59.

From a comparison of the stability of neutral, low coordinated phosphorus systems, $-\underline{P}=$ with their isoelectronic, cationic sulphur counterparts (e.g. $Me_2N-\underline{S}=O^+$ is a very stable cation [83,87], Me_2NPO cannot be isolated), a systematic investigation of the chemistry of three-coordinate sulphur(VI) cations is expected to lead to a variety of new cations.

5. Three-coordinate sulphur(VI) anions

The generation of three-coordinate sulphur(VI) anions seems to be even more difficult than the synthesis of cations, discussed previously. Owing to the lack of appropriate starting materials, only a few reports on such anions are found in the literature. The first evidence for the existence of a three-coordinate sulphur(VI) anion was presented by Appel and Ross [88]. From the reaction of *S,S*-dimethyl sulphur diimide with KNH_2 in liquid ammonia, salt **148** was isolated (Scheme 60). It was characterised by elemental analysis and its hydrolysis products. At 100 °C, loss of NH_3 leads to **149** (Scheme 61), for which **149a** or **149b** might be possible structures (Scheme 62). Characterisation of **149** is extremely difficult because of its pyrophoric and explosive nature.



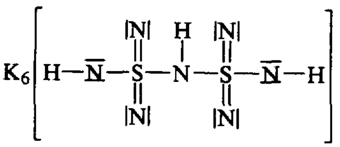
147 **148**

Scheme 60.

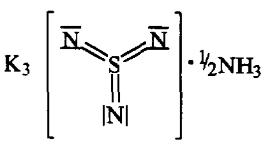
$$2\,\mathbf{148}\ \underset{NH_{3(liq)}}{\overset{-3NH_3\,(100°)}{\rightleftharpoons}}\ \underset{\mathbf{149}}{[K_6S_2N_6]\cdot NH_3}$$

Scheme 61.

An obvious way to sulphur triimide anions is the Si–N bond-cleavage in $S(NSiMe_3)_3$ by ionic fluorides. TAS-fluoride, $(Me_2N)_3S^+Me_3SiF_2^-$ [89] for example, reacts with the sulphur diimide $Me_3SiNSNSiMe_3$ to give the corresponding mono-anion in quantitative yield [90] (Scheme 63).



149a



149b

Scheme 62.

$$\underset{\textbf{150}}{TASF + Me_3SiNSNSiMe_3} \xrightarrow[-2Me_3SiF]{} \underset{\textbf{151}}{TAS^+\,Me_3SiNSN^-}$$

Scheme 63.

Salt **152**, with the mono-anion, might be formed in the reaction of Scheme 64, but further investigations are required for an unequivocal characterisation [91].

$$TASF + (Me_3SiN)_3S \xrightarrow[-2Me_3SiF]{} \underset{\textbf{152}}{TAS^+\,(Me_3SiN)_2SN^-}$$

Scheme 64.

While bis(imino)oxo anions have not been reported in the literature, a few controversial reports on the $[NSO_2]^-$ anion are found [92,93]. The parent acid, free $HNSO_2$, has not yet been isolated. Its existence as an unstable intermediate in the synthesis of $SO_2(NH_2)$ from SO_3 and NH_3 or by condensation reactions of $SO_2(NH_2)_2$ to $(HNSO_2)_n$ has been merely postulated [94,95]. The oligomers $(HNSO_2)_n$ ($n=3$, 4, 6) [96–98] and the polymeric chain have been known for many years.

In 1982, Roesky and co-workers reported on the preparation of Cs^+NSO_2- **153**, along with the analogous PPN^+ and PPh_4^+ salts [92] from the diimide **150** and CsF in wet $CHCl_3$ (Scheme 65). Subsequent work by Chivers et al. cast doubt on the nature of the anion [93]. They repeated the reported preparation of $Cs^+NSO_2^-$ and,

$$\underset{\textbf{150}}{Me_3SiNSNSiMe_3} + CsF \xrightarrow{[H_2O]} \underset{\textbf{153}}{Cs^+NSO_2^-} + 2Me_3SiF$$

$$\textbf{153} + Ph_4P^+Cl^- \longrightarrow \underset{\textbf{153a}}{Ph_4P^+NSO_2^-} + CsCl$$

$$\textbf{153} + Ph_3NPNPPh_3{}^+Cl^- \longrightarrow \underset{\textbf{153b}}{Ph_3NPNPPh_3{}^+NSO_2^-} + CsCl$$

Scheme 65.

by assignment of the IR and ^{14}N NMR spectra, showed the product to be Cs^+NSO^- containing significant amounts of $S_3N_3^-$ and small amounts of $S_3N_3O^-$.

Reaction of **153** with $RhH(CO)(PPh_3)_3$ gives the NSO complex **154** (Scheme 66), characterised by single-crystal X-ray diffraction [99]. This is an unusual reaction where the metal-centre remains unoxidised but S(VI) is reduced to S(IV). More recent reports of reactions of **153** with transition metal complexes are described to give NSO_2-containing products (no structure determinations were performed) [100] (Schemes 67 and 68).

$$\underset{\textbf{153}}{Cs^+NSO_2^-} + RhH(CO)(PPh_3)_3 \longrightarrow \underset{\textbf{154}}{Rh(CO)(NSO)(PPh_3)_3}$$

Scheme 66.

$$[M(CO)F(PPh_3)_2] + \underset{\textbf{153}}{Cs^+NSO_2^-} \longrightarrow \underset{\textbf{155}}{[M(CO)(NSO_2)(PPh_3)_2]} + CsF$$

$M = Rh, Ir$

Scheme 67.

$$[M'(NS)Cl_3] + \underset{\textbf{153}}{2Cs^+NSO_2^-} \longrightarrow \underset{\textbf{156}}{Cs_2[M'(NS)(NSO_2)_2Cl_3]}$$

$M' = Ru, Os$

Scheme 68.

Despite a recent report on the structure of $[Rh(MACSM)(COCH_3)(NSO_2)(PPh_3)]$ ($MACSM^-$ = methyl ester of 2-amino-1-cyclopentene-1-dithiocarboxylate ion) [101], obtained by an irreproducible hydrolysis of $[Rh(MACSM)(CO)(PPh_3)]$ in which the SO (130.9(6) pm) and SN (122.4(5) pm) bond distances given for the ligand are unrealistic, the question of the existence of the NSO_2^- ligand remains unanswered.

6. Conclusions

Although $(Me_3SiN)_3S$ [1] was prepared earlier than $(Me_3SiN)_2PN(SiMe_3)$ [3], the chemistry of stable three-coordinate sulphur(VI) species is rather poorly developed in comparison with its isocoordinated phosphorus(V) counterpart [102]. The main progress in sulphur chemistry was made more than 15 years ago. Since then, exciting advancements in other areas of low-coordination main-group chemistry have been reported. New, sterically demanding groups have been introduced and new synthetic methods have been developed. Rapid progress occurred particularly in phosphorus chemistry. This was possible owing to ^{31}P NMR spectroscopy, an excellent tool for the detection of new species, and supported by the progress in computational chemistry [103]. Because NMR is not an easily applicable technique in sulphur chemistry, and ^{14}N NMR spectroscopy is of very little use, characterisation of sulphur, and sulphur–nitrogen compounds is dependent upon X-ray crystallography. The developments in this field, e.g. of new techniques in low-temperature crystallography, will be of great help in the future.

The chemistries of three-coordinate sulphur(VI) and phosphorus(V) correlate very nicely. In both systems protic reagents will add to the element–nitrogen bond with expansion of the coordination sphere, oligomerisation is observed, (2+2) cycloaddition is a main reaction pathway and (2+1) cycloadditions are also known. Besides this, in phosphorus chemistry, (2+3) cycloadditions and the formation of coordination compounds have also been established.

In view of the similarity of the chemistries of these two systems, it is rather surprising that the approaches for the syntheses of three-coordinate S(VI) and P(V) described in the literature are completely different. The sulphur derivatives are almost exclusively prepared from relatively hard to prepare, highly coordinated precursors with reduction of the coordination number. The corresponding phosphorus species, however, were prepared from more readily available low coordinated P(III) derivatives, mainly by oxidative iminations with azides or *N*-chlorosilyl amines. Oxidative iminations of sulphur diimides and thionyl imides should be possible in the light of the formation of R_FNSO_2 amine adducts, from R_FNSO and $R_3N{=}O$, as described in Section 2.6.2.

More structural determinations and theoretical investigations are necessary to understand the bonding situation, the reactivity and the chemistry of sulphur triimides and their oxo-analogues, of thiazyl oxide derivatives, $N{\equiv}S(O)X$, and their imino counterparts, $N{\equiv}S({=}NR)X$. The difficult field of three-coordinate cations and anions is almost unstudied. It appears that the chemistry of three-coordinate S(VI)N species is still in its infancy.

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